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I am submitting herewith a dissertation written by John Thomas Ellis entitled "The Effect of Ion Damage and Annealing on Superconducting Transition Metal-Nitride Compounds." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

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THE EFFECT OF ION DAMAGE AND ANNEALING ON SUPERCONDUCTING
TRANSITION METAL-NITRIDE COMPOUNDS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
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John Thomas Ellis

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To Liz

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ABSTRACT

Thin films of the B1 phase superconducting compounds vanadium nitride and titanium nitride have been formed. This was accomplished by heating the previously evaporated pure metal films in high purity nitrogen gas. The resistivity at room and low temperature, the superconducting transition temperature T_C , and the upper critical field of these films were measured using a four probe d.c. resistive technique and found to be similar to those measured on bulk samples of the same compound. The films were then irradiated with nitrogen ions and the effect of lattice damage on these parameters was determined. It was found that the dependence on ion fluence of the residual resistivity and the transition temperature obeyed saturating exponential functions that could be derived from a simple defect production and annealing model. The renormalized electronic density of states $N^*(0)$ was calculated as a function of ion fluence, while the band density of states $N_b(0)$ was calculated using the electron lifetime model. The electron-phonon coupling constant was determined from these densities of states and from the McMillan equation for T_C . The results do not agree and it is shown that spin fluctuations cannot be used to explain the discrepancy. It is argued that some mechanism, other than lifetime reduction of the band density of states, is responsible for the observed effects. This is in contrast to the high temperature A15 superconductors in which the electron lifetime model yields large reductions in $N_b(0)$. It is thought that any other mechanism present in these materials would be overshadowed by this large reduction. Subsequent annealing studies were performed on these

samples. The results indicate that the radiation damage effects are, to a large extent, reversible. It is also found that annealing in vacuum at high temperatures results in loss of nitrogen and thus degradation of the properties of the material. From the ion damage and annealing results and from thermodynamic properties found in the literature it is argued that the bonding in TiN is almost three times stronger than in VN.

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I. INTRODUCTION

The effect of disorder, induced by irradiation, on the properties of superconducting compounds and alloys has been the subject of much research in recent times. The desire to use high field superconducting magnets in high energy accelerators and in fusion energy applications necessitates the knowledge of these effects. Besides the technological applications, studies of the effect of disorder can also help in attaining a better understanding of the mechanisms of superconductivity in the materials. Irradiation studies using neutrons or ions are extremely useful to this end since, using them, one can introduce regulated amounts of defects.

One important class of superconductors that have been studied extensively are the body centered cubic (b.c.c.) alloys of niobium. Among these are the systems Nb-Ta (Swarts et al., 1966), Nb-Ti (Okada et al., 1976; Schmelz et al., 1975; Coffey et al., 1967; and Wohllleben, 1973), and Nb-Zr (Coffey et al., 1967). Many of these alloys have been used in the construction of high field magnets used in research and development applications at the present. In general it was found that the superconducting transition temperature T_C and the upper critical magnetic field H_{C2} of these materials are little affected by irradiation.

Another important class of superconductors in which irradiation effects have been studied extensively are the compounds with the A15 or W_3O structure. These compounds have very high transition temperatures and upper critical fields. One of the A15 compounds, Nb_3Ge , has a transition temperature of 23.2 K (Gavaler, 1973; Testardi

et al., 1974 and 1975), the highest on record. The effects of irradiation by neutrons and ions in many of these compounds have been discussed by Sweedler et al., (1979); Dynes et al., (1977); and Ghosh et al., (1978). These materials in general exhibit drastic decreases in transition temperature with disorder, in some cases as much as 80% or more. In most of the high T_C A15 compounds the Fermi energy lies on a large peak in the density of electronic states. Reductions of this peak due to electron scattering by radiation generated defects have been cited as the reason for the large changes in T_C .

A third class of superconductors which have interesting properties for technological as well as purely scientific reasons are those with the B1 or rocksalt (NaCl) structure. Many of these compounds also possess high transition temperatures and upper critical fields; in fact, the ternary B1 compound $NbNb_{0.7}Co_{0.3}$ has a transition temperature of 17.8 K (Williams et al., 1967) which is exceeded by only a few A15 compounds. Unlike the b.c.c. alloys and the A15 compounds, irradiation effects have been studied in few B1 compounds. The Fermi energy in most of the superconducting B1 compounds lies on the side of a large peak in the density of electronic states; thus it is expected that the density of states at the Fermi energy, in contrast to the A15 compounds, will be little affected by radiation damage.

The first radiation damage work on B1 materials was done by Dew-Hughes and Jones (1980). They irradiated the compounds TiN, NbC, and Nb(CN) with fast neutrons and discovered that the transition temperature only decreased by 6 to 27%, much less than the A15

compounds. This finding suggested that the B1 compounds may be useful technologically since they possibly combine the radiation insensitivity of the b.c.c. alloys with the high temperature and field characteristics of the A15 compounds. Since the Dew-Hughes and Jones work a few of the B1 compounds have also been studied using ions. Among these are MoC irradiated with He ions, in which the transition temperature was found to change only slightly (Ruzicka et al., 1984), NbC irradiated with Ar and He ions (Kobayashi et al., 1984 and 1984), and NbN irradiated with Ar ions (Jung, 1984).

Another interesting facet to the B1 phase compounds comes from recent theoretical investigations of their superconducting properties. Rietschel et al. (1980) performed band structure calculations and solved the Eliashberg equations to determine the transition temperature of the compounds VN, NbN, ZrN, and TiN. They calculated for VN a transition temperature value of 32.3 K, which is well above the highest reported value of 9.25 K (Zhao et al., 1984), while they calculate T_C values much closer to the measured values for the other compounds. In this paper Rietschel et al. argue that spin fluctuations, due to long range magnetic interactions caused by an enhanced spin susceptibility of the electrons, cause the suppression of T_C observed in experimental investigations. Subsequent theoretical investigations on the B1 compounds VN, NbN, TaN, CrN, MoN, and WN (Papaconstantopoulos et al., 1985) also find high values for the transition temperature of VN but argue against spin fluctuations as a source for the discrepancy.

This later theoretical work, along with others, predicts a transition temperature for B1 MoN of 29.4 K (Pickett et al., 1981; Klein and Pickett, 1982; and Papaconstantopoulos et al., 1985). Other theoretical work indicates that this compound is unstable (Boyer et al., 1986); however, it has been formed (Linker et al., 1984), although in a very disordered state as indicated by very high resistivities, and found to have a transition temperature of about 3 K. Subsequently, other B1 phase MoN thin films have been formed with a transition temperature of 11 K (Yamamoto et al., 1985) and 12.7 K (Ihara et al., 1985); however, these materials had a substantial concentration of nitrogen vacancies. These theoretical and experimental findings on MoN indicate that a study of the effects of disorder in B1 compounds would be beneficial to understanding the superconductive mechanism in these materials.

Due to the above mentioned considerations, a program of research has been performed to study the effects of lattice disorder in B1 phase compound superconductors. Thin films of the B1 phase compounds vanadium nitride and titanium nitride have been synthesized and irradiated with nitrogen ions in order to determine, in a controlled manner, the effects of lattice damage on the superconducting and normal state properties. The superconducting transition temperature T_C , the room temperature and low temperature or residual resistivities, $\rho(300\text{ K})$ and ρ_0 , respectively, the X-ray diffraction pattern, and the upper critical magnetic field $H_{C2}(T)$ have been measured as a function of lattice damage induced by these ion irradiations. From these measured parameters several microscopic

quantities have been calculated. Upon completion of the irradiation study, the ion damaged samples have also been annealed in vacuum or in a nitrogen atmosphere. The same parameters were then measured to determine if these damage effects are reversible and to provide insight on the types of defects produced by the irradiations.

From this ion damage and annealing investigation we have examined the measured and deduced quantities and proposed a simple, empirical defect production and annealing model to explain the observed behavior of the residual resistivity and the transition temperature. We have also compared the present results with existing theoretical treatments of the effects of disorder on the microscopic properties of these materials. From this comparison it is argued that spin fluctuations in VN cannot account for the differences observed between existing theory and the present results.

II. EXPERIMENTAL ASPECTS

A. APPARATUS FOR CHARACTERIZATION OF THE SAMPLES

To measure quantities such as the superconducting transition temperature, the electrical resistivity at various temperatures, and the upper critical magnetic field, an apparatus is needed which combines electrical resistance measurement capabilities, high magnetic fields and variable sample temperatures. To meet these requirements a cryostat has been designed and constructed, the basic features of which are: (1) operating temperatures from 1.5 to 300 Kelvin, (2) magnetic fields up to 8 Tesla, (3) ease of sample change and (4) a straightforward resistance measurement technique. In this section the cryostat will be described followed by a discussion of measurement techniques and procedures.

1. Description of the Apparatus

The apparatus described herein is designed to measure the above mentioned properties of thin film or foil samples; however, it can also be used to measure bulk samples if the sample dimensions are such that it can fit on the sample holder. The apparatus is shown schematically in Figures II.1 and II.2. Figure II.1 shows the removable sample rod. Samples are mounted on the bottom of a copper sample block at the end of the rod. The samples are held in place by Apiezon N grease which also provides good thermal contact between sample and block. Electrical contact to the samples is made through a pogo board which utilizes spring loaded "pogo" contacts made by the PYLON company. This board, made from phenolic board coated on one

Figure II.1. The sample rod. The indicated components are as follows: A; electrical feed-through; B, Ladish flange; C, radiation shields; D, centering device; E, sample block; F, heater; G, heat sinking ares; H, sample mounting area; and I, copper shield.

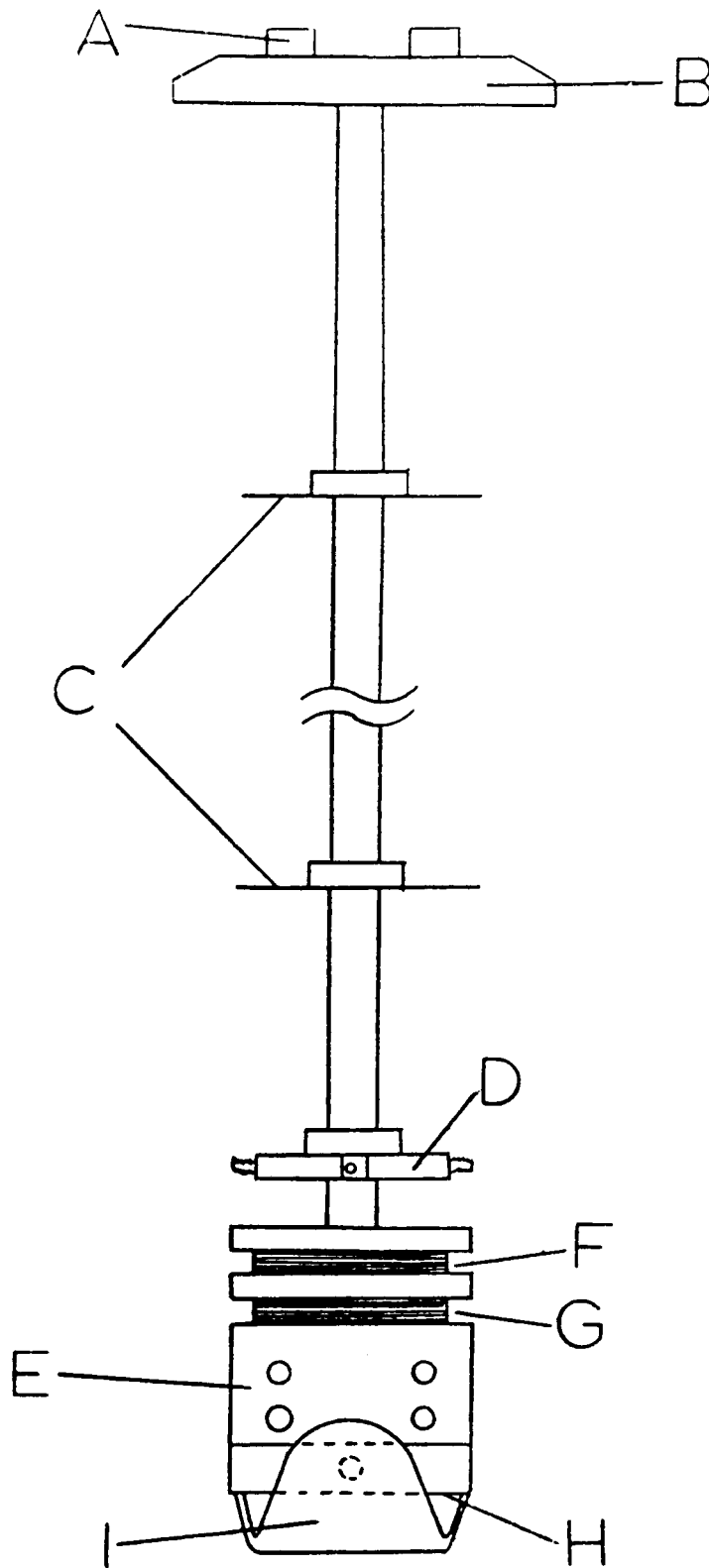


Figure II.1

Figure II.2. The cryogenic apparatus. The indicated components are as follows: A, Ladish flange which mounts to the Ladish flange in Figure II.1; B; electrical feed-through; C, needle valve control knob; D, liquid nitrogen jacket; E, needle valve; F, radiation shields; G, vacuum wall; H, capillary; I, magnet; J, vaporizer; K, vacuum wall around sample space; and L, sample space.

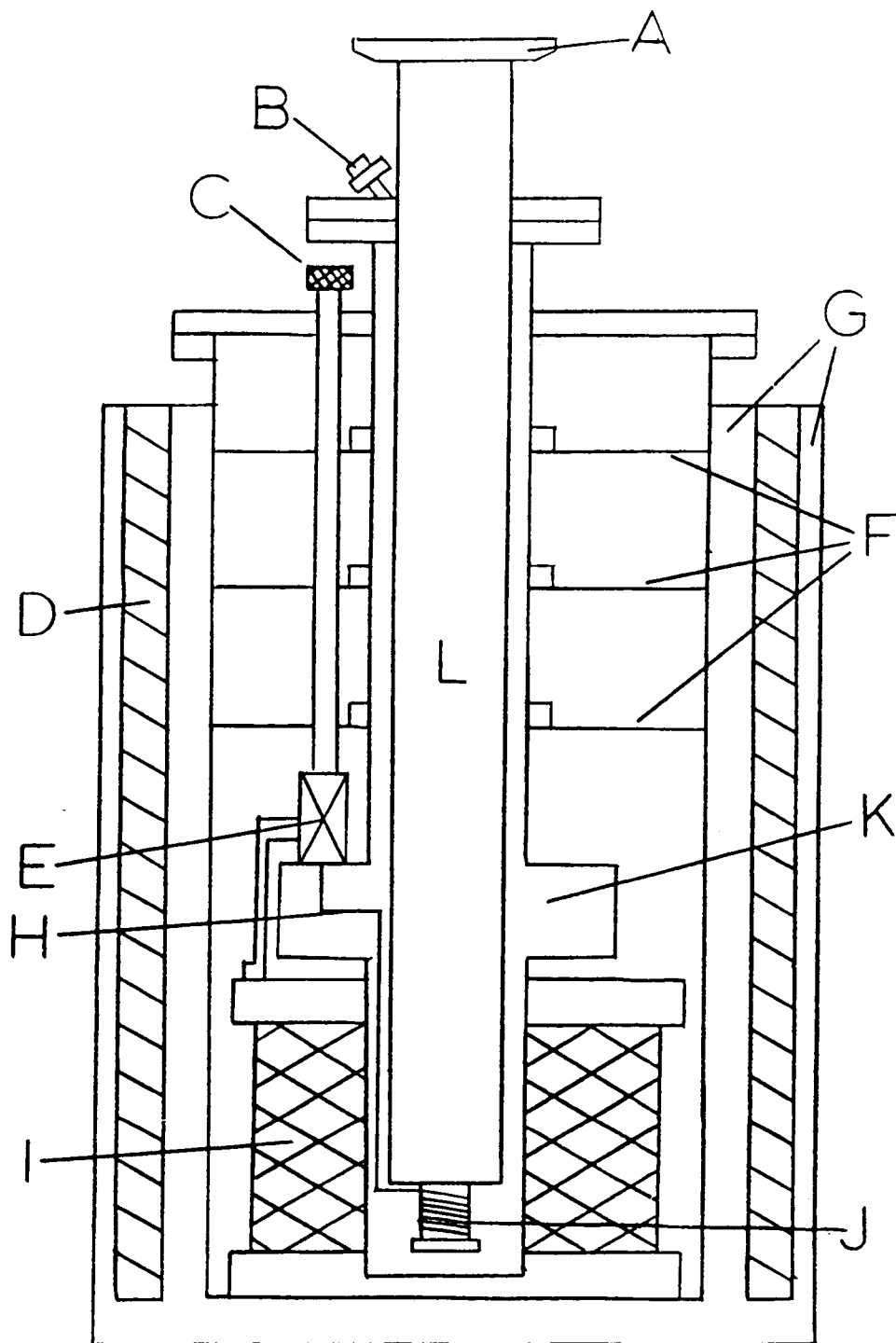


Figure II.2

side with copper, is attached to the sample block by copper screws on either end of the sample. A shield, made of copper sheet, is attached to the side of the sample block and loops down below the sample. Its purpose will be described later.

The sample block contains various resistance thermometers and a heater. The heater is made of Tophet "C" wire, 17 Ω per foot, and is wrapped around the sample block as shown. It is used in conjunction with a uncalibrated, 220 Ω at room temperature, Allen-Bradley resistor and an Artronix model 5301-E temperature controller to form a temperature control circuit. The block also contains a Wahl wire-wound Pt resistance thermometer for temperature measurement from 30 to 300 K and a Lakeshore model CGR-1-1000 calibrated carbon glass thermometer for measurement from 1.4 to 40 K. The leads for the thermometers are heat-sunk to the sample block, as shown in Figure II.1, in order to prevent conduction of heat down the leads. This block is clamped to the end of a 3/8 inch diameter thin walled stainless steel tube using a clamp collar. On the tube, just above the sample block, is a centering device made of aluminum. It consists of four legs with threaded holes down their centers, each hole having a nylon screw in it. Centering is achieved by adjustment of the screws. Above this are three equally spaced radiation shields. These shields, made of copper, are used to prevent thermal radiation from making its way down to the sample and thus causing an undue heat load. At the top of the sample rod is a Ladish flange, size tube o.d.-2, which mates to a similar flange on top of the cryostat, as shown in Figure II.2. The lead wires for the above-mentioned heater and

resistance thermometers run up the sample rod, through holes in the radiation shields, to the flange at the top. Electrical connection through this flange is made using four hermetically sealed, 7-pin feed-throughs mounted on the flange.

Figure II.2 shows the cryostat which consist of a conventional stainless steel liquid helium dewar with a liquid nitrogen jacket, a high field superconducting magnet and the sample chamber with its various hardware for temperature control. The sample chamber is composed of an inner stainless steel wall, inside diameter of 1.5 inches, surrounded by a vacuum jacket and an outer stainless steel wall. Mounted on the outer wall is a needle valve which allows liquid helium, from the helium bath, to enter a stainless steel capillary and travel to a "vaporizer" device at the bottom of the inner chamber. This needle valve is controlled by the valve stem which is extended and emerges through a flange near the top of the outer wall. A dip tube is attached to the needle valve in order to facilitate helium flow after the helium level is below the valve.

The vaporizer is made from a one inch diameter cylindrical copper block. This block has had various steps, ridges and holes machined into it to accommodate a heater, a thermometer and a place to heat-sink their leads. The capillary from the needle valve is wound around the center portion of the block then is soldered into a hole in the bottom. This hole runs the length of the block and allows liquid helium from the bath to flow through the vaporizer and into the sample chamber. A wire-wound heater is wrapped on top of the capillary in order to boil and heat the liquid helium if desired. An Allen-

Bradley, 220 Ω at room temperature, carbon thermometer is also mounted on the block to monitor the temperature of the vaporizer and, along with the heater, is connected to an Artronix model 5301-D temperature controller so that the temperature of the vaporizer can be controlled.

The sample chamber is inserted into the bore of an 8 Tesla, high homogeneity, superconducting magnet, manufactured by American Magnetics Incorporated. It is equipped with a persistent switch which is basically a superconducting shunt across the magnet coil. This shunt is thermally connected to a heater which can drive the shunt normal. When energizing the magnet, the heater is turned on. The finite resistance of the shunt in parallel with the superconducting magnet forces the current to flow into the magnet. Once the desired magnet current is reached, the heater is turned off, reactivating the short, thus allowing one to remove the supply current and save liquid helium.

The magnet is energized through a pair of vapor cooled leads, also made by American Magnetics. The vapor cooled leads are constructed with small passages running their length with openings at their top and bottom. When the magnet is operated, the He gas, boiling off the liquid He bath, is forced to flow through these passages to exit the cryostat, thus cooling the leads. These leads pass through three copper radiation shields, mounted on the sample chamber. The leads then exit the cryostat via the top flange.

The circuit for operating the magnet is shown in Figure II.3. At the top, the vapor cooled leads are connected in series with a 0.01 Ω standard resistor, which is used to measure the current through the

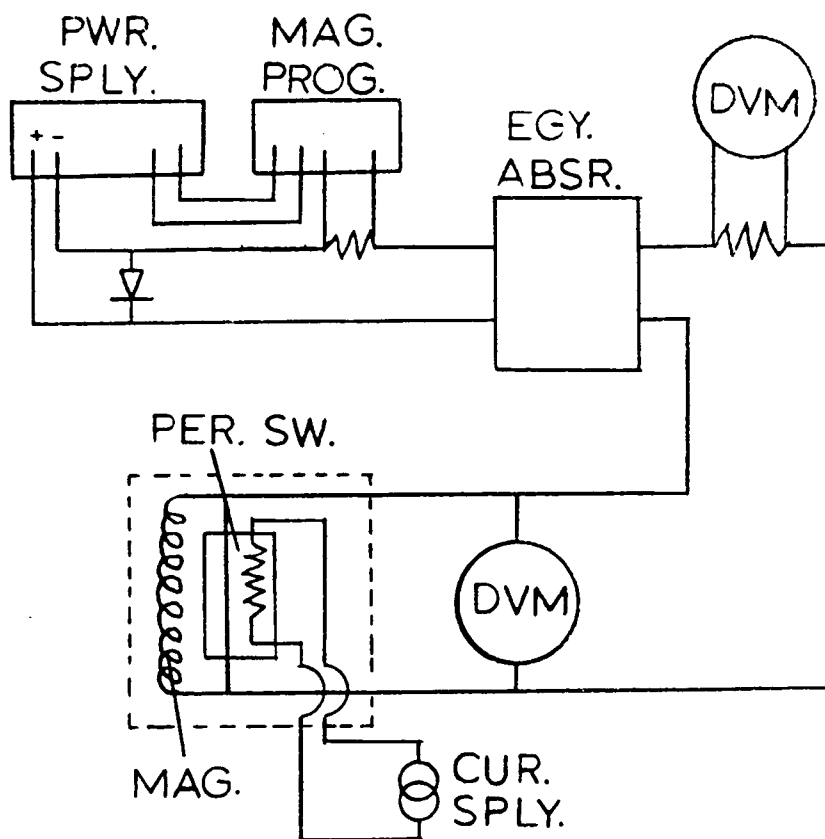


Figure II.3. The wiring diagram for the magnet energizing circuit. The area inclosed in the dotted line is inside the cryostat.

magnet by measuring the voltage across it. This combination is connected to an energy absorber whose function is to dissipate energy when removing current from the magnet, thus protecting the power supply. The energy absorber is connected in series with a 1 m Ω shunt and a Hewlett-Packard model 6260B, 0 to 100 A, power supply. The power supply is controlled by an American Magnetics, model 400A, magnet programmer which uses the shunt as a current monitor. A Wahl Pt resistance thermometer is mounted on top of the magnet in order to monitor the temperature of the magnet.

2. Temperature Measurement and Control

Measurement of the sample temperature is achieved, as mentioned above, by use of a wire wound platinum and a carbon glass resistance thermometer. The platinum thermometer is calibrated from room temperature to 30 K and the carbon glass from 40 K to 1.4 K. In each case the temperature is determined by comparing the resistance of the thermometer to a resistance versus temperature calibration table. The circuit diagram for this measurement is shown in Figure II.4 where the dashed box indicates the part of the circuit actually within the cryostat.

The platinum and carbon glass thermometers are wired in series with a Cryo Cal, model CS 1000B, constant current supply and a 100 Ω standard resistor. This arrangement allows the use of only one current source for both thermometers and, by measuring the voltage across the standard and applying Ohm's law, a method of monitoring the current through the them. Voltage leads from each thermometer are connected to opposite sides of a double pole, double throw switch.

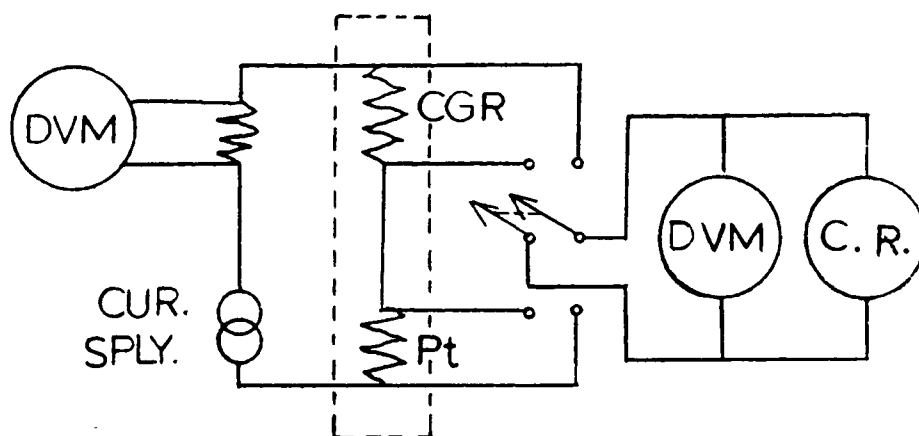


Figure II.4. The wiring diagram for the thermometer resistance measurement circuit. The area inside the dotted line is inside the cryostat.

The center of the switch is then connected in parallel with a Keithley, model 197, digital volt meter and the x-axis of a Houston Instruments, model 2000, x-y recorder. By throwing the switch one can select which thermometer's voltage is to be measured. By knowing the voltage and current of a resistance thermometer and using Ohm's law, the resistance of the thermometer, and thus the temperature of the sample, is determined.

Two methods of temperature control are used depending on whether one desires to maintain a constant temperature (method 1) or to vary the temperature (method 2). In method 1, the liquid He bath is maintained at some pressure above atmospheric, typically about 100 Torr gauge. This is achieved by closing off all but one of the ports from which the He boil-off gas usually escapes. The remaining port is then attached to a pressure relief valve set at the appropriate pressure. The needle valve, described above, is then opened allowing liquid He to flow through the capillary into the vaporizer and into the sample chamber, thus cooling the vaporizer and sample rod. This is done until liquid He has collected in the sample chamber and filled to above the sample block, at which time the needle valve is closed.

The liquid He is then removed using the temperature control circuits of the sample block and vaporizer, shown in Figure II.5. The sample block controller is set in the full control mode in which the controller is sensitive to the amount of deviation of the thermometer from the set-point (heater power is proportional to the deviation), the rate of change of the deviation from the set-point (heater power

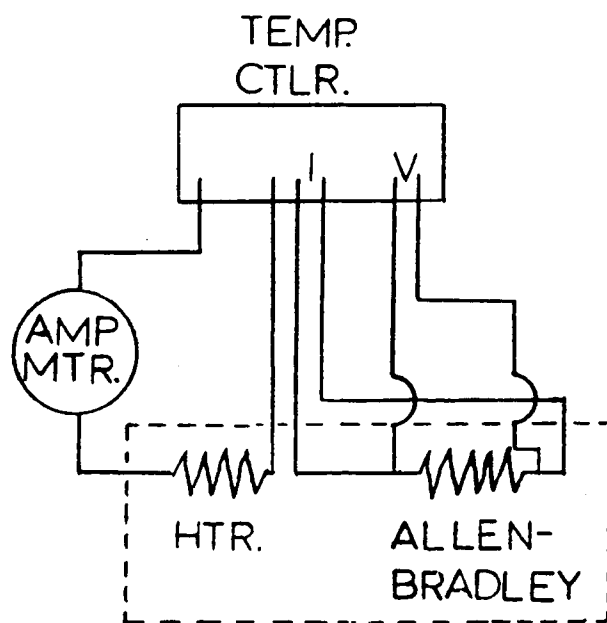


Figure II.5. The wiring diagram for the sample block and vaporizer temperature control circuits. They are equivalent circuits. The area inside the dotted line is inside the cryostat.

is proportional to the rate of change) and also resets the amount of power to the heater to keep the deviation very small (by use of a servo motor connected to the heater power output rheostat). This controller is set to control at 1000 Ω on the Allen-Bradley carbon resistor (approximately 9.5 K) while the vaporizer controller is used only as a current supply and is set to deliver 200 mA to the vaporizer heater. This is done until all the liquid He in the sample chamber and vaporizer is boiled away.

At this point the needle valve is opened slightly, typically 1/4 to 1/2 turn, allowing liquid He to again flow into the vaporizer; however, this time the vaporizer controller is used to control its temperature at approximately the desired value. This boils the incoming He liquid and heats it to the temperature of the vaporizer. This heated He gas then leaves the vaporizer and enters the sample chamber where it envelops the sample block. Here the gas contacts the shield, described in section 1, which prevents the gas from directly blowing on the sample and thus prevents thermal gradient problems that might arise. Once the temperature of the sample block is stabilized, the sample temperature can be fine tuned using the sample block temperature controller.

In method 2 the He bath is also held at an elevated pressure in the same manner as in method 1. The needle valve is opened and liquid He is allowed to flow into the sample chamber, cooling and filling it until the sample block is covered. The needle valve is then closed. Heat is applied to the sample block, as before, with the controller set in the full control mode and set to control at 1000 Ω . This is

continued until the liquid He has boiled down below the sample block, leaving a small pool of liquid He between the block and the bottom of the sample chamber, and the block's temperature is controlled at about 9.5 K (1000 Ω).

The temperature can then be varied smoothly from 6 K to about 10 K by changing the temperature controller on the sample block to proportional mode, where the power output to the heater is proportional to the deviation of the resistance of the thermometer from the set point, and varying the set point. To sweep the temperature to values lower than about 6 K, the sample heater is turned off and the temperature is controlled by pumping on the sample chamber using a vacuum pressure regulator. The reduction in pressure causes the pool of liquid He below the sample block to boil thus causing cold gas to pass over the block and therefore cooling it. The temperature can be varied quite smoothly from 7 K down to about 1.4 K by controlling the pressure in the sample chamber, either pumping to reduce pressure or introducing He gas to raise the pressure. To vary the temperature above about 10 K, one must again use the temperature controller in the full mode and vary the set-point.

3. Characterization of Samples

The samples are characterized by the room temperature and low temperature (or residual) electrical resistivities, $\rho(300)$ and ρ_0 , respectively, the superconducting transition temperature T_C and the temperature dependent upper critical magnetic field $H_{C2}(T)$. All these parameters are actually determined by measuring the electrical

resistance of the sample. The circuit for sample resistance measurement is shown in Figure II.6.

The sample is wired in series with a Lakeshore Cryotronics, model 120, constant current source, which can supply currents of 1 μ A to 100 mA, and a 1 Ω standard resistor, used to check the current. As described previously in section 1, voltage and current leads are connected to the sample by spring-loaded pogo contacts, shown in Figure II.7. The current is introduced through the two outside contacts and the voltage leads are connected to the two inside contacts. The voltage leads from the pogo board are connected in parallel with a Keithley, model 181, digital nanovoltmeter and the y-axis of the Houston Instruments x-y recorder mentioned in section 2. The sample resistance is then determined by passing a current, typically 100 μ A, through the sample and measuring the voltage across the sample. Applying Ohm's law, the resistance is then the voltage divided by the current.

The resistivity ρ is calculated from the resistance R by the formula:

$$\rho = R A/l,$$

where A is the cross sectional area of the sample, given by the width times the thickness, and l is the gauge length of the pogo board (ie., the distance between the two voltage contacts) shown in Figure II.7. The width of the sample is determined by the evaporation mask used in forming the sample (this will be described in the next section) and is either 0.159 cm or 0.233 cm. The thickness is measured using a stylus type device made by Tencor, Inc. The estimated error in thickness

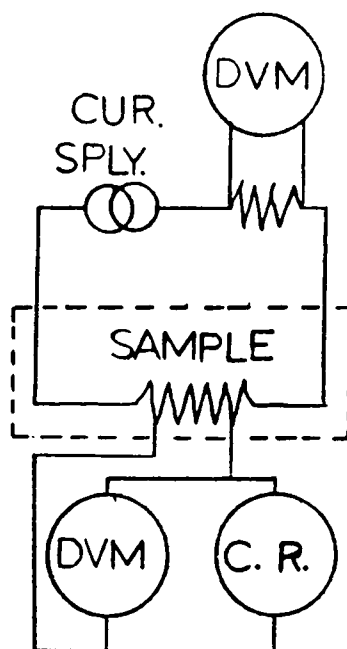


Figure II.6. The wiring diagram for the sample voltage measuring circuit. The area inside the dotted line is inside the cryostat.

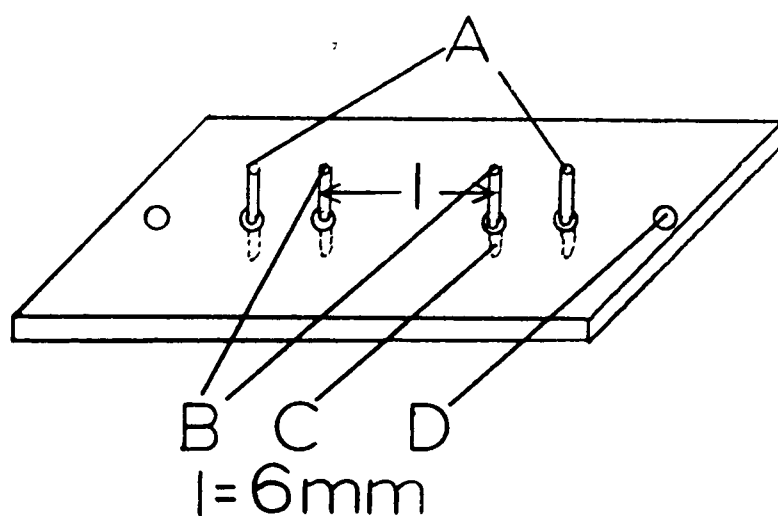


Figure II.7. The pogo board. This is used to make electrical contact to the thin film samples. The features are as follows: A, current contacts; B, voltage contacts; C, spring loaded pogo pins; and D, screw holes.

using this instrument is ± 10 nm or about $\pm 10\%$, depending on the sample thickness. Using the above-described temperature control methods, the resistivity can be measured at any temperature from room temperature to 1.4 K.

The superconducting transition temperature T_C is determined by measuring the low temperature resistance as a function of temperature. This is accomplished by using the previously described temperature control method (method 2) and the x-y recorder to trace the resistance versus temperature curve. At the superconducting transition, the resistance decreases to zero. T_C is defined as that temperature at which the resistance falls to 50% of its normal state value. The width of the transition ΔT_C is defined as the difference between the temperature at 90% the normal state resistance and the temperature at 10% the normal state value.

The upper critical magnetic field as a function of temperature is the curve, in H-T space, that defines the phase boundary between the normal and superconducting states; that is, at a given temperature, it is the field at which the sample goes from the superconducting state to the normal state. $H_{C2}(T)$ is then found by measuring T_C in a magnetic field applied perpendicular to the plane of the film. Once T_C is measured at several different applied fields, the H_{C2} vs. T curve may be plotted, thus the above-mentioned phase boundary is determined.

The procedure for this measurement is as follows. First, T_C is determined as described above. The temperature is then raised above T_C and a magnetic field is applied. The transition temperature in

this field is then measured as described above. Thus, this defines a point in H-T space on the phase boundary. The procedure is then repeated again at another field, and so on. This produces the needed H_{C2} vs. T curve.

B. X-RAY DIFFRACTION

X-ray diffraction studies of the samples were conducted using the facilities at the Solid State Division of Oak Ridge National Laboratory. Here a Guinier thin film diffractometer (Linker, 1984, p. 30; Weiner, 1966) was used, suitably modified so that the film samples could be rotated about an axis perpendicular to the plane of the film in order to average out texture. A Guinier diffractometer is arranged so that the angle between the incident X-ray beam and the sample is very small (on the order of 2 degrees). This makes the effective thickness of the film much greater compared to near normal incidence.

Using X-ray diffraction the lattice constant can be determined since the X-rays reflect off the crystal planes in the sample and diffract according to Bragg's law (Bragg, 1913). The resulting allowed reflections are governed by the expression, for materials with cubic space lattices,

$$\lambda = 2d \sin \theta,$$

$$\text{where } d = \frac{a_0}{(h^2 + l^2 + k^2)^{1/2}},$$

2θ is the angle of the reflection relative to the incident beam, and a_0 is the lattice constant. The indices h, k, and l are the indices for the set of crystal planes which produced the given reflection.

The values that h, k, and l can have is determined by the crystal

structure of the lattice (Kittel, 1967, p. 63). For B1 phase (rocksalt) materials, which have a face centered cubic space lattice, h , k , and l must be either all odd or all even. By measuring the angles of the reflections and applying Bragg's law, one may determine the lattice constant of a given material.

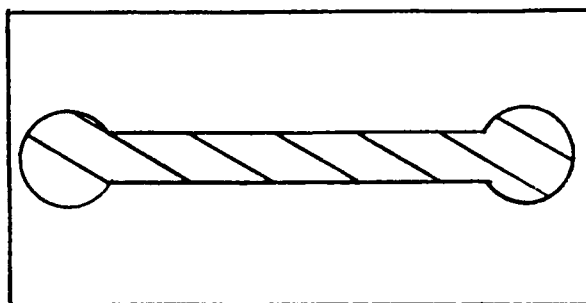
C. SAMPLE PREPARATION

This section describes the sample preparation procedures and techniques employed to produce the vanadium nitride and titanium nitride thin film samples used in this study. Since the methods of preparation for both compounds are the same, differing only in details such as production parameters, the general procedures will first be described. This will be followed by two subsections concerning the details pertinent only to each compound.

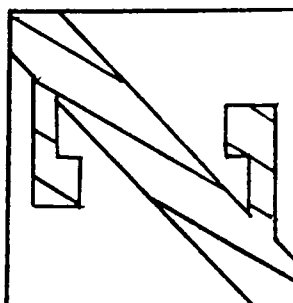
Thin film samples of VN and TiN were formed by heating films of the pure metal, previously evaporated onto sapphire substrates, in one atmosphere of nitrogen gas. The thin films of the pure metal were prepared by electron-beam evaporation. This was carried out at facilities in the Health and Safety Research Division of the Oak Ridge National Laboratory. Their apparatus consisted of a cryopumped pyrex bell jar containing a Thermionics Laboratories, Inc., 3 kw, electron-beam evaporation unit, a quartz crystal thickness monitor and various substrate holding hardware. The electron gun and evaporation hearth unit was surrounded by a chimney made of stainless-steel shim stock, which prevented any of the evaporated material from condensing on the sides of the bell jar. The top of the chimney was fitted with a

shutter, moveable from the outside, that covered all but a small portion of chimney's top opening. The bell jar rested on a stainless-steel collar, sealed with a viton ring, which was fitted with several 2 3/4 in. O.D. conflat flanges. These flanges provided feed through capability from the outside. This system was rough pumped by first a carbon vane pump, which reduced the pressure to about 200 Torr, and then by a liquid nitrogen cooled sorption pump, which brought the system down to about 10 mTorr, and then pumped by an Air Products, water cooled, cryo-pump. This provided pre-evaporation pressures of 7×10^{-8} to 2×10^{-7} Torr while introducing no oil vapor usually associated with mechanical pumps.

The sapphire substrates were single crystal ribbons of Al_2O_3 , 1/2 in. by 2 in. by 0.025 in., purchased from the Saphikon company. These ribbons were cut into two sizes, 1/2 in. by 1/2 in. and 1 in. by 1/2 in. Prior to evaporation, these were cleaned in a 1:1 solution of trichloroethane 1,1,1 and iso-propyl alcohol using an ultra-sonic cleaner, after which they were rinsed in distilled water followed by iso-propyl alcohol and dried with a heat gun. The substrates were then placed into one of the two substrate holders depending on size. These holders were constructed to mask the substrates in order to produce films with geometries convenient to resistivity measurements (ie., films with uniform rectangular cross sections). These film patterns are shown in Figure II.8. The substrate holders were fitted with a type K thermocouple (chromel-alumel) and a detachable heater plate, used to measure the temperature of and heat the substrates, respectively, during evaporation. The heater plate incorporated a



(A)



(B)

Figure II.8. The evaporated film pattern. The top figure (A) is for 1 in. by 1/2 in. substrates and (B) is for 1/2 in. by 1/2 in. substrates.

stainless-steel capillary filled with nichrome wire insulated by an MgO sleeve. This capillary was twisted in a serpentine fashion and spot welded onto a stainless-steel plate which could be bolted onto the substrate holder. The entire substrate holder assembly is cleaned in an identical manner to the substrates prior to assemblage.

The substrate holder assembly was held above the evaporation chimney by a clamp system similar to a laboratory ring stand. The thickness monitor was positioned so that it was at the same distance from the evaporation source as the substrates and over the small opening made by the chimney and shutter. This provided a way to set up the evaporator (ie., set the deposition rate or outgas the source) without opening the shutter and exposing the substrates. The leads for the heater and thermocouple exited the system through a high vacuum feed through attached to one of the conflat flanges and were connected to a variac and a voltmeter, respectively. After the substrate holder assembly was mounted, the system was evacuated overnight.

The evaporation procedure was started by slowly increasing the power to the electron gun. This caused localized heating at first, evidenced by a small red spot on the source material, then thermal equilibrium was reached. As the power was further increased, material began to evaporate as evidenced by the thickness monitor. The power was increased until the desired evaporation rate (or the maximum rate attainable, which ever was lowest) was reached. Evaporation in this mode was continued for several minutes to ensure that the source material was outgassed of any impurities and to deposit some of the

source material on the walls of the system to act as a getter for any trace oxygen in the system. The power to the electron gun was then reduced and turned off to allow the cryo-pump to pump away any gas released from the source or the system.

After a few minutes, when the system pressure had reached a minimum again, the power to the electron gun was turned up again in the same manner as before to the desired evaporation rate. Simultaneously, the thickness monitor was reset to zero and the shutter was opened, beginning the actual deposition of the films. This was continued until a thickness of 100 nm was indicated on the thickness monitor, at which time the electron gun power was shut off. This produced films of the pure metal, of nominally 100 nm thickness, which were highly reflective, silvery in color, and generally metallic in character.

The pure metal films were then studied at low temperature to quantify their quality. The residual resistance ratio Γ , defined as the ratio of the room temperature resistance to the resistance at 4.2 K (or the resistance just above the superconducting transition, whichever was higher), the T_C and the transition width were used as quality parameters for the vanadium films while only Γ could be used for titanium films since T_C for bulk Ti is 0.39 K, well below our lower limit in temperature. Values of these will be discussed in the following subsections since they vary considerably for V and Ti.

The nitrides were formed by heating the pure metal films in nitrogen gas. This was performed in an all metal, ultra high vacuum (UHV), annealing furnace. The furnace consisted of a stainless-steel

vacuum chamber, equipped with various sizes of conflat flanges, which was connected through a 6 in. I.D. pumping line and a 6 in. gate valve to a CTI-Cryogenics, model CRYO-TORR 8, UHV cryo-pump. Through an all metal valve on the bottom of the pumping line (called the roughing valve), the furnace was connected to a rough pumping manifold equipped with three liquid nitrogen cooled sorption pumps, a carbon vane pump and, through a liquid nitrogen cold trap, to a direct drive rotary mechanical pump.

A variable leak valve and an all metal mini valve (called the gas inlet valve) were connected to the front of the vacuum chamber by a 1.33 in O.D. (mini) conflat flange. These valves were attached to a 1/4 in. stainless-steel tube coming from a gas handling manifold. This manifold had three Matheson, model 3803, ultra high purity gas regulators used to introduce gasses into the furnace.

The samples were heated by use of rf induction heating of a metal tube containing the samples. Heat was provided by a double layer copper coil entering through an UHV rf feed through on a 2 3/4 in. conflat flange. The coil was made of 3/16 in. O.D. copper tubing wound on a 2 in. O.D. mandrel, thus producing a 2 in. I.D. coil. The coil was attached to the feed through by modified Cajon VCR gland fittings (modified in that they are only available in stainless-steel so they were made out of copper at the Solid State Division machine shop at ORNL). Outside the vacuum chamber, the copper lines from the feed through were connected to a 9 kw rf generator. The copper lines of the coil and feed through provide good electrical conduction as well as carrying cooling water. Samples were heated by placing them

inside a metal tube (called a susceptor) which was suspended inside the coil. Rf power was then applied to the coil inducing currents in the susceptor. These currents create Joule heat in the susceptor and thus heat the samples by radiation. Using this apparatus temperatures of up to 2000°C can be obtained, depending on the size and type of susceptor, size of the sample and atmosphere in the furnace at the time of heating.

The susceptor used to nitride the samples in this case was made from a sheet of 0.003 in. thick, 99.8% pure, molybdenum metal. The sheet was wrapped around a 5/8 in. O.D. form and fastened together using a sheet metal type lap joint to form a tube. This Mo tube was then cut to three inches in length and one end was closed by making cuts up the length of the tube, about 1/2 in., and folding the resulting strips over and in. The Mo susceptor was then attached to a Mo rod by running a Mo wire through matching holes near the top of the susceptor and the bottom of the rod and twisting to tighten. The Mo rod was then connected to a stainless-steel tube, fitted with a set screw, by sliding it inside and tightening the screw. The opposite end of this tube was threaded and screwed into a hole in a ceramic (Al_2O_3) standoff. The standoff was also threaded and screwed into a blank 2 3/4 in. conflat flange. When in operation, this flange mated to a similar flange on top of the vacuum chamber so as to center the susceptor in the rf coil. Before use the Mo susceptor was outgassed at 1600°C for a few hours until the pressure in the vacuum chamber reached a minimum.

The process of nitriding the metal films was started by placing the films, after they were rinsed in trichloroethane 1,1,1, followed by iso-propyl alcohol, in the Mo susceptor and inserting the above described susceptor assembly into the vacuum chamber. The gas inlet valve was then opened so both the gas lines and the chamber could be evacuated at the same time. Evacuation was then begun by opening the roughing valve and opening one of the sorption pumps, previously cooled in liquid nitrogen, to the roughing manifold. This pumped the system down to about 20 mTorr in about fifteen minutes. Next the roughing valve was closed and the gate valve was opened connecting the cryo-pump to the vacuum chamber. This resulted in an immediate pressure drop to about 5×10^{-6} Torr as read by a nude ion gauge inside the vacuum chamber.

After pumping overnight the pressure was typically 3 to 5×10^{-9} Torr. This pressure could be improved by baking the system. The entire system, except the cryo-pump and roughing system, had been previously wrapped with heater tapes which were connected to a large variac. The vacuum chamber was covered with a fiberglass shroud used to promote even heating. The variac was attached to a timer which would shut the power to heater tapes off after a prescribed time. In this case, the system was baked for twelve hours and allowed to cool, after which typical pressures of 8 to 9×10^{-10} Torr were observed. However, it was generally felt that this additional procedure was unnecessary and it was omitted.

After a satisfactory pressure was reached, the gas inlet valve was closed. To remove any oxygen that may have inadvertently leaked

into the regulator, the gas lines were flushed by the following method. The lines and the roughing manifold were connected so that one could use the rotary pump and nitrogen cold trap to pump out the gas lines. The lines were then filled, from a gas cylinder connected to the regulator, with about 800 Torr of 99.9995% pure nitrogen gas, as read by a Datametries Barocel pressure transducer attached to the lines. A valve connecting the regulator and the gas cylinder was then closed and the N₂ gas was pumped away using the cold trap and rotary pump. This was then repeated four times for a total of five flushings.

The gate valve was then closed and the gas inlet valve was opened, filling the vacuum chamber with N₂ to approximately 1 atmosphere. Once the chamber was full, the gas inlet valve was closed and the gas lines were evacuated using the cold trap and rotary pump. After turning on water to the rf generator and coil, the generator was turned on and the susceptor, and thus the metal films, were heated to the appropriate temperature for 10 minutes, after which the rf generator was shut off. This amount of time was determined empirically after several nitridings. The time can be estimated (Fromm and Gebhardt, 1976); however, the resulting times are much less than that actually required.

The temperature of the susceptor was determined using one of two optical pyrometers. For temperatures of less than about 1100°C a Leeds and Northrop, model 8622-C, infrared pyrometer was used, which one looked through, at the susceptor, and adjusted a filament temperature until the susceptor and filament were at the same

temperature. For temperatures of 1100°C and higher a Capintec, Inc., two color pyrometer was used which gave a digital read-out of the temperature in Celsius degrees.

Once the susceptor and samples, now nitrides, were judged to be cool they were removed from the furnace. This was determined by measuring the temperature of the top of the vacuum chamber, since the hot susceptor would, and did, cause convection currents in the N₂ gas, heating the top of the chamber more than the rest. This measurement was usually made by touching the surface with one's hand.

1. Vanadium Nitride

The source material for all the vanadium films was 99.99% pure vanadium metal. The metal, which was in the form of small pieces, was first arc melted into ingots of approximately 10 grams, after which they were cut into quarters. Prior to evaporation the vanadium metal pieces were etched in a mixture of H₂O and HNO₃ in a ratio of 1 to 1, which removed a surface layer of metal along with any impurities that may have accumulated on the surface.

Three evaporation runs were made. The first two were performed with the substrates at ambient temperature, while the third was done, using the heater, with the substrates at 230°C. The film deposition rate was 1.8, 2.0, and 3.3 nm/sec, respectively, for the three runs. The pressure during evaporation for the three runs was 3.4×10^{-7} Torr, 2.2×10^{-7} Torr and 3.5×10^{-7} Torr. In all three cases, the resulting films were silver in color and highly reflective.

The two evaporations made with substrates at ambient temperature produced films which were very similar in quality, as one would

expect. The residual resistance ratios of these films ranged from to 2.71 to 2.92, while T_C ranged from 4.10 to 4.39 K (T_C of bulk V metal is 5.38 K as quoted in Kittel, 1976, p. 356), with transition widths of 0.06 to 0.18 K. The films deposited onto 230°C substrates were of higher quality with consistent resistance ratios of 3.9, T_C values of 4.80 K and transition widths of 0.05 K.

Nitriding temperatures of 775°C to 1400°C were used in an attempt to optimize the conditions for VN formation. This produced a wide range of T_C values ranging from 3.45 K to a maximum at 8.84 K; the highest value reported for bulk VN is 9.25 K (Zhao et al., 1984). The optimum nitriding temperature was found to be 825°C. Films formed below this temperature had the lowest T_C and residual resistivity values. Samples formed above 825°C also had lower T_C values; however, T_C decreased slowly with increasing nitriding temperature and, except for the films formed at 1400°C, still had T_C values greater than or equal to 7.9 K and residual resistivities of less than about 80 $\mu\Omega$ -cm.

The films nitrided at 1400°C had transition temperatures of about 4 K and residual resistivities on the order of 300 $\mu\Omega$ -cm. All of the VN films were highly reflective and pale golden in color, representative of B1 phase (rocksalt structured) vanadium nitride (Ajami and MacCrone, 1975). X-ray diffraction studies showed only peaks associated with the B1 phase except for an occasional peak from the sapphire substrate.

It has been shown that VN_x samples have transition temperatures that increase as x approaches 1 (Toth et al., 1966, and Ajami and MacCrone, 1975) and, in separate work, it has been shown, through

equilibrium nitrogen vapor pressure measurements, that, in one atmosphere of N_2 , x decreases with increasing temperature (Kieda et al., 1984). This may be a possible explanation for the observed nitriding temperature dependence; however, X-ray diffraction studies were inconclusive in that the expected decrease in lattice constant was not observed.

Some correlation was also observed between the quality of the starting V film and the resulting VN film. While the quality of the V metal films appeared to be correlated with the substrate temperature, this had no effect on the resulting VN. However, the quality of a VN film did appear to be dependent on the pressure during evaporation of the V film from which it was formed. All the VN samples used in this study were formed from V metal evaporated onto ambient temperature substrates.

2. Titanium Nitride

For evaporation source material for the titanium metal films 99.999% pure titanium was used. The titanium metal, cut from a rod into sections of approximately 1/2 in. in length, was etched in Titanium Etchant TFT, manufactured by the Transene Company, Inc., for etching Ti films in the microelectronics industry.

Three evaporations were performed with substrate temperatures of 150°C, 350°C and ambient. The pressures during these evaporations were 2.9×10^{-7} Torr, 2.0×10^{-6} Torr and 7.0×10^{-7} Torr, respectively, while the deposition rate was 3.5 nm/sec for all runs. All the resulting Ti films were highly reflective and silver in color. Films from the three evaporations had r values of 5.00, 2.00 and 2.30,

respectively, indicating that the quality of the Ti film is more strongly dependent on the residual gas pressure during evaporation than substrate temperature.

In an attempt to optimize the nitriding conditions, temperatures of 950°C to 1400°C were used. These produced films with transition temperatures of 3.19 K to 4.49 K, bulk TiN has been observed with a T_C of 5.5 K (Pessall et al., 1967), with the films with the highest T_C values being formed at 1250°C. The quality of the TiN films, unlike VN, were correlated with the substrate temperature, as well as the pressure, during Ti deposition, with the best films, as judged by the transition temperature, being formed from the titanium films made in the second evaporation run. The TiN films formed from the Ti evaporated onto ambient temperature substrates were of poor quality. All the films were highly reflective and bright golden in color as has been reported for TiN (Toth, 1971, p.7) and X-ray diffraction showed only B1 phase peaks.

D. ION INDUCED DAMAGE EXPERIMENTS

All ion irradiations performed in this study were carried out on the ion implantation equipment at the Surface Modification and Characterization Facility of the Solid State Division at the Oak Ridge National Laboratory. This consists of a 35 to 500 kV linear accelerator with variable source material capability. The beam, exiting the accelerator, proceeds through beam steering components where the beam can be electromagnetically rastered to increase its

diameter. From there it enters the implantation chamber through an aperture, of 3.77 cm² area, which defines the maximum implanted area.

The dose of ions striking the sample during an irradiation is measured in terms of the fluence of incident ions. Fluence is defined as the number of ions per square centimeter incident upon the target. The implantation sample holder is connected to counting electronics which integrate the beam current over the time of irradiation in order to measure the amount of accumulated charge. By knowing the area of the ion beam and the charge of the ion species, one can determine the fluence of a particular irradiation once the accumulated charge is measured. The implantation sample holder is surrounded by a cylindrical grid, held at a negative potential, which acts as a suppressor for secondary electrons emitted from the sample, thus aiding in a reliable fluence determination. The beam can be diverted electromagnetically when not in use to prevent accidental irradiation of the sample.

All irradiations were performed with nitrogen ions in order to introduce no new chemical impurities. To produce a fairly uniform damage energy profile two beam energies were used for each implantation. These were 45 and 340 keV ions in a ratio of 1 to 15. Energy deposition profiles, calculated from the computer program E-DEP-1 (Manning and Mueller, 1974) for these energies, are discussed in section III,A.

The samples, during irradiation, were kept at room temperature at all times. The pressure in the implantation chamber during irradiation was approximately 1×10^{-6} Torr. The 45 keV ions were

produced by accelerating N^+ ions through 45 kV while the 340 keV ions were obtained by accelerating N^{++} ions through 170 kV. The average current of incident ions was less than or equal to 3 μA , thus no greater than 0.5 watts of power was delivered to the sample at any time.

E. ANNEALING EXPERIMENTS

In an attempt to determine whether the damage induced by the ion irradiations was reversible, as had been indicated previously (Thompson et al., 1985), an annealing study was undertaken. Selected irradiated samples of VN and TiN were annealed at progressively higher temperatures, either in vacuum or in a nitrogen atmosphere. The anneals were performed in the UHV annealing furnace described in section C. All anneals were performed at constant temperature for 10 minutes, after which the samples were characterized before another anneal was performed.

The temperature of the susceptor and samples was measured with the optical pyrometers, as described in section C, for temperatures greater than or equal to 800°C. The above mentioned Mo susceptor was used in this temperature range. For temperatures less than 800°C a susceptor made of tantalum was used. This susceptor was fabricated from a cylindrical rod of Ta metal 7/8 in. in diameter and 2 1/2 in. long. A hole, 0.525 in. (in order to accommodate 1/2 in. wide substrates) and off center, was drilled in one end to a depth of 2 in. A tapped hole was fashioned in the top of the rod so a 1/8 in. Ta rod

could be screwed into it. This small rod was then attached to a 2 3/4 in. conflat flange in the same manner as described in section C.

The conflat was equipped with a 1/16 in. Cajon Ultra-Torr fitting so that a type K thermocouple, sheathed in a 1/16 in. O.D. monel capillary, could be passed through it into the vacuum chamber. This thermocouple was inserted into a 1/16 in. hole in the top of the susceptor, just deep enough so that the end of the thermocouple was at the middle of the susceptor. The thermocouple, after exiting the vacuum chamber, was connected to a temperature/voltage converter, model TC-253, made by the Beckman Co., which was calibrated to accept the voltage from a type K thermocouple, compensate it for room temperature, and output a voltage proportional to temperature, 1 mV per degree C. This converter was connected to a digital voltmeter so that the sample and susceptor temperature could be read directly. This arrangement was used to measure temperatures up to 800°C; however, it was calibrated up to 1100°C.

1. Vacuum Anneals

Before heating the samples, the vacuum chamber was pumped out overnight during which it was baked to remove any water molecules adhering to the surface, thus causing the pressure to be high. This was accomplished in the manner described in section C. The next day after the chamber had cooled off, pressures of 7 to 10 X 10⁻¹⁰ Torr were observed.

The samples were annealed at temperatures from 200°C to 1600°C in constant temperature steps. Below 500°C in vacuum the temperature was very difficult to control; therefore, the temperature was taken to be

the average temperature over ten minutes. After heating for 10 minutes the furnace power was shut off and the samples and susceptor were allowed to cool at the natural rate of the furnace under vacuum to about 80°C before they were removed. In vacuum this took about 30 minutes at temperatures below approximately 800°C and up to an hour for higher temperatures.

2. Nitrogen Anneals

Before annealing in nitrogen, the vacuum chamber was pumped out overnight; however, it was not baked. This resulted in pressures of 2 to 5×10^{-9} Torr. The vacuum chamber was back-filled with approximately 1 atm. of 99.9995% pure N₂ gas in the same manner as described in section C. Anneals were performed in constant temperature steps at temperatures of 200°C to 1500°C. After heating, the power was shut off and the samples and susceptor were allowed to cool. The samples were not removed until they reached 80°C. This required approximately 10 minutes, much faster than in vacuum due to the extra heat conduction provided by the gas.

III. THEORETICAL BACKGROUND

A. RADIATION DAMAGE

In order to quantify the amount of damage produced by ion irradiation the energy deposited in the lattice from the bombarding ions must be determined. This is achieved by calculating the energy lost in slowing down the ion. The first part of this section will present a brief description of the calculations involved and how they were made. The second part will describe the actual irradiation process.

1. Energy Deposition

In order to determine the amount of energy transferred to the lattice atoms one must first calculate the damage energy deposition profile; that is, the amount of energy deposited in the lattice to create atomic displacements per unit depth in the film as a function of depth. This is accomplished by calculating the amount of energy lost by a projectile ion in collisions with the target ions. From this the range of the ion (that is, the distance the ion travels in the target) and the dispersion in the range (the RMS standard deviation in the range) can be calculated. Then, from these quantities, the damage energy deposition profile may be determined. This process has been described in detail in the literature (Billington and Crawford, Jr., 1961; Carter and Colligon, 1968; Thompson, 1969), thus the following is a synopsis of this procedure followed by a discussion of the production of defects.

Consider the interaction of a beam of energetic ions with a solid target as a series of binary collisions. The specific energy loss of the incident ion dE/dx , where E is the energy of the ion and x is the depth within the target, is then defined as the energy lost by that ion per unit depth into the target and is given by (Bohr, 1948)

$$\frac{dE}{dx} = S N = N \int T d\sigma, \quad (\text{III.1})$$

where S is the stopping cross section per target atom, N is the number of scattering centers (target atoms) per unit volume and T is the energy transferred from the ion to the target atom. The collision consists of two types, elastic (due to collisions of the ion with the nucleus of the target atom) and inelastic (due to the excitation of the electrons of the target atom by the incident ion), which are assumed to be not correlated (Lindhard et al., 1963b). Thus the two contributions can be separated and we can write

$$\frac{dE}{dx} = \left(\frac{dE}{dx}\right)_e + \left(\frac{dE}{dx}\right)_n = N(S_e + S_n), \quad (\text{III.2})$$

where the subscripts e and n indicate electronic and nuclear stopping, respectively.

The electronic stopping cross section is quite complex. At high incident ion energies S_e has a maximum at v_1 given by $v_1 = v_0 Z_1^{2/3}$, where $v_0 = e^2/\hbar$, the Bohr velocity, and Z_1 is the atomic number of the incident ion (Lindhard et al., 1963b; this work is known as the LSS theory). Above this velocity (which, for nitrogen ions, is 8×10^8 cm/sec or 4.6 MeV) S_e decreases as $1/E$. In the lower energy regions, which were used in this work, the electronic stopping cross section is

found to be proportional to the square root of the energy (Lindhard and Scharff, 1961):

$$\frac{d\varepsilon}{d\rho} = k\varepsilon^{1/2},$$

where ε and ρ are reduced energy and range variables, respectively, as introduced by Lindhard et al. (1963b) and are given by

$$\varepsilon = E \frac{aM_2}{Z_1 Z_2 e^2 (M_1 + M_2)} \text{ and}$$

$$\rho = RN^4 \pi a^2 \frac{M_1 M_2}{(M_1 + M_2)^2}$$

where Z and M are atomic numbers and masses, respectively, the subscripts 1 and 2 referring to projectile and target, respectively, R is the range of the ion, and a is the Thomas-Fermi screening length given by

$$a = 0.885 a_0 (Z_1^{2/3} + Z_2^{2/3})^{-1/2},$$

where $a_0 = 0.53 \text{ \AA}$ = Bohr Radius. The constant of proportionality k is projectile and target dependent and is given by

$$k = 0.079 Z_1^{1/6} \frac{Z_1 Z_2}{Z}^{1/2} \frac{M_2}{M_0^{3/2}}, \text{ where}$$

$$Z^{2/3} = Z_1^{2/3} + Z_2^{2/3}, \text{ and}$$

$$M_0 = \frac{M_1 M_2}{M_1 + M_2}.$$

The nuclear stopping cross section is then given by

$$S_n = \int_{T_d}^{T_m} T d\sigma(E, T), \quad (\text{III.3})$$

where T_m is the maximum energy transferred to a target atom, T_d is the minimum energy necessary to displace a target atom (usually called the displacement energy) and $d\sigma$ is the differential cross section for energy transfer to the target atom for transferred energies between T

and $T + dT$ for a projectile with initial energy E . Since the beam energies are usually on the order of tens to hundreds of keV and T_d is on the order of 20 eV, T_d is most often set equal to zero for this calculation. The nuclear stopping cross section is derived by considering the collision as a classical two body scattering problem. The differential cross section for scattering is $d\sigma = 2\pi p dp$ where p is the impact parameter. The cross section for energy transfer is derived by relating the impact parameter to the scattering angle θ and then relating θ to the transferred energy T . This is accomplished by use of the general solution for the motion of 2 bodies in a central force field. The connection between the scattering angle and p is given by the scattering integral (Goldstein, 1965, pp. 58-85)

$$\theta = \pi - 2p \int_{r_{\min}}^{\infty} \frac{dr}{r^2(1 - V(r)/E_r - p^2/r^2)^{1/2}},$$

where r = the interatomic distance,

$r_{\min}$ = the minimum approach distance,

$E_r = \frac{M_2}{M_1 + M_2} E$, and

$V(r)$ = the interatomic potential.

Since this is a conservative system, the connection between T and θ can be obtained by considering asymptotic values of the momentum and energy and applying the conservation laws. This results in

$$T = T_m \sin^2 \theta / 2, \quad T_m = \frac{4M_1 M_2}{(M_1 + M_2)^2} E.$$

In order to solve the scattering integral some form for the interatomic potential must be assumed. The integral can be analytically solved for potentials of the form $V(r) = C/r^s$ (Lindhard et al., 1968), where C is a constant and $s = 0$ (hard core potential),

1 (Coulomb potential), 2 (Nielsen potential), and so on; however, the potentials that best describe the true interatomic potential are derived from the Thomas-Fermi statistical model of the atom. This potential is given by

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \phi(r/a),$$

where a is the Thomas-Fermi screening length and $\phi(r/a)$ is the screening function which is complex. Using this potential and their reduced range and energy parameters introduced above, Lindhard et al. (1963b) solved the scattering integral numerically and obtained the differential cross section

$$d\sigma = \pi a^2 f(t^{1/2}) \frac{dt}{2t^{3/2}}$$

where $t = \epsilon^2 \sin^2 \theta / 2$ and $f(t^{1/2})$ is a numerically evaluated function.

Winterbon et al. (1970) have approximated this function with

$$f(t^{1/2}) \approx \lambda t^{1/6} [1 + (2 \lambda t^{2/3})^{2/3}]^{-3/2}$$

$$\lambda \equiv 1.309.$$

Inserting this differential cross section into equation III.3 gives a universal expression for the nuclear stopping cross section (Lindhard et al., 1963b)

$$S_n = -4\pi a^2 \frac{M_1}{M_1 + M_2} \frac{Z_1 Z_2 e^2}{a} \left(\frac{d\epsilon}{d\rho} \right)_n,$$

$$\text{where } \left(\frac{d\epsilon}{d\rho} \right)_n = \frac{\ln \epsilon}{2\epsilon(1 - \epsilon^{-3/2})}.$$

The total specific energy loss is then calculated by substituting these values for S_e and S_n into equation III.3.

The range of the ion and related parameters may now be determined from the specific energy loss; however, a discussion of range concepts

is first necessary. The range R is defined as the actual distance traversed by the ion along its path through the target material. Since each individual ion will have a different history of collisions, it is expected that there will be some distribution of ranges for any given projectile ion energy. This distribution is assumed to be Gaussian (Lindhard et al., 1963b) with a maximum at $\langle R \rangle$, the average range, and RMS deviation $\langle \Delta R \rangle$, the range dispersion. The distribution is defined by

$$f(r) = [(2\pi)^{1/2} \langle \Delta R \rangle]^{-1} \exp\{-(r - \langle R \rangle)^2 / 2 \langle \Delta R \rangle^2\},$$

where r is the distance along the ion path. A quantity of more experimental interest is the projected range R_p , which is defined as the distance the ion travels within the target as measured from the surface of the target along the incident direction of the ion. This quantity also will have some distribution, assumed to be Gaussian, defined by

$$f(x) = [(2\pi)^{1/2} \langle \Delta R_p \rangle]^{-1} \exp\{-(x - \langle R_p \rangle)^2 / 2 \langle \Delta R_p \rangle^2\},$$

where $\langle R_p \rangle$ is the average projected range, $\langle \Delta R_p \rangle$ is the dispersion in the projected range, and x is the distance from the surface of the target measured parallel to the direction of incidence.

The average range, range dispersion, average projected range, and the projected range dispersion can be derived as follows (Lindhard et al., 1963b). Let $p(R, E)dR$ be the probability that the total range lies between R and $R + dR$. Then

$$\int_0^{\infty} p(R, E) dR = 1 \text{ and } \langle R^m \rangle = \int_0^{\infty} p(R, E) R^m dR.$$

Suppose the particle with energy E moves a distance δR through a medium containing N atoms per unit volume, then there is a probability

$N\delta R d\sigma$ for a collision with energy transfer T specified by $d\sigma$ which contains both electronic and nuclear contributions. If the collision takes place the particle has the probability $p(R-\delta R, E-T)$ of obtaining the total range R . Multiplying this by the probability of collision we get the contribution to the probability of the total range R from this collision. Next, sum over all possible collisions and add the probability that no collision takes place, $(1-N\delta R/d\sigma)p(R-\delta R, E)$, to obtain the expression

$$p(R, E) = N\delta R \int d\sigma p(R-\delta R, E-T) + (1-N\delta R \int d\sigma) p(R-\delta R, E).$$

Taking the limit as $\delta R \rightarrow 0$ we obtain

$$\frac{\partial p(R, E)}{\partial R} = N \int d\sigma \{p(R, E-T) - p(R, E)\} \quad (\text{III.4})$$

which is the basic integral equation for the probability distribution of the range.

To derive the moments of the range $\langle R^m \rangle$ multiply equation III.4 by R^m and integrate by parts. This gives

$$m \langle R^{m-1}(E) \rangle = N \int d\sigma \{ \langle R^m(E) \rangle - \langle R^m(E-T) \rangle \}, \quad (\text{III.5})$$

thus the average range is given by setting $m = 1$

$$1 = N \int d\sigma \{ \langle R(E) \rangle - \langle R(E-T) \rangle \}. \quad (\text{III.6})$$

To solve this integral equation make a series expansion in T , since the energy transferred to a target atom in a collision is small compared to E . Keeping only first order terms (for a comparison to values obtained using higher order terms see Lindhard et al., 1963b pp. 22-23)

$$\langle R(E) \rangle = \int_0^E \frac{dE'}{NS(E)} = \int_0^E \frac{dE'}{(dE/dx)}$$

where $S(E) = \int T d\sigma$ as before and dE/dx is just the specific energy loss from before.

The range dispersion is calculated from

$$\langle \Delta R^2 \rangle = \langle R^2(E) \rangle - \langle R(E) \rangle^2,$$

thus the second moment of R must be calculated from equation III.5.

Next, multiply equation III.6 by $2\langle R(E) \rangle$ and subtract it from the second moment yielding

$$\int d\sigma \{ \langle \Delta R^2(E) \rangle - \langle \Delta R^2(E-T) \rangle \} = \int d\sigma \{ \langle R(E) \rangle - \langle R(E-T) \rangle \}^2.$$

Now make a series expansion in T , as before, and keep only the first order terms on both sides of the equation. This results in

$$S(E) \frac{d \langle \Delta R^2 \rangle}{dE} = \Omega^2(E) \left(\frac{d \langle R \rangle}{dE} \right)^2$$

$$\text{where } \Omega^2 = \int T^2 d\sigma.$$

Substituting the value for $\langle R \rangle$ from before one obtains

$$\langle \Delta R^2 \rangle = \frac{1}{N^2} \int_0^E \frac{dE' \Omega^2(E')}{S^3(E')} = \int_0^E \frac{dE' N \Omega^2(E')}{(dE'/dx)^3}.$$

The average projected range may be derived from the same equations as the average range with some modification. Equation III.6 then becomes

$$1 = N \int d\sigma \{ \langle R_p(E) \rangle - \langle R_p(E-T) \rangle \cos \theta \}$$

where θ is the scattering of the ion. If we again use a series expansion in T this equation becomes

$$1 = \langle R_p(E) \rangle N \int d\sigma (1 - \cos \theta) + \frac{d \langle R_p(E) \rangle}{dE} N \int d\sigma T \cos \theta.$$

Lets define the transport mean free path λ_{tr} and the transport stopping cross section S_{tr} as

$$\frac{1}{\lambda_{tr}} = N \int d\sigma (1 - \cos \theta) \quad \text{and} \quad S_{tr} = \int d\sigma T \cos \theta.$$

The $\langle R_p \rangle$ equation becomes

$$1 = \frac{\langle R_p(E) \rangle}{\lambda_{tr}(E)} + \frac{d\langle R_p(E) \rangle}{dE} N \text{ Str}(E) ,$$

which has the solution

$$\langle R_p(E) \rangle = \int_0^E \frac{dE'}{N \text{ Str}(E')} \exp \left\{ \int_E^{E'} \frac{dE''}{\lambda_{tr}(E'') N \text{ Str}(E'')} \right\} .$$

The projected range dispersion is much more complicated to derive. If one treats the second moment of the projected range, the square of the average range projected on the plane perpendicular to the direction of incidence must be introduced as well as the square of the average distance between the starting and ending points (see Figure III.1); therefore, the five equations needed for finding $\langle \Delta R_p \rangle$ are given below and the reader is referred to Lindhard et al. (1963b). The equations are

$$2\langle R_p(E) \rangle = N \int d\sigma \{ \langle R_C^2(E) \rangle - \langle R_C^2(E-T) \rangle \} ,$$

$$2\langle R_p(E) \rangle = N \int d\sigma \{ \langle R_r^2(E) \rangle - [1 - (3/2)\sin^2\theta] \langle R_r^2(E-T) \rangle \} ,$$

$$\langle R_C^2 \rangle = \langle R_p^2 \rangle + \langle R_{\perp}^2 \rangle , \text{ and } \langle R_r^2 \rangle = \langle R_p^2 \rangle - (1/2) \langle R_{\perp}^2 \rangle .$$

With these quantities determined the energy deposition profile may now be calculated. In order to proceed the distribution of ion energies $E_1(x)$ at depth x must be known. This is determined by assuming that $E_1(x)$ is related to the projected range distribution $f(x)$ (Kulcinski et al., 1971). It should be noted at this point that the energy transferred to the electrons in the slowing down of the projectile ion is not available to do damage to the target lattice; that is, the energy transferred to the electrons only excites them, thus possibly producing heat in the target, but does not contribute to displacing any target atoms. However, the energy absorbed by the

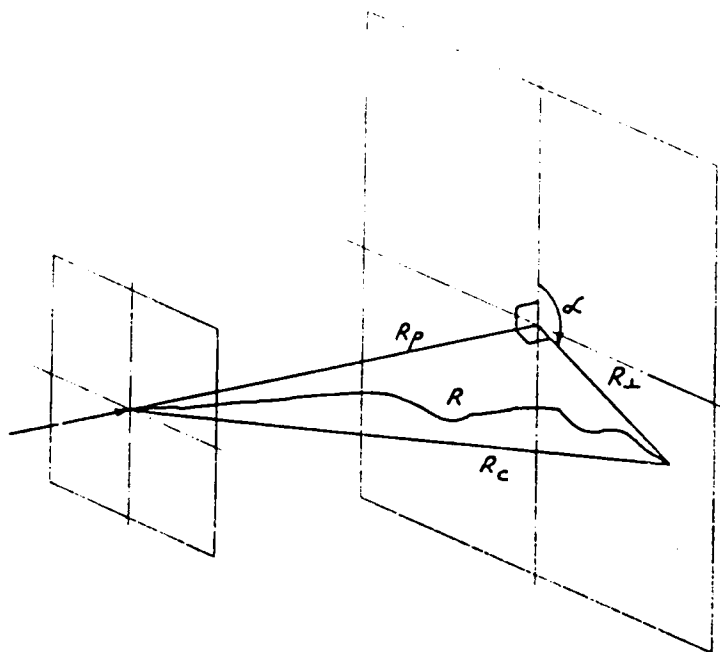


Figure III.1. A schematic diagram of the projected range R_p . It includes the range projected on the plane perpendicular to the direction of incidence $R_\perp$, and the distance between the starting and ending points for an ion traveling through a solid (Lindhard et al., 1963b).

electrons does reduce the amount of energy available for atomic displacement thus it must be considered in the energy deposition profile.

With this in mind the damage energy deposition profile $(dE/dx)(x)$, that is the energy deposited in the target lattice to displace atoms in units of energy per unit depth per ion with a given initial energy, is given by (Lindhard et al., 1963a)

$$\frac{dE}{dx}(x) = \int_x^\infty f(x') \left(\frac{dE}{dx} \right)_1(E_1(x'-x)) \frac{dR(x'-x)}{dx'} dx',$$

where R is the range. The specific energy loss $(dE/dx)_1$ is very similar to that described above and is given by

$$\left(\frac{dE}{dx} \right)_1(E) = \int_{T_d}^{T_m} T n(T) d\sigma,$$

where, as before, T_d is the energy required to displace an atom and T_m is the maximum energy transferred. The differential cross section includes only the elastic (nuclear) term calculated from the Thomas-Fermi potential above. The function $n(T)$ (Lindhard et al., 1963a) is included to account for the energy lost to inelastic collisions with the electrons and is given by (Robinson, 1971)

$$n(T) = [1 + kg(\epsilon)]^{-1},$$

$$\text{where } g(\epsilon) = \epsilon + 0.40244 \epsilon^{3/4} + 3.4008 \epsilon^{1/6}.$$

In this expression ϵ is the reduced energy parameter of Lindhard et al. (1963b), given above, for energy T and k is the constant of proportionality from the expression for energy transfer to the electrons. Thus the damage energy deposition profile is determined.

The above mentioned calculations were actually performed using the computer software package E-DEP-1 (Manning and Mueller, 1974).

Using this program, one inputs the projectile ion's energy, atomic number and atomic mass, the atomic number and atom mass of each of the constituent atoms in the target along with the atomic densities (targets with multiple atomic species may be used). The software outputs a table of deposited energy per unit depth vs depth as well as all the average projected range data for the given projectile-target combination. All irradiations were performed with nitrogen ions in order to introduce no new chemical impurities. Fairly uniform damage energy profiles are obtained by using 45 and 340 keV beam energies for each irradiation in a ratio of 1 to 15. Energy deposition profiles, calculated from E-DEP-1 for these energies, are shown in Figure III.2 for VN and Figure III.3 for TiN. Using these profiles an average deposited energy per unit depth per incident ion of 706 MeV/cm-ion for VN and 637 MeV/cm-ion for TiN is calculated.

2. Defect Production

Once the damage energy profile is known the amount of damage suffered by the target lattice can be estimated. Assuming the damage energy profile is fairly uniform it can be approximated by a uniform (that is, flat as a function of depth) profile equal to the deposited energy, averaged over the thickness of the film. This value is the average deposited energy per unit depth per incident ion, $\langle dE/dx \rangle$. The number of ions incident upon the target in a given irradiation is called the fluence ϕ and is in units of ions per square centimeter. By multiplying the fluence by $\langle dE/dx \rangle$ one obtains the total amount of energy per unit volume, the energy density, deposited in an irradiation. This is then divided by the atomic density of the target

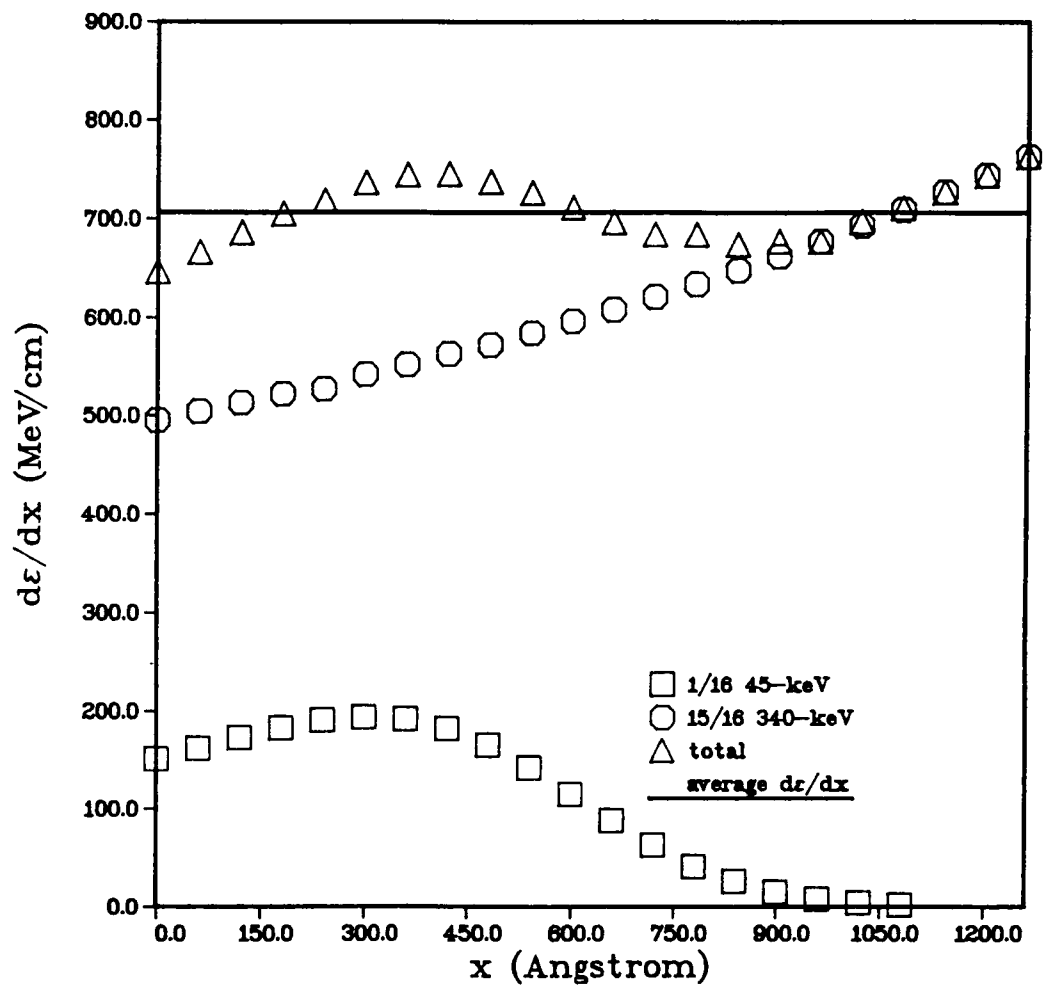


Figure III.2. The damage energy deposition profile for vanadium nitride.

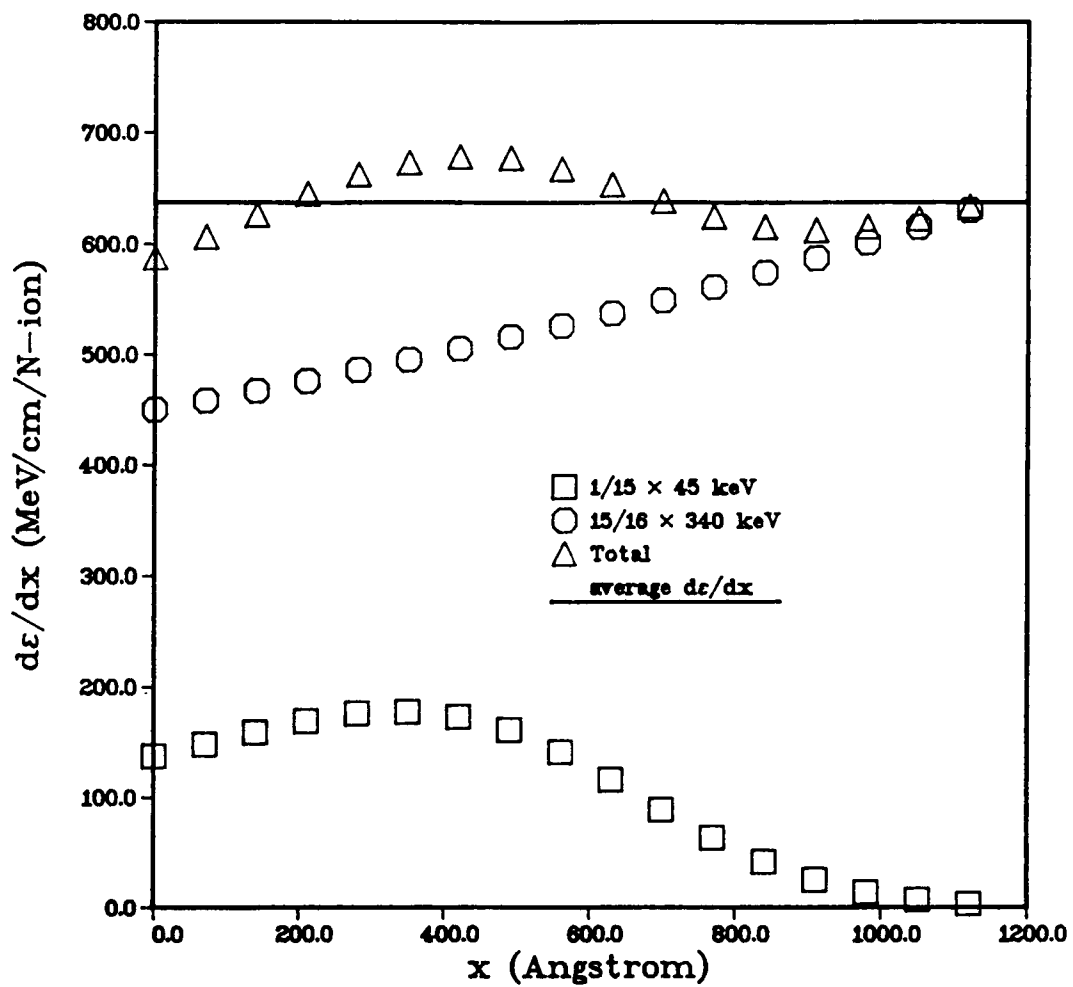


Figure III.3. The damage energy deposition profile for titanium nitride.

to get the amount of energy per target atom E_A deposited in the target. The number of displaced atoms N_d is then calculated from (Kinchin and Pease, 1955)

$$N_d = \frac{0.8 E_A}{2 T_d},$$

where T_d is the energy necessary to displace a target atom. The complication that arises is that T_d is not a well known quantity and is very difficult to determine. In this study, as is the case in the literature (for example, Kobayashi et al., 1985), an estimate of 20 eV was used.

Another problem that arises is that this formula does not take into account any annealing or saturation effects. Since the ion irradiation experiments were carried out at room temperature there is a finite probability that some of the defects produced may be annealed out during the irradiation process; that is, there may be enough thermal energy to enable recombination of vacancies and displaced atoms (interstitials). Saturation effects are similar to annealing effects in that they involve recombination of vacancies and interstitials. Here, so many displacements have been produced that any additional displaced atoms easily find their way to a vacancy thus producing no increase in the number of defects. These complications must be accounted for empirically.

B. SUPERCONDUCTIVE TRANSITION TEMPERATURE

The theoretical development involved in the calculation of the superconducting transition temperature is a very complicated one. It involves the electronic properties, the phononic properties, and the

interaction between these two systems for a given material. In this section we will present a relatively simple discussion of the basic theory involved in these calculations. An thorough review of the theory of the transition temperature is given by Allen and Mitrovic' (1982), while a much more brief and readable overview is given by Butler (1981).

The original quantum mechanical work on the calculation of the superconducting transition temperature was presented in the landmark work of Bardeen, Cooper, and Schrieffer (1957). In this work, known as the BCS theory, they showed that if an attractive interaction exists between the conduction electrons in a metal, no matter how small, then a state exists where the electrons form pairs, called Cooper pairs (Cooper, 1956), which are bound states made up of an electron in band state k with spin up and an electron in band state $-k$ with spin down (the time reversed state). The total energy of this pair was found to be less than the sum of the energies of the states from which the electrons came.

The attractive interaction responsible for the superconducting transition comes about indirectly through the interaction of the electrons with phonons. In a very simplified picture this can be understood by the following scenario. As an electron passes through the lattice of positively charged ions it attracts them causing them to move in toward the electron. However, due to the large mass of the ions, their response is slow and the electron will have moved away by the time they have reached their maximum displacement. This time is about 10^{-13} seconds ($\approx 1/\omega_{ph}$, where ω_{ph} is a typical phonon frequency)

and in this time the electrons, traveling at about 10^8 cm/s, will have traveled several hundred lattice spacings. Therefore, the electron will leave a wake of positively charged lattice polarization far behind it. A second electron will see this positive charge and be attracted to it resulting in a net attraction between the electrons. The Coulomb repulsion of the two electrons is greatly reduced since the slow response of the lattice allows the two electrons to be separated by a large distance.

This attractive interaction can be derived from a simple physical picture. In the following we have generally followed the scheme of Butler (1981). Consider an electron in a crystal lattice at a position x at time t . This electron will feel a force caused by the potential fields of the surrounding ions at positions $\{R_l\}$. If the potential at position x is $V(x, \{R_l\})$, then by translational invariance $V(x+\delta, \{R_l\}) = V(x, \{R_l+\delta\})$. Then the total force exerted on the lattice in the direction α by the electron is given by

$$F_{\alpha}^T = V_{\alpha} V(x, \{R_l\}) = - \sum_l \frac{\delta V(x, \{R_l\})}{\delta R_{l\alpha}}.$$

The force on an ion at R_l in the direction α due to an electron at (x, t) is then $F_{l\alpha}(t) = -\delta V / \delta R_{l\alpha}$.

The force exerted on an ion at position l and time t will propagate through the lattice causing the other ions to be displaced. The function that generates the displacement in direction β of the ion at $R_{l'}$ at time t' due to a force exerted in the direction α on the ion at R_l at time t is called the lattice Green's function or propagator $D_{\beta\alpha}(l', l; t'-t)$ and the displacements are given by

$$u_{1'\beta}(t') = \sum_{1\alpha} \int dt D_{\alpha\beta}(1',1;t'-t) F_{1\alpha}(t) .$$

The calculation of this for a harmonic lattice is given in Reissland (1973). The change in energy of an electron at (x',t') due to these displacements is then

$$\delta V = \sum_{1'\beta} \frac{\delta V(x',\{R_1\})}{\delta R_{1'\beta}} u_{1'\beta}(t) ,$$

and the change in energy of an electron at (x',t') due to an electron at (x,t) for time Δt is

$$v(x',t';x,t) = - \sum_{1'\beta,1\alpha} \frac{\delta V(x')}{\delta R_{1'\beta}} D_{\beta\alpha}(1',1;t'-t) \frac{\delta V(x)}{\delta R_{1\alpha}} \Delta t .$$

This interaction can be converted to a function of energy and momentum by noting that the electron with wave function $\psi_k(x)\exp(i\epsilon_k t/\hbar)$ is annihilated at (x,t) while an electron with wave function $\psi_{k'}(x)\exp(i\epsilon_{k'} t/\hbar)$ is created there and the same holds true for the electron at (x',t') except for time reversal. The electron spins are ignored here because they are not affected by the electron-phonon interaction. Then the interaction can be written

$$v(k,k';\epsilon_k-\epsilon_{k'}) = \frac{1}{V_a^2} \int d^3x' \int d^3x d\tau \sum_{11'\beta\alpha} \psi_{-k'}^*(x') \frac{\delta V(x')}{\delta R_{1'\beta}} \psi_{-k}(x') \\ \times D_{\beta\alpha}(1',1,\tau) \psi_k^*(x) \frac{\delta V(x)}{\delta R_{1\alpha}} \psi_k(x) \exp[i(\epsilon_k-\epsilon_{k'})\tau/\hbar],$$

where V_a is the volume per atom. By using the Bloch property of the wave function $\psi_k(x+R_1) = \psi_k(x) \exp(ik \cdot R_1)$, time reversal symmetry $\psi_k(x) = \psi_{-k}^*(x)$, and the translational symmetry of $V(x,\{R_1\})$ one can write

$$\int d^3x \psi_k^*(x) \frac{\delta V(x)}{\delta R_{1\alpha}} \psi_k(x) = \exp[i(k-k') \cdot R_1] V_a I_{\alpha k'k},$$

where $I\alpha_{k'k}$ is the electronic part of the electron-phonon matrix element. Using this equation and the expression for the phonon propagator

$$D_{\beta\alpha}(l',l;t'-t) = -\theta(t'-t) \sum_{qj} \frac{\epsilon_j^\beta(q)\epsilon_j^\alpha(q)}{M\omega_j^2(q)} \\ \times \sin[\omega_j^2(q)(t'-t)] \exp[iq \cdot (R_l - R_{l'})],$$

where $\theta(t'-t)$ is the Heavyside step function, $\epsilon_j(q)$ are the phonon polarization vectors and $\omega_j^2(q)$ are the phonon frequencies (Reissland, 1973), one can write the electron-phonon interaction as

$$v(k',k;\epsilon_{k'}-\epsilon_k) = \sum_j |g_{jkk'}|^2 \frac{2\hbar\omega_j^2(q)}{(\epsilon_{k'}-\epsilon_k)^2 - (\hbar\omega_j^2(q))^2},$$

$$\text{where } |g_{jkk'}|^2 = \hbar \sum_{\alpha\beta} \frac{\epsilon_j^\alpha(q)\epsilon_j^\beta(q)}{2M\omega_j^2(q)} \frac{I\alpha_{k'k}}{I\beta_{kk'}},$$

is the square of the electron-phonon matrix element.

Obtaining the phonon mediated electron-electron interaction is only part of the problem in the calculation of the transition temperature. The bound state is obtained by considering the repeated electron-phonon interaction. To do this we shall define $\Delta(k',k;\epsilon_{k'}-\epsilon_k)$ as the total scattering amplitude for electrons in states k and $-k$ to interact and be scattered into states k' and $-k'$. Then the repeated interaction can be represented, in a very simplified notation, algebraically as

$$\Delta = v + vKv + vKvKv + \dots$$

where v represents the electron-electron interaction, given above, and K represents the lowest order approximation to the two particle pair propagator. This may be formally summed to give $\Delta = v + vK\Delta$ (see Butler, 1981). The bound state is formed when the scattering amplitude diverges or equivalently when the equation $\Delta = vK\Delta$ has a

nontrivial solution. Inserting the appropriate indices in this equation we get

$$\Delta(k', k; \epsilon', \epsilon) = \sum_{k''} \int d\epsilon'' v(k', k; \epsilon' - \epsilon'') K(k'', \epsilon'') \Delta(k'', k; \epsilon'', \epsilon).$$

To solve this equation one needs the lowest-order pair propagator

$$K(k, \epsilon) = \frac{1}{(\epsilon - \epsilon_k)} \frac{1}{(-\epsilon - \epsilon_{-k})}.$$

In order to convert this zero-temperature formalism into a formalism useful at finite temperatures we shall use a trick introduced by Matsubara (1955) in which the energies are replaced by the imaginary integral quantities $\epsilon \rightarrow i\epsilon_n = i(2n + 1)\pi k_B T$ (called the Matsubara frequencies). Inserting this we get

$$\Delta(k, k'; \epsilon_n, \epsilon_{n'}) = k_B T \sum_{n''} \sum_{k''j} |g_{jkk''}|^2 \frac{2\hbar\omega_{j_{k-k''}}}{(\epsilon_n - \epsilon_{n''})^2 + (\hbar\omega_{j_{k-k''}})^2} \times \frac{1}{\epsilon_{n''}^2 + \epsilon_{k''}^2} \Delta(k'', k'; \epsilon_{n''}, \epsilon_{n'}).$$

We may now replace the sum over k'' by an integral over energy and an integral over constant energy surfaces in k -space. To do this we make the following change:

$$\sum_k \rightarrow \int d\epsilon \frac{V_a}{(2\pi)^3} \int \frac{dk}{\hbar v_k}.$$

Now we suppress the k' and $\epsilon_{n'}$ arguments and assume that the band structure does not change much over the range of $\pm \omega_{\max}$ around the Fermi surface, where $\omega_{\max}$ is the maximum phonon frequency. This assumption allows the surface integral to be placed at the Fermi energy and the $\epsilon_{n''}$ integral may be done analytically. This yields

$$\Delta(k, n) = \frac{V_a}{N(0)(2\pi)^3} \int \frac{dk'}{\hbar v_{k'}} \sum_{n'} \frac{\lambda_{kk'}(n-n')}{|2n' + 1|} \Delta(k', n'),$$

where we have defined a set of temperature dependent electron-phonon coupling functions

$$\lambda_{kk'}(m) = N(0) \sum_j |g_{jkk'}|^2 \frac{2\hbar\omega_{j\mathbf{k}-\mathbf{k}'}}{(2\pi mk_B T)^2 + (\hbar\omega_{j\mathbf{k}-\mathbf{k}'})^2},$$

and $N(0)$ is the density of electronic states at the Fermi energy (in units of states per energy). The scattering amplitude is usually called the superconducting gap function and these equations are called the linearized gap equations. The gap function represents half the energy gap between the superconducting and normal states (half because there are two electrons in a Cooper pair).

The variation of the gap function with $\mathbf{k}$ along the Fermi surface is known as the gap anisotropy. In our case, and in many materials, impurities and other defects cause much of the anisotropy to be smeared out due to scattering of the electrons, thus the $\mathbf{k}$ dependence of the gap is removed and the integral in $\mathbf{k}$ -space can be evaluated. It is found to just give a factor of $N(0)$ in the gap equation since

$$N(0) = \frac{V_a}{(2\pi)^3} \int \frac{d\mathbf{k}}{\hbar v_{\mathbf{k}}},$$

Then the isotropic gap equation is

$$\Delta(n) = \sum_{n'} \frac{\lambda(n'-n)}{|2n' + 1|} \Delta(n'),$$

where $\lambda(m)$ is a temperature dependent generalization of the isotropic mass enhancement parameter

$$\lambda(m) = \langle \langle \lambda_{kk'} \rangle_{\mathbf{k}} \rangle_{\mathbf{k}'} = 2 \int \frac{\alpha^2(\omega) F(\omega) \omega d\omega}{\omega^2 + (2\pi mk_B T)^2},$$

and where $\langle \rangle_{\mathbf{k}}$ mean a Fermi surface average. The function $\alpha^2 F(\omega)$ is called the phonon spectral function or the Eliashberg function (Eliashberg, 1960 and 1961) and $F(\omega)$ is the phonon density of states.

As mentioned at the beginning of this section this is a simple approach to the theory of the superconducting transition temperature and as such two very important effects have been left out, the Coulomb repulsion of the two electrons in the pair and the electron-phonon mass enhancement of the electrons. The Coulomb repulsion effectively reduces the electron-phonon enhancement parameter $\lambda(m)$. This can be treated in the manner of Morel and Anderson (1962) in which that they argue that since the electrons are separated by a large distance the interaction will be small and can be represented by a parameter similar to the electron-phonon coupling parameter, namely

$$\mu = N(0) \langle \langle V_{C_{kk'}} \rangle_{k,k'} \rangle,$$

where $V_{C_{kk'}}$ is the effective screened Coulomb interaction; however, due to retardation, this is rescaled and the number that enters the theory is actually

$$\mu^* = \frac{\mu}{1 + \mu \ln(\omega_{el}/\Theta_D)},$$

where ω_{el} measures the Coulombic response frequencies and Θ_D is the Debye temperature. This is very difficult to calculate theoretically and is usually found empirically or estimated. At the end of this section we will see that T_C is actually only weakly dependent upon this parameter.

The mass renormalization $Z(n)$ is determined by summing over the mass enhancement parameter in the following manner (see Allen and Mitrovic', 1982):

$$Z(n) = 1 + \frac{1}{|2n + 1|} \sum_{n'} \lambda(n-n'), \quad (III.7)$$

and the isotropic gap equation is given by

$$Z(n)\Delta(n) = \sum_{n'} \frac{\lambda(n-n') - \mu^*}{|2n' + 1|} \Delta(n') . \quad (\text{III.8})$$

These equations are known as the isotropic Eliashberg equations.

An equation for the transition temperature was derived from the Eliashberg equations by McMillan (1968) in a very ingenious manner. He first solved the equations by making the assumption that the gap was equal to a constant at low n and equal to a different constant at high n . From this he determined that the renormalization was given by

$$Z(0) = 1 + \lambda \text{ and}$$

$$Z(\infty) = 1 ,$$

where λ is the zero temperature value of $\lambda(m)$, called the electron-phonon coupling constant. From this approximation he determined an expression for T_C which contained adjustable parameters.

In order to determine these parameters he then numerically solved the Eliashberg equations. To do this he had to assume some form for $\alpha^2(\omega)F(\omega)$. At the time he was interested in the b.c.c. transition metals and their alloys, therefore he chose the phonon spectrum $F(\omega)$ for Nb as determined from neutron scattering measurements and took α to be a constant. The expression for T_C , found by solving the Eliashberg equations, was then fit to the numerical data and the adjustable parameters were determined. This resulted in the famous McMillan equation

$$T_C = \frac{\Theta_D}{1.45} \exp \left[- \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right] .$$

A problem with this equation is that it is restricted to systems that have a phonon spectrum similar to that of Nb. It was found empirically (Allen and Dynes, 1975) that this restriction could be

lifted if the prefactor to the exponential were replaced by $\omega_{\log}/1.20$ where $\omega_{\log}$ is given by

$$\omega_{\log} = \exp\langle \ln(\omega) \rangle,$$

$$\langle \ln(\omega) \rangle = \frac{2}{\lambda} \int d\omega \alpha^2 F(\omega) \frac{\ln(\omega)}{\omega}.$$

This results in the modified McMillan equation

$$T_C = \frac{\omega_{\log}}{1.20} \exp \left[- \frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right], \quad (\text{III.9})$$

which has been used with success in calculating T_C for many materials.

Recently, however, calculations of the band structure of d-band compounds result in transition temperatures that are much too high (Rietschel and Winter, 1979; Rietschel et al., 1980; and Papaconstantopoulos et al., 1985). Often the culprit blamed for this is spin fluctuations or paramagnons. In some metals, where the spin susceptibility is strongly exchange enhanced (Gladstone et al., 1969), there can exist, at low temperatures, medium-range spin order among the electrons. This corresponds to an effective attraction of parallel spins and a repulsion of anti-parallel spins, which counteracts the Cooper pairing required for superconductivity (Allen and Mitrovic', 1982).

The theory leading to the Eliashberg equations has been modified to include electron-paramagnon interactions by Berk and Schrieffer (1966); however, the formalism is very complicated thus for our purposes we shall use the approach of Daams et al. (1981) where, in the isotropic Eliashberg equations, the electron-phonon coupling parameter is reduced by the parameter λ_{sf} , called the spin fluctuation

parameter, which measures the electron-paramagnon interaction. This results in the equations

$$Z^*(n) = 1 + \frac{1}{|2n+1|} \sum_{n'} \frac{\lambda(n-n')}{1 + \lambda_{sf}},$$

$$Z^*(n)\Delta(n) = \sum_{n'} \frac{\lambda(n-n') - \lambda_{sf} - \mu^*}{1 + \lambda_{sf}} \frac{\Delta(n')}{|2n'+1|}.$$

The resulting equation for the transition temperature including the effect of spin fluctuations is the following expression:

$$T_C = 1.13 \Theta_D \exp \left[- \frac{1 + \lambda + \lambda_{sf}}{\lambda - \mu^* - \lambda_{sf}} \right]. \quad (\text{III.10})$$

C. UPPER CRITICAL MAGNETIC FIELD

The effect of an applied magnetic field on the properties of a superconductor has been studied almost from the origin of the discovery of the superconducting state. A phenomenological description valid only near the transition temperature was originally proposed by Ginzburg and Landau (1950). They found that the energy of formation of a superconductor-normal interface could, under certain circumstances, become negative and thus allow the penetration of magnetic flux into a bulk superconducting sample. This situation is known as type II superconductivity and the materials in which this occurs are called type II superconductors. Abrikosov (1957) examined this situation in detail and showed that the superconducting to normal transition in type II materials is second order since the superconducting order parameter goes continuously to zero at the upper critical field (H_{C2}) with increasing field.

Gor'kov (1958, 1959a, and 1959c) later presented a Green's function approach to the BCS theory. From this reformulation he

generalized to the case of a position dependent Cooper pair wave function $\Delta(r)$ (or gap function). Then, in the limit of zero magnetic field, he demonstrated that the BCS theory, which is a microscopic theory, reduced to the phenomenological Ginzburg-Landau theory where the pair wave function is the same as the Ginzburg-Landau order parameter.

Since the gap function goes continuously to zero it was possible to investigate theoretically the upper critical field as a function of temperature at all temperatures by linearizing the Gor'kov equations, which he derived from BCS theory, for small $\Delta(r)$. When this was done a homogeneous integral equation is obtained, with the upper critical field being related to its lowest eigenvalue. Many people have studied this equation, mostly in special cases. Gor'kov (1959b) was the first to do this in the case of infinite mean free path and zero temperature. He found that the eigenvalue equation satisfied a variational principle and calculated a lower bound for H_{C2} at zero temperature. The eigenvalue equation was solved at all temperatures by Maki (1964) and de Gennes (1964) in the limit as the mean free path goes to zero (called the dirty limit).

Helfand and Werthamer (1966) solved the Gor'kov equation for all temperatures and all mean-free-paths; however, they did not include paramagnetic effects due to interactions of the electron spin (Pauli paramagnetism) with the applied magnetic field or spin-orbit scattering due to impurities. Clogston (1962) and Chandrasekhar (1962) have previously pointed out the importance of the electron Zeeman energy in high field superconductors. Their argument was that

the electron spin paramagnetism causes the free energy of the normal state to be lowered relative to the superconducting state, thus lowering the critical field for the transition. Spin-orbit scattering occurs when the electrons, after scattering from impurities, experience a spin flip. This causes an effective reduction in the spin susceptibility of the normal state relative to the superconducting state (Fetter and Hohenberg, 1969), therefore increasing the free energy of the normal state relative to the superconducting state and thus counteracting the effects of Pauli paramagnetism.

Werthamer, Helfand, and Hohenberg (1966) (generally called the WHH theory) solved the Gor'kov equation including these additional interactions by generalizing the results of Helfand and Werthamer (1966). This is the theory generally used for high field superconductors; therefore, we shall present it here. The WHH theory is very complicated so we shall only present a brief outline of the processes involved in obtaining the end-product; the original work provides more detail if needed. There also exist other explanations of the theory in the literature by Werthamer (1969), Fetter and Hohenberg (1969), and Saint-James and Sarma (1969).

The WHH paper begins with several initial assumptions. First, they neglect any strong coupling and assume the BCS model for electron-electron coupling. This is equivalent to assuming that the electron-phonon interaction is constant within an energy ω_D (Debye frequency) of the Fermi energy and zero elsewhere. They further assumed that the spin flip scattering rate is much less than the total

scattering rate. They also performed their analysis in position space rather than momentum space.

We will begin by first considering the case where no paramagnetic effects or spin-orbit scattering exists (following Helfand and Werthamer, 1966). The Hamiltonian for this system is then

$$H = \int d^3r \psi^\dagger(\underline{r}) \left[-\frac{1}{2m} (\nabla - ie\underline{A})^2 \right] \psi(\underline{r}) + \\ \int \int d^3r d^3r' \psi^\dagger(\underline{r}) V'(\underline{r}, \underline{r}') \psi(\underline{r}') + \\ \frac{1}{2} g \int d^3r \psi^\dagger(\underline{r}) \psi^\dagger(\underline{r}) \psi(\underline{r}) \psi(\underline{r}),$$

where ψ and $\psi^\dagger$ are field operators, $\underline{A}$ is the vector potential, g is the BCS electron-electron coupling constant, V' is the impurity potential and the underlines indicate vector quantities. The units used here are $\hbar = c = k_B = 1$. The first integral is due to the motion of a charged particle in a magnetic field. The second integral is due to the scattering of electrons by impurities. The final integral is due to the attractive interaction between electrons which results in the superconductive transition. If $g = 0$ this is the Hamiltonian for a non-superconducting system.

At a second order phase transition where the superconducting gap function $\Delta(\underline{r})$ goes continuously to zero the critical field is the largest field for which there is an eigenfunction of the linear homogeneous integral equation (Gor'kov, 1958 and 1959a)

$$\ln(T_C/T) \Delta(\underline{r}) = \int d^3r' X(\underline{r}, \underline{r}') \Delta(\underline{r}').$$

The kernel $X(\underline{r}, \underline{r}')$ was derived by Rickayzen (1965) by considering electron scattering from static, short-ranged impurities of random distribution and dilute concentration in the method developed in the

field-free case by Edwards (1958) and Abrikosov and Gor'kov (1960).

The result is

$$X(\underline{r}, \underline{r}') = \sum_n \left[\frac{\delta^3(\underline{r} - \underline{r}')}{|2n + 1|} - S_\omega(\underline{r}, \underline{r}') \right], \quad (\text{III.11a})$$

where S_ω satisfies the equation

$$S_\omega(\underline{r}, \underline{r}') = S_\omega^0(\underline{r}, \underline{r}') + (2\pi T)^{-1} \int d^3r_1 S_\omega^0(\underline{r}, \underline{r}_1) S_\omega(\underline{r}_1, \underline{r}') \quad (\text{III.11b})$$

and S_ω^0 is defined by

$$S_\omega^0(\underline{r}, \underline{r}') = \frac{T}{2v_F |\underline{r} - \underline{r}'|^2} \times \exp \left\{ - \left(\frac{2\omega}{v_F} + \frac{1}{\tau} \right) |\underline{r} - \underline{r}'| + 2ie \int_{\underline{r}'}^{\underline{r}} \underline{A}(\underline{s}) \cdot d\underline{s} \right\}, \quad (\text{III.11c})$$

where τ is the electron scattering time and the frequencies are the Matsubara frequencies defined, as in the previous section, by $\omega = (2n + 1)\pi T$ (Matsubara, 1955).

Werthamer et al. (1966) modified this result to the case where paramagnetic effects and spin-orbit scattering are present by considering the Hamiltonian

$$H = \int d^3r \psi^\dagger(\underline{r}) \left[- \frac{1}{2m} (\nabla - ie\underline{A})^2 - \mu \underline{\sigma} \cdot \underline{H} \right] \psi(\underline{r}) + \iint d^3r d^3r' \psi^\dagger(\underline{r}) V(\underline{r}, \underline{r}') \psi(\underline{r}') + \frac{1}{2} g \int d^3r \psi^\dagger(\underline{r}) \psi^\dagger(\underline{r}) \psi(\underline{r}) \psi(\underline{r}),$$

Where the second term in the first integral is due to the paramagnetic susceptibility of the electrons with μ being the Bohr magneton, $\underline{\sigma}$ the Pauli spin vector, and $\underline{H}$ the magnetic field. The term V in the second integral now contains spin flip scattering as well as non-spin flip scattering. (for the details of this potential see the appendix of Werthamer et al., 1966.) Using this Hamiltonian they constructed a 2

X 2 matrix Green's function equation, averaged over impurities (Abrikosov et al., 1963), for the Gor'kov equation and thus generalized equations III.11 to obtain

$$\ln\left(\frac{T_C}{T}\right) \Delta(\underline{r}) = \sum_n \int d^3r' \left[\frac{\delta^3(\underline{r}-\underline{r}')}{|2n+1|} - \frac{1}{2} \text{tr} S_\omega(\underline{r}, \underline{r}') \right] \Delta(\underline{r}'), \quad (\text{III.12a})$$

$$S_\omega(\underline{r}, \underline{r}') = S_\omega^0(\underline{r}, \underline{r}') + \int d^3r_1 S_\omega^0(\underline{r}, \underline{r}_1) \frac{N(0)}{T (\delta^3(0))^2}$$

$$\times \int d^3r_2 \langle V(\underline{r}_1, \underline{r}_2) S_\omega(\underline{r}_1, \underline{r}') \tilde{V}(\underline{r}_2, \underline{r}_1) \rangle, \text{ and} \quad (\text{III.12b})$$

$$S_\omega^0(\underline{r}, \underline{r}') = \frac{T}{2v_F |\underline{r}-\underline{r}'|^2} \exp \left\{ -(2i\mu\sigma \cdot \underline{H} \sin(\omega) + 2|\omega| + \tau^{-1}) \frac{|\underline{r}-\underline{r}'|}{v_F} + 2ie \int_{\underline{r}}^{\underline{r}'} \underline{A}(\underline{s}) \cdot d\underline{s} \right\}, \quad (\text{III.12c})$$

where the trace is only in spin space. The quantity $\tau^{-1} = \tau_1^{-1} + \tau_2^{-1}$ where τ_1 is the spin-independent scattering time and τ_2 is the spin-orbit scattering time. The tildes on the impurity potentials indicate time reversal (that is $\omega \rightarrow -\omega$ and $\sigma \rightarrow -\sigma$) and the angle brackets indicate impurity averages.

To proceed WHH next introduces the auxiliary function $\phi(\underline{r})$ defined as the eigenfunction of the kernel S_ω^0 , with eigenvalue s_ω^0 , so that

$$s_\omega^0 \phi(\underline{r}) = \int d^3r' S_\omega^0(\underline{r}, \underline{r}') \phi(\underline{r}'). \quad (\text{III.13})$$

Then, if ϕ is independent of spin and ω , it is also a solution to the III.12a and we may set $\Delta(\underline{r}) = \phi(\underline{r})$ yielding

$$\ln(T_C/T) = \sum_n \left[\frac{1}{|2n+1|} - \frac{1}{2} \text{tr} s_\omega \right]. \quad (\text{III.14})$$

From equation III.12b we get

$$s_{\omega} = s_{\omega}^0 + s_{\omega}^0 [N(0)/T(\delta 3(0))^2] \int d^3 r_1 \langle V(\underline{r}, \underline{r}_1) s_{\omega} \nabla(\underline{r}_1, \underline{r}) \rangle.$$

Now the spin dependence of s_{ω} is explicitly shown by setting

$$s_{\omega} = s_{\omega}(1) + s_{\omega}(2) \underline{\sigma} \cdot \hat{H} \sin \omega, \quad (\text{III.15})$$

$$s_{\omega}^0 = s_{\omega}^0(1) + s_{\omega}^0(2) \underline{\sigma} \cdot \hat{H} \sin \omega,$$

where $\hat{H}$ is a unit vector in the direction of the field. Then the above equation becomes (see the analysis of the impurity potential in the appendix of Werthamer et al., 1966)

$$s_{\omega} = s_{\omega}^0 \left\{ 1 + [\tau^{-1} s_{\omega}(1) + (\tau^{-1} - (4/3)\tau_2^{-1}) s_{\omega}(2) \underline{\sigma} \cdot H \sin \omega] / 2\pi T \right\}. \quad (\text{III.16})$$

Using III.12c and III.15, WHH evaluated s_{ω}^0 using III.14 and found the result that $s_{\omega}^0(1)$ and $s_{\omega}^0(2)$ are the real and imaginary parts, respectively, of the function I_{ω} defined by

$$I_{\omega} \equiv \left\{ 2\pi T / [v_F (2eH)^{1/2}] \right\} J(\alpha_{\omega}), \quad (\text{III.17})$$

where J is given by

$$J(z) = 2 \int_0^{\infty} d\omega \exp(-\omega^2) \frac{1}{2i} \ln \left[\frac{1 + iz\omega}{1 - iz\omega} \right], \quad (\text{III.18})$$

$$\alpha_{\omega} = v_F (2eH)^{1/2} (2|\omega| + \tau^{-1} + 2i\mu H)^{-1}.$$

Through a rather lengthy algebraic manipulation of equation III.16, using III.17 and III.18, they solved it yielding

$$(1/2) \text{tr } s_{\omega} = \left\{ [\text{Re}(I_{\omega}^{-1} - (\tau^{-1} - (4/3)\tau_2^{-1})/2\pi T)^{-1}] - 1 - (4/3)(2\pi T\tau_2)^{-1} \right\}^{-1}. \quad (\text{III.19})$$

Equations III.14 along with equations III.17 through III.19 now give the theoretical relationship between H and T at a second order transition, that is at H_{C2} , for all temperatures and all mean free paths including paramagnetic effects and spin-orbit scattering.

In the case of our samples of vanadium nitride and titanium nitride, as well as most high field and high temperature

superconductors, we are most interested in the so called dirty limit where the electronic mean free path becomes very small or equivalently the scattering time is very short. This can be best characterized by the transport collision parameter (Helfand and Werthamer, 1966)

$$\lambda_{tr} = 0.882\xi_0/l = \hbar/2\pi k_B T_C \tau,$$

where ξ_0 is the Ginzburg-Landau coherence length (a measure of the spacial extent of the Cooper pair), l is the mean free path and we have added the factors of $\hbar$ and k_B . If this parameter is much greater than one, the dirty limit is justified. For our samples we estimate this parameter to be about 10 for both VN and TiN in the cleanest samples.

Werthamer et al. (1966) introduced the dimensionless variables

$$t = T/T_C, \quad h = (2eH/c)(v_F^2 \tau / 6\pi k_B T_C),$$

$$\alpha = 3\hbar/2m v_F^2 \tau, \quad \lambda_{so} = \hbar/3\pi k_B T_C \tau_2,$$

where we have added the required values of $\hbar$, k_B , and c . The parameter α was first introduced by Maki (1964) and is a measure of the paramagnetic effect on the upper critical field (it is often called the Maki parameter) while λ_{so} is a measure of the spin-orbit scattering rate since it is proportional to the reciprocal of the spin-orbit scattering time τ_2 . Inserting these new variables in the above equations for $H_{C2}(T)$ and applying the dirty limit one obtains the series

$$\ln(1/t) = \sum_n \left\{ \frac{1}{|2n+1|} - \left[|2n+1| + \frac{h}{t} + \frac{(\alpha h/t)^2}{|2n+1| + (h + \lambda_{so})/t} \right]^{-1} \right\}. \quad (\text{III.20})$$

This may be rewritten in the more analytical form

$$\ln(1/t) = \left(\frac{1}{2} + \frac{i\lambda_{SO}}{4\gamma} \right) \psi \left(\frac{1}{2} + \frac{h + (1/2)\lambda_{SO} + i\gamma}{2t} \right) + \left(\frac{1}{2} - \frac{i\lambda_{SO}}{4\gamma} \right) \psi \left(\frac{1}{2} + \frac{h + (1/2)\lambda_{SO} - i\gamma}{2t} \right) - \psi(1/2), \quad (\text{III.21})$$

where $\gamma = [(\alpha h)^2 - (0.5 \lambda_{SO})^2]^{1/2}$ and $\psi(z)$ is the complex digamma function (Abramowitz and Stegun, 1965, p. 258; and appendix A, p. 89 in Allen and Mitrovic', 1982) defined as the derivative with respect to z of the natural logarithm of the gamma function $\Gamma(z)$.

Two interesting parameters which can be obtained from this theory are the value of the upper critical field extrapolated to zero temperature, $H_{C2}(0)$, and the slope of the upper critical field at $t = 1$ ($T = T_C$), H_{C2}' . The slope of the upper critical field may be obtained by first taking the derivative of equation III.21 with respect to temperature. This is accomplished with the formulas for the polygamma function, the multiple derivatives of the digamma function, found in Abramowitz and Stegun (1965, p. 260) and by use of the chain rule. The resulting expression, independent of α and λ_{SO} , is

$$\frac{-1}{T_C} = \psi^{(1)}(1/2) \frac{1}{2} \frac{dh}{dT} \Big|_{T_C},$$

where $\psi^{(1)}$ means the first derivative. Using the expression for this quantity from Abramowitz and Stegun (1965, pp. 260 and 807) it is found to equal $\pi^2/2$, thus we find that

$$\frac{dh}{dT} \Big|_{T_C} = \frac{-4}{T_C \pi^2}. \quad (\text{III.22})$$

From the definition of h we see that

$$\frac{dh}{dT} \Big|_{T_C} = \frac{ev_F^2 \tau}{3\pi c k_B T_C} \frac{dH_{C2}}{dT} \Big|_{T_C} = \frac{ev_F^2 \tau}{3\pi c k_B T_C} H_{C2}',$$

thus applying equation III.22 we find

$$H_{C2}' = - \frac{12ck_B}{\pi e v_F^2 \tau} \quad (\text{III.23})$$

The residual resistivity is given by the equation (Butler, 1981)

$$\rho_0 = \frac{3}{2e^2 N(0) v_F^2 \tau},$$

where $N(0)$ is the density of electronic states at the Fermi energy in units of states per erg per cm^3 per spin, while the coefficient of the electronic heat capacity is given by (Orlando et al., 1979)

$$\gamma = (2/3) \pi^2 k_B^2 N(0).$$

Making these substitutions into equation III.23 and making the appropriate unit conversions results in

$$H_{C2}' = - 4.48 \times 10^4 \rho_0 \gamma,$$

where ρ_0 is in units of $\Omega\text{-cm}$, γ is in $\text{erg}/(\text{cm}^3\text{-K}^2)$, and H_{C2}' is in Oe/K . Using the above formulas, the Maki parameter α can also be expressed in terms of experimentally accessible parameters as

$$\alpha = \frac{3e^2 \rho_0 \gamma}{2m\pi^2 k_B^2} = 5.2758 \times 10^{-5} (-H_{C2}').$$

Since these equations have not considered any renormalization of the parameters due to the electron mass enhancement, it has been pointed out (Orlando et al., 1979) that this can be done by replacing the normal state parameters in the above equation by there renormalized values. The transport properties are not affected by mass renormalization (Butler, 1981) since it cancels out in the appropriate equations; however, the electronic heat capacity is renormalized by the factor $1+\lambda$, where λ is the electron-phonon coupling constant. Thus the equation for H_{C2}' becomes

$$H_{C2}' = - 4.48 \times 10^4 \rho_0 \gamma^*,$$

where the asterisk indicates the renormalized value. Therefore, using this formula, the coefficient of the renormalized electronic heat capacity, and thus the renormalized density of states at the Fermi energy, can be calculated from the upper critical field slope and the residual resistivity.

The value of $H_{C2}(0)$ is easily obtained by first employing the asymptotic expansion of the digamma function for large arguments. Using this the term $\ln(t)$ can be subtracted from both sides yielding

$$2[\psi(1/2) + \ln(2)] = \ln[h^2(1 + \alpha^2) + \lambda_{SO} h] - (\lambda_{SO}/\gamma) \tan^{-1}[\gamma/(h + (1/2)\lambda_{SO})].$$

In the case of VN and TiN, as will be seen in section IV, the best fits to WHH theory occur for $\lambda_{SO} = 0$, thus making this substitution we obtain

$$2[\psi(1/2) + \ln(2)] = \ln[h^2(1 + \alpha^2)].$$

Solving this for h we obtain

$$h(0) = \frac{1}{2e\gamma(1 + \alpha^2)^{1/2}},$$

where γ is Euler's constant equal to 0.577219... (Abramowitz and Stegun, 1965, p. 255). Now let us define the parameter h^* by

$$h^*(T) = \frac{h(T)}{T_C h'} = \frac{H_{C2}(T)}{T_C H_{C2}'},$$

and thus by equation III.22 we see that $h^* = (\pi^2/4)h$. Substituting this into the above equation and evaluating the constants we find

$$H_{C2}(0) = 0.69267 \frac{T_C H_{C2}'}{(1 + \alpha^2)^{1/2}},$$

Thus the value of the upper critical field at zero temperature may be determined from the transition temperature, the slope of H_{C2} at T_C , and the Maki parameter.

D. ELECTRON LIFETIME MODEL

The properties of many transition metals and their compounds have been found to depend strongly on the degree of electron scattering present in the material, whether it is due to phonons, defects, or impurities. A simple model for estimating these effects is the electron lifetime model, or ELM, first introduced by Testardi and Mattheiss (1978). It has since been used with success to predict the effects of finite electron lifetimes on the normal and superconducting state properties of many A15 compounds and b.c.c. transition metals (Testardi and Mattheiss, 1978; Mattheiss and Testardi, 1979; and Soukoulis and Papaconstantopoulos, 1982). It has also been used in attempts to predict similar effects in the B1 phase compound MoN (Papaconstantopoulos and Pickett, 1985) which has been predicted to have a transition temperature of 29.4 K (Papaconstantopoulos et al., 1985), but which has never been observed.

The effect of frequent scattering of electrons (a short electron lifetime) can, for particles near the Fermi energy, be considered in an approximate fashion through the uncertainty principle (Wiesmann et al., 1978). This is accomplished by assuming that

$$\Delta E \tau = \hbar,$$

where ΔE is the broadening of the bands near the Fermi energy due to the electron scattering time τ . If $F(E)$ is a quantity whose energy dependence is known near the Fermi energy for the perfect crystal, then the electron lifetime effects are included by the convolution

$$F(E, \Delta E) = \int S(E, E', \Delta E) F(E', 0) dE',$$

where $S(E, E', \Delta E)$ is a broadening function which depends on the energy width $\Delta E = \hbar/\tau$. Testardi and Mattheiss (1978) have shown that the form of this broadening function is not very crucial; however, Dingle (1952) demonstrated that the proper function is a Lorentzian of half-width ΔE . For our calculations we have used a Lorentzian of the form

$$S(E, E', \Delta E) = \frac{\Delta E}{\pi[(E - E')^2 + \Delta E^2]} .$$

The lifetime can be calculated from the electrical resistivity ρ and the Drude plasma frequency, Ω_p since the quantities are given by

$$\rho = \frac{m}{ne^2\tau} \quad \text{and} \quad \Omega_p^2 = \frac{4\pi ne^2}{m} ,$$

where m is the electron mass and n is the density of electrons. Thus the energy width is given by

$$\frac{\hbar}{\tau} = \frac{\Omega_p^2 \rho}{4\pi\hbar} ,$$

Therefore, using these equations, we can obtain the desired quantities, determined from band structure calculations for a perfect crystal, as a function of resistivity.

It should also be noted that problems can occur due to the far reaching wings of the Lorentzian broadening function. The actual curves for a given quantity obtained from band structure calculations are always finite in energy. Since the Lorentzian has such wide wings it can sample, especially at high resistivities, energies where no data exist. To account of this we have normalized all our calculations by the factor

$$\int_{E_{\min}}^{E_{\max}} S(E, E', \lambda E) dE' ,$$

where $E_{\min}$ and $E_{\max}$ define the range over which there exist data.

In the context of the present work we are interested in the effect of residual resistivity on the density of states at the Fermi energy for vanadium nitride and titanium nitride. To apply the ELM we must first know the density of states for the given material as a function of energy. For TiN we have used the result of Marksteiner et al. (1986). For VN we have used the shape of the density of states curve determined by Marksteiner et al. (1986) but have chosen to use the absolute value of the density of states at the Fermi energy $N(0)$ calculated by Papaconstantopoulos et al. (1985) since they have also calculated some of the superconducting properties using this density of states. This was accomplished by displacing upward the curve of Marksteiner et al. to match the $N(0)$ of Papaconstantopoulos et al. In the case of VN, as well as TiN, the Fermi energy lies on the side of a large peak.

The Drude plasma frequency for VN was calculated from the band structure by D.A. Papaconstantopoulos (private communication) and found to be 7.1 eV. This is very similar to the value of 7 eV determined by Pfluger et al. (1984) by modeling the results of electron-energy-loss-spectroscopy for both VN and TiN; therefore, we have also used this value for TiN.

The resulting density of states at the Fermi energy as a function of the residual resistivity is shown in Figure III.4 for both VN and TiN. In both cases, the density of states goes through a weak maximum at low resistivity. This is due to the broadening function sampling the large peak above the Fermi energy in both materials. After the

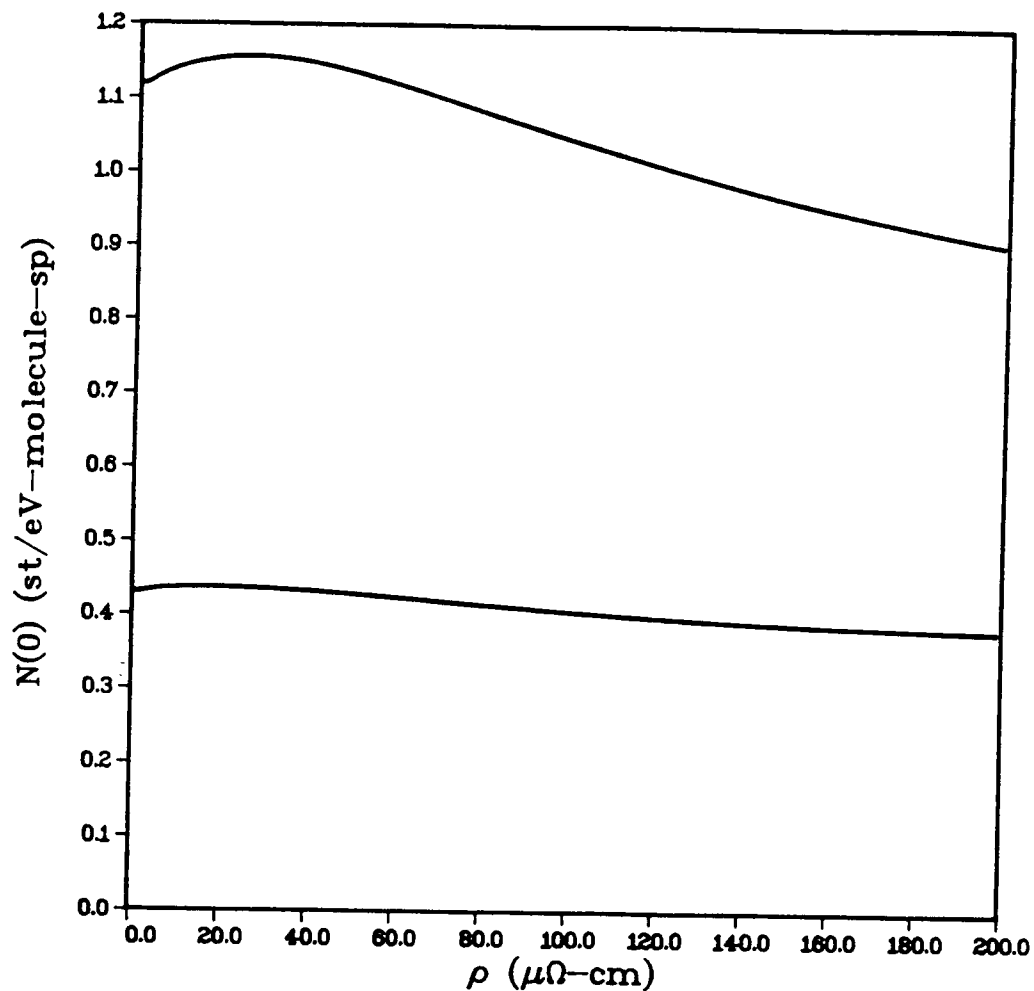


Figure III.4. The electron lifetime model result for the electronic density of states at the Fermi energy as a function of the resistivity. The upper curve is for VN and the lower curve is for TiN.

maximum the density of states slowly decreases; however, the changes are very small, only about 20% for VN and 10% for TiN at 200 $\mu\Omega$ -cm.

It should be noted that no effect of electron lifetime on the plasma frequency has been included. This is because we have no way to do so for these materials. However, such calculations have been made for many A15 compounds and some b.c.c. metals (Testardi and Mattheiss, 1978; Mattheiss and Testardi, 1979; and Soukoulis and Papaconstantopoulos, 1982). In most cases the plasma frequency was found to decrease with increasing resistivity. If this were also true for the present materials, then the curves of the density of states versus resistivity would be even flatter.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

In this section the effects of nitrogen ion irradiation and subsequent annealing on thin films of vanadium nitride and titanium nitride will be discussed. This will be followed by a comparison of the two systems. This section is divided into three subsections; in the first two subsections the effects of irradiation and annealing on the individual properties of each system will be discussed, an empirical model will be presented to describe the observed behavior, and the results will be compared with existing theory. In the last section the similarities and differences between the two systems will be discussed along with possible generalizations to all B1 phase, interstitial compound superconductors.

A. VANADIUM NITRIDE

This subsection is concerned with the effects of nitrogen ion irradiation and post-irradiation annealing on the vanadium nitride system. It is divided into three subsections which discuss the properties of the samples as they were formed, as a function of ion irradiation and as a function of annealing, respectively.

1. As-Formed Samples

The vanadium nitride samples, after preparation and before ion irradiation or annealing, had a wide range of properties. In this subsection we will describe those properties and discuss the other properties that can be deduced from them. The possibility of correlations between the measured parameters will also be explored.

Some of these details have been given above in the section on formation of the VN films; however, they will be summarized here for continuity.

The first property of interest is the transition temperature T_C . The VN samples, as formed, possessed T_C values ranging from 3.45 to 8.84 K; however, we will discuss below only the five samples with a T_C value of greater than 8.0 K since these are more representative of the best B1 phase VN and were the ones used in the ion irradiation and annealing experiments. The transition widths of these better samples, 0.12 to 0.27 K, were not correlated with the transition temperature.

The residual resistivity ρ_0 of the samples ranged from 30.7 $\mu\Omega\text{-cm}$ for the sample with the highest T_C to 66.0 $\mu\Omega\text{-cm}$ for the sample with a T_C of 8.10 K. As implied, the transition temperature was definitely correlated with the resistivity; however, it was not correlated in a way that could be extrapolated to zero residual resistivity. Thus an estimation of the maximum T_C could not be made for VN.

The upper critical field H_{C2} of the as formed samples was measured, as described above, as a function of temperature. For all samples the resulting upper critical field curves were found to be described by WHH theory, in the dirty limit, without the inclusion of paramagnetic limiting or spin orbit scattering (Werthamer et al., 1966). The slope of the upper critical field at T_C , H_{C2}' , ranged from 15.7 to 20.1 kOe/K. This parameter was roughly correlated T_C in that the sample with the highest T_C value had the lowest H_{C2}' ; however, it is better to observe that the three films with the highest transition temperature had roughly the same value of H_{C2}' .

The X-ray diffraction experiments performed on the virgin samples showed only lines associated with B1 phase VN, with the exception of an occasional line from the sapphire substrate. Values for the lattice constant a_0 obtained from these measurements ranged from 0.4138 to 0.4145 nm. For bulk material, the lattice constant for stoichiometric vanadium nitride has been reported to be 0.41398 nm and was observed to decrease with composition to 0.40662 nm for $\text{VN}_{0.72}$, which is the lower limit of the B1 phase (Toth, 1971). As mentioned above, the transition temperature is strongly dependent on stoichiometry and therefore the lattice constant (Ajami and MacCrone, 1975); however, our films show no correlation of T_C and a_0 in the manner described in the literature. A possible explanation for this is that the substantially low T_C values observed, down to 3 K, are due to carbon and/or oxygen impurities occupying the nitrogen sites in the B1 lattice, thus making the nitrogen content less stoichiometric. However, the ionic radii of carbon and oxygen are both similar to that of nitrogen, thus their inclusion would not be expected to change the unit cell size drastically. It should also be mentioned that the lattice constant of $\text{VC}_{0.87}$ is 0.4166 nm (Storms and McNeal, 1962) and that oxygen impurities have been found to be very detrimental to the transition temperature in vanadium metal (De Schutter et al., 1985).

The measured lattice constants are perhaps weakly correlated with T_C since the sample possessing the highest T_C also has the smallest lattice constant; however, all the lattice constants are larger than the bulk stoichiometric value and vary in the opposite direction to that expected from compositional variations, that is, larger a_0 values

are correlated with lower T_C values. This is probably due to strains induced in the material when VN, with an f.c.c. space lattice, is formed from vanadium metal, which has a b.c.c. space lattice, since there is a volume expansion of 27.5%. These initially measured parameters are shown in Table IV.1.

The upper critical field extrapolated to zero temperature, $H_{C2}(0)$, was found to be approximately constant for all samples. The average value of $H_{C2}(0)$ was 100 kOe, $\pm 6.4\%$, using the extrapolation formula derived in section III, C. The coefficient of the electronic heat capacity γ^* , renormalized by many-body corrections, which was calculated from H_{C2}' and ρ_0 , ranged from 6.32 to 12.2 mJ/mole-K². These values are in qualitative agreement to values obtained by direct heat capacity measurements (9.18 mJ/mole-K² by Geibel et al., 1985) and to values calculated from band structure calculations (10.7 mJ/mole-K² by Papaconstantopoulos et al., 1985; please note that the value published in this paper was found to be in error during the course of the current investigation). These values were also correlated with the transition temperature, which is to be expected since they depend, as does T_C , on the density of states and the electronic mass enhancement (or the electron-phonon coupling constant) λ . The values of $H_{C2}(0)$ and γ^* , along with values of the renormalized density of states at the Fermi energy, calculated from γ^* , are shown in Table IV.2.

In addition to these parameters, Table IV.2 includes values of the Ginzburg-Landau coherence length $\xi_{GL}(0)$ and penetration depth $\lambda_{GL}(0)$ at zero temperature. These are calculated from the standard

Table IV.1. Initial parameters of the VN samples.^a

Sample	T_C	ΔT_C	ρ_0	Γ	H_{C2}'	a_0
3-VN#1	8.28	0.12	48.6	1.54	20.1	.4144
13-VN#2	8.66	0.29	35.0	1.69	16.1	.4142
14-VN#1	8.84	0.24	30.7	1.85	15.7	.4138
14-VN#2	8.75	0.27	33.6	1.76	16.2	.4142
20-VN#1	8.10	0.27	66.0	1.30	17.5	.4145

^aThe units are T_C in K, ΔT_C in K, ρ_0 in $\mu\Omega\text{-cm}$, H_{C2}' in kOe/K, and a_0 in nm.

Table IV.2. Superconducting properties calculated from the initial parameters for VN.^a

Sample	$H_{C2}(0)$	γ^*	$N^*(0)$	$\xi_{GL}(0)$	$\lambda_{GL}(0)$
3-VN#1	121	9.86	2.09	4.45	156
13-VN#2	97.3	11.0	2.33	4.86	129
14-VN#1	95.8	12.2	2.58	4.88	120
14-VN#2	99.1	11.5	2.43	4.82	126
20-VN#1	99.9	6.32	1.34	4.82	183

^aThe units are $H_{C2}(0)$ in kOe, γ^* in mJ/mole-K², $N^*(0)$ in states/eV-V atom-spin, and $\xi_{GL}(0)$ and $\lambda_{GL}(0)$ in nm.

formulas, in the dirty limit, (Orlando et al., 1979)

$$\xi_{GL}(0) = 8.57 (\gamma^* \rho_0 T_C)^{-1/2} \text{ and}$$

$$\lambda_{GL}(0) = 6.42 \times 10^4 (\rho_0/T_C)^{1/2},$$

where $\xi_{GL}(0)$ and $\lambda_{GL}(0)$ are in nm, γ^* is in erg/cm³-K², ρ_0 is in Ω -cm, and T_C is in K. The coherence length is a measure of the spatial extent of the Cooper pairs and the penetration depth is a measure of the attenuation length of the magnetic field inside a superconductor. As is seen in the table, the coherence length is approximately constant for all samples while the penetration depth varies with the resistivity.

2. Irradiation Studies

This subsection is concerned with the effect of lattice damage, induced by irradiation with nitrogen ions, on the superconducting and normal state properties of the VN films. Since the resistivity is the parameter most obviously affected by defects in the lattice, it will be discussed first, followed by the transition temperature, the upper critical field and the microscopic properties.

Resistivity. The electrons in a metal are scattered by several different mechanisms. Among these are scattering by phonons (eg., lattice vibrations due to the internal energy of the system at a finite temperature), impurities and other defects such as grain boundaries, vacancies in the lattice and atoms in interstitial positions (for an excellent review of scattering of electrons see Fisk and Webb, 1981). At room temperature all these mechanisms are at work; however, at low temperatures the phonon portion of the

scattering is suppressed since few phonon modes are accessible. The residual resistance ratio Γ , defined above, is a convenient parameter to quantify the relative amount of defect scattering at low and room temperatures, as well as the phonon scattering at room temperature.

If we assume the scattering mechanisms are all independent, Matthiessen's rule applies (Fisk and Webb, 1981) and one can write the total resistivity ρ_{tot} as

$$\rho_{\text{tot}} = \rho(T) + \rho_0,$$

where $\rho(T)$ is the temperature dependent part of the resistivity, due to electron-phonon scattering, and ρ_0 is the residual resistivity due to impurities, grain boundaries, etc. The residual resistance ratio is then given by

$$\Gamma = 1 + \rho(T)/\rho_0.$$

Thus Γ in a very good sample will be quite large since ρ_0 will be very small.

Figure IV.1 shows Γ versus incident ion fluence ϕ for the VN samples studied, plotted on a semi-log scale for convenience. Here it is seen that in every case Γ decreases monotonically until it saturates at or near 1.0. Considering the above equation for Γ , this behavior must be due to either an increase in ρ_0 , a decrease in $\rho(T)$, or both. In actuality both terms are changing. The residual resistivity changes due to defects produced during irradiation. The changes in the thermal part may be due to changes in the phononic properties of the material or Matthiessen's rule may not be valid; however, the decrease is probably due to the saturation of the resistivity observed in many d- and f-band metals (Allen, 1980). A

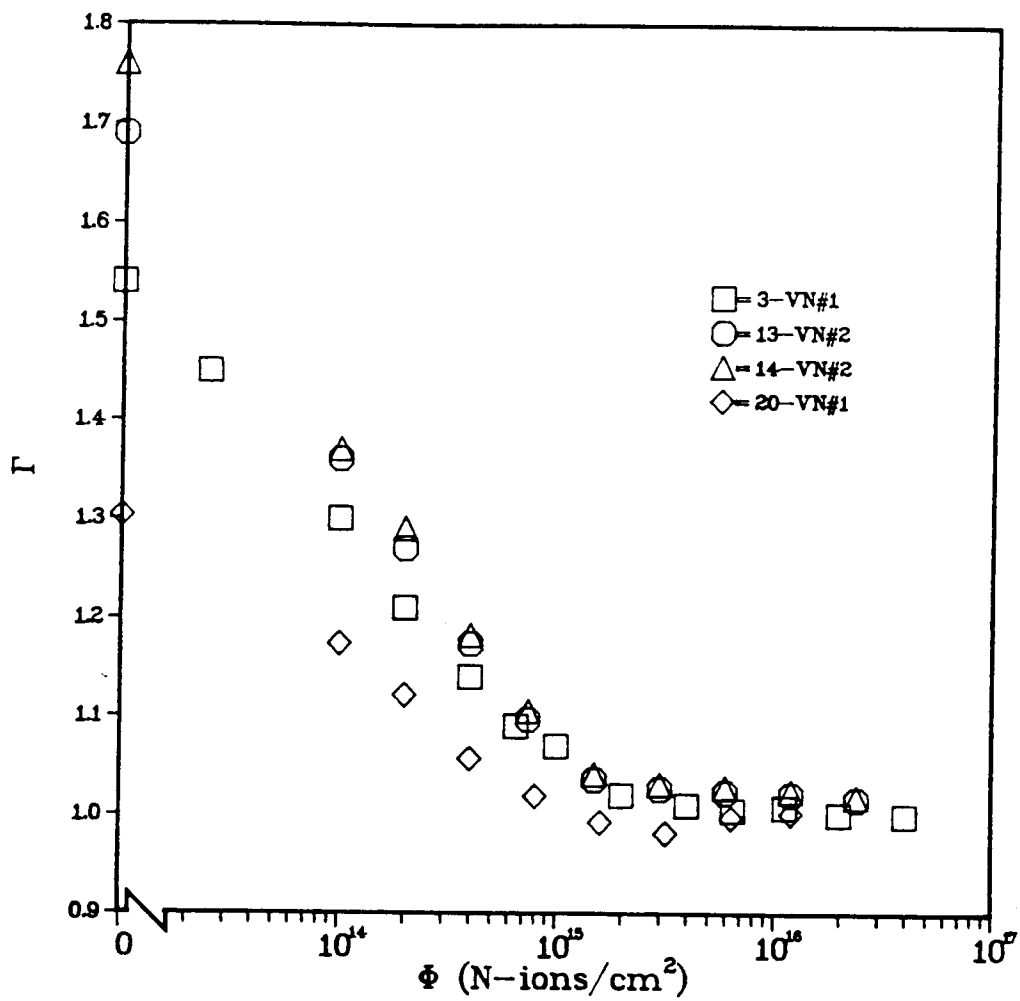


Figure IV.1. The residual resistance ratio Γ versus the incident ion fluence Φ for VN.

detailed study of the temperature dependence of the resistivity would be needed to study this behavior, which is not within the scope of this work.

The residual resistivity is plotted in Figure IV.2 versus the fluence. Here we see that ρ_0 increased with fluence as one would expect. It increased rapidly at first then saturated at fluences greater than about 6×10^{15} N-ions/cm². This fluence corresponds to a deposited energy density of 37.5 eV/atom, using the conversion to deposited energy calculated in Section II, A. Assuming, as previously mentioned, 20 eV as the minimum displacement energy per atom, this corresponds to about 1.9 displacements per atom. The small increases in resistivity above 1.5×10^{16} N/cm² are believed due to ion mixing of the sapphire substrate with the VN film. The saturation value of the resistivity was found to be sample dependent.

The behavior of ρ_0 was found to fit an exponentially saturating function of the form

$$\rho_0(\phi) = \rho_0(0) + \Delta\rho (1 - \exp[-\phi/b]), \quad (\text{IV.1})$$

where $\rho_0(0)$ is the resistivity of the unirradiated sample, $\Delta\rho$ is the total change in resistivity (ie., the saturated value minus the initial value) and b is a decay constant. Fits made to this function, using the experimentally determined values for $\rho_0(0)$ and $\Delta\rho$, were performed yielding decay constants for the various samples. These fits were quite good with an average RMS deviation of about 3.7 $\mu\Omega\text{-cm}$ (or about 4.5%). The decay constant b was found to be sample independent and had an average value of 6.68×10^{14} N/cm² or 4.18 eV/atom. This corresponds to about 0.21 displacements per atom.

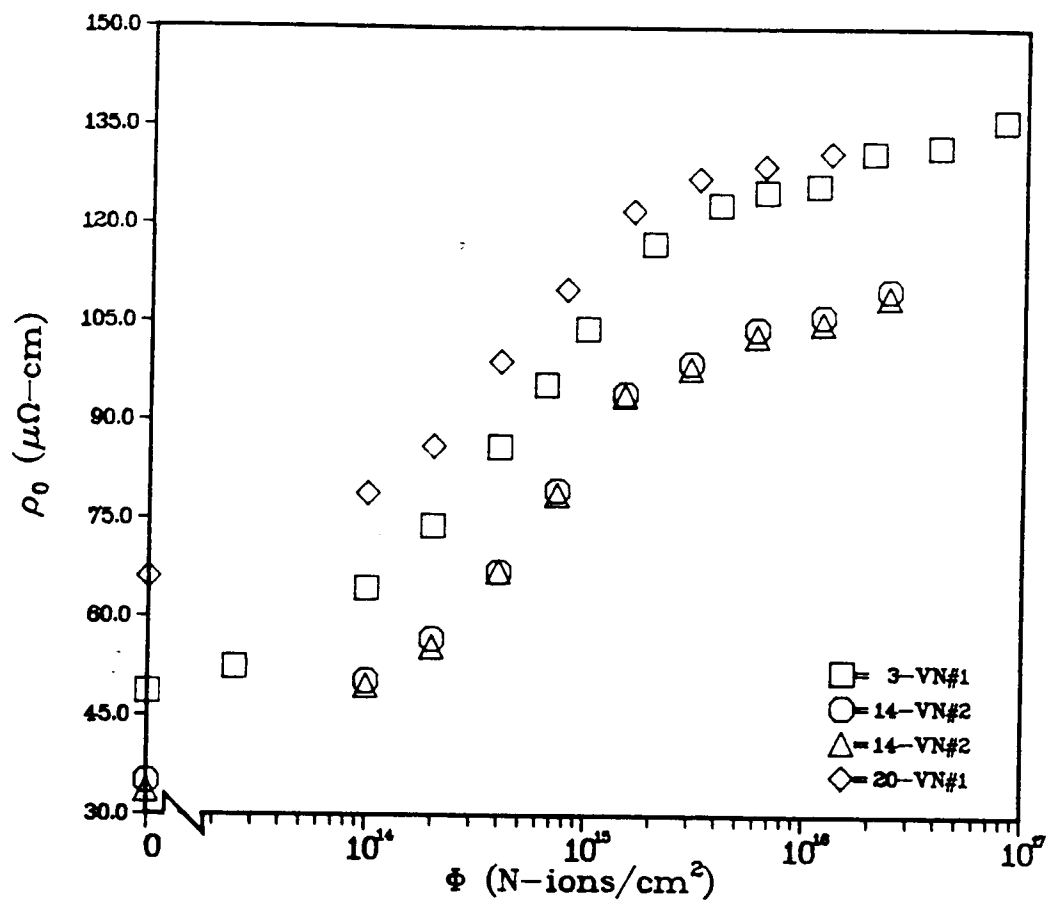


Figure IV.2. The residual resistivity versus the incident ion fluence for VN.

A simple defect production and annealing model is now proposed to explain the behavior of $\rho_0(\phi)$. Suppose the residual resistivity was made up of two terms, one due to scattering of electrons by impurities ρ_I , called the impurity term, and the other due to defects such as vacancies and interstitial atoms (ie., displaced atoms) ρ_D , called the defect term. This second term, of course, will also contain the scattering due to grain boundaries as well. Then the residual resistivity can be written as

$$\rho_0 = \rho_I + \rho_D. \quad (\text{IV.2})$$

The impurity term is assumed to be constant as a function of fluence. The defect term is, however, fluence dependent and it is assumed that this term is proportional to a defect density c_D . That is

$$\rho_D = k c_D, \quad (\text{IV.3})$$

where k is a constant of proportionality.

Now the dependence of the defect density on the fluence is needed. This is introduced through the assumption that the rate of increase of the defect density with respect to the fluence is given by

$$\frac{dc_D}{d\phi} = B - \frac{c_D}{b}.$$

The first term B represents the direct damage production rate in the lattice by the incoming ion. The second term c_D/b is an annealing or saturating rate proportional to the defect density and represents a maximum defect density that the lattice will support. This second term accounts for the saturation behavior of the resistivity.

This equation now needs to be integrated in order to extract c_D . Upon rearrangement this yields

$$c_D = c_D^i + (bB - c_D^i) [1 - \exp(-\phi/b)],$$

where c_D^i is the initial defect density before irradiation. Thus we see that bB is actually the saturation defect density. By applying equation IV.3 we see that kc_D^i is the initial defect resistivity, ρ_D^i , and lbB is the saturated defect resistivity, ρ_D^S , and the defect resistivity is given by

$$\rho_D = \rho_D^i + (\rho_D^S - \rho_D^i)[1 - \exp(-\phi/b)]. \quad (\text{IV.4})$$

One now needs to find some way to separate the impurity part from the defect part in the measured resistivities.

Let us consider the initial unirradiated residual resistivity $\rho_0(0)$, which is equal to $\rho_I + \rho_D^i$. As mentioned above, the transition temperature is correlated with the residual resistivity. As a first approximation let us assume that the sample with the highest T_C has no resistivity due to impurities, thus any reduction in T_C is due to defect scattering as discussed in section III,D. Also let us assume that this initial defect resistivity is the same for all samples since they were all formed in the same manner. Then the initial defect term is $30.7 \mu\Omega\text{-cm}$ and the impurity terms for each sample are determined by subtracting this value from $\rho_0(0)$. These values are shown in Table IV.3.

According to our model, the saturation defect resistivity, $\rho_D^S = kbB$, should be the same for all samples since bB is a constant; therefore, set ρ_D^S equal to the ρ_D^S value of the sample with the highest initial T_C and lowest initial residual resistivity, that is, sample 14-VN#2 which had $\rho_D^S = 102 \mu\Omega\text{-cm}$, as determined above and shown in Table IV.3. The impurity and initial defect terms are then determined from

Table IV.3. The values of ρ_I and ρ_D^S for VN using $\rho_{Di} = 30.7 \mu\Omega\text{-cm}$ for VN.^a

Sample	$\rho_0(0)$	$\rho_0(\infty)$	ρ_I	ρ_D^S
3-VN#1	48.6	126	17.9	108
13-VN#2	35.0	106	4.30	102
14-VN#2	33.6	105	2.90	102
20-VN#1	66.0	131	35.3	96.0

^aAll units are in $\mu\Omega\text{-cm}$.

$$\rho_I = \rho_0(\infty) - 102 \mu\Omega\text{-cm} \text{ and } \rho_D^i = \rho_0(0) - \rho_I,$$

where $\rho_0(\infty)$ is the experimentally measured resistivity at saturation (ie., at fluences greater than 1×10^{16} N-ions/cm²). These values are shown in Table IV.4 and the resulting $\rho_D (= \rho_0(\phi) - \rho_I)$ data are plotted in Figure IV.3 versus the fluence.

Using equations IV.2, IV.3, and IV.4, we may now write the resistivity equation as

$$\rho_0(\phi) = \rho_I + \rho_D^i + (102 \mu\Omega\text{-cm} - \rho_D^i)[1 - \exp(-\phi/b)],$$

where ρ_I and ρ_D^i are sample dependent and $b = 6.68 \times 10^{15}$ N-ions/cm², which completely describes the fluence and sample dependence of the residual resistivity. It should be noted that the impurity term, as determined from this model, is correlated with the initial transition temperature in that the sample with the lowest initial T_C has the highest ρ_I , or rather the largest amount of impurities. This is consistent with our speculation on the causes of the variation in T_C in part 1 of this section.

Many of the high T_C , transition-metal compound, superconductors exhibit a saturating behavior in the resistivity at elevated temperatures (Allen, 1980; and Gurvitch et al., 1980). This behavior has been empirically found to be described by the parallel resistor model (Wiesmann et al., 1977; Allen, 1980; and Gurvitch, 1981) given by

$$\frac{1}{\rho_{\text{exp}}} = \frac{1}{\rho_{\text{ideal}}} + \frac{1}{\rho_{\text{max}}},$$

where ρ_{exp} is the experimentally measured resistivity, ρ_{ideal} is the resistivity of an ideal metal, as is given by the Boltzmann equation (Butler, 1980), and ρ_{max} is a parallel resistance which is constant

Table IV.4. The values of ρ_I and ρ_D^i for VN using $\rho_D^S = 102 \mu\Omega\text{-cm}$ for VN.^a

Sample	$\rho_0(\infty)$	ρ_I	ρ_D^i
3-VN#1	126	24.0	24.6
13-VN#2	106	4.0	31.6
14-VN#2	105	3.0	30.6
20-VN#1	131	29.0	37.0

^aAll units are in $\mu\Omega\text{-cm}$.

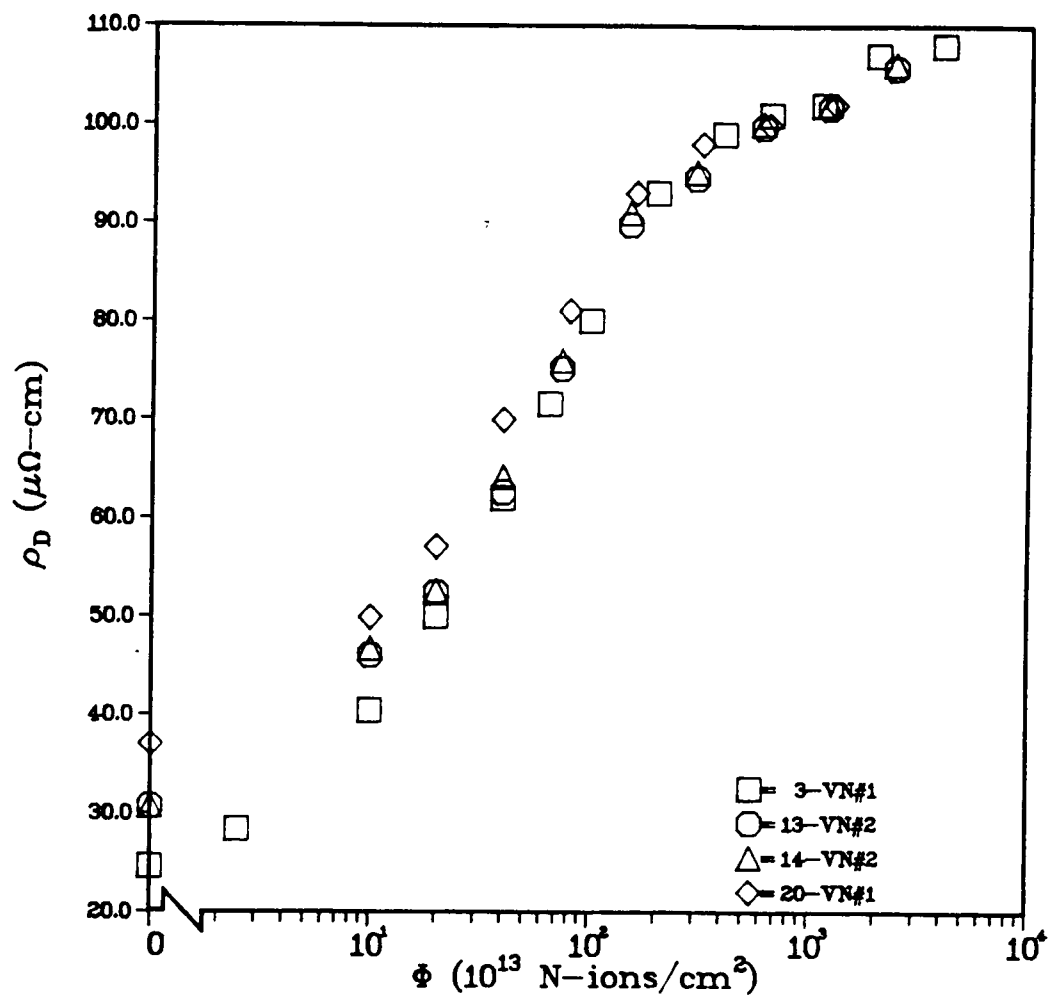


Figure IV.3. The defect part of the residual resistivity versus the incident ion fluence for VN.

and sample independent for a given material, and accounts for the saturation with increasing temperature. This model has been considered theoretically (Laughin, 1982; and Chakraborty and Allen, 1978 and 1979) and has been applied to VN experimentally by Zasadzinski et al. (1985). Zasadzinski et al. measured the resistivity as a function of temperature up to room temperature and fit their data to this model, finding a $\rho_{\max}$ of 230 $\mu\Omega\text{-cm}$. With this in mind we have applied this model to our residual resistivity data.

To apply the model we use the form

$$\frac{1}{\rho_0(\Phi)} = \frac{1}{\rho_0^P(\Phi)} + \frac{1}{\rho_{\max}}, \quad (\text{IV.5})$$

where the subscripts have the same meanings as before with the superscripts referring to the parallel resistance model. Our defect production and annealing model is then applied, as before, to $\rho_0^P(\Phi)$. The development of this model is shown in the Appendix. The values of $\rho_{\max}$ obtained by fitting to this model (see the Appendix) were approximately the same for all samples and showed no correlation with any of the measured parameters. The average value was 401 $\mu\Omega\text{-cm} \pm 7.3\%$.

The parallel resistivity may now be removed yielding the "ideal" resistivity by inverting equation IV.5. The values of $\rho_0^P(0)$, $\Delta\rho^P$, and $\rho_0^P(\infty)$ obtained are shown in Table IV.5 and ρ_0^P is plotted versus the fluence in Figure IV.4. This data was fitted to the defect production and annealing model as before in order to determine the decay constant. The fits were good with a RMS standard deviation of 5.0 $\mu\Omega\text{-cm}$ (or 4.3%) which is approximately the same as without the parallel resistance model. The decay constant was the same for all

Table IV.5. The resistivity values for VN with the parallel resistivity removed.^a

Sample	$\rho_0 P(0)$	$\Delta \rho P$	$\rho_0 P(\infty)$
3-VN#1	55.3	129	184
13-VN#2	38.3	106	144
14-VN#2	36.7	105	142
20-VN#1	79.0	116	195

^aThese are calculated using $\rho_{\max} = 401 \mu\Omega\text{-cm}$ as described in the text.

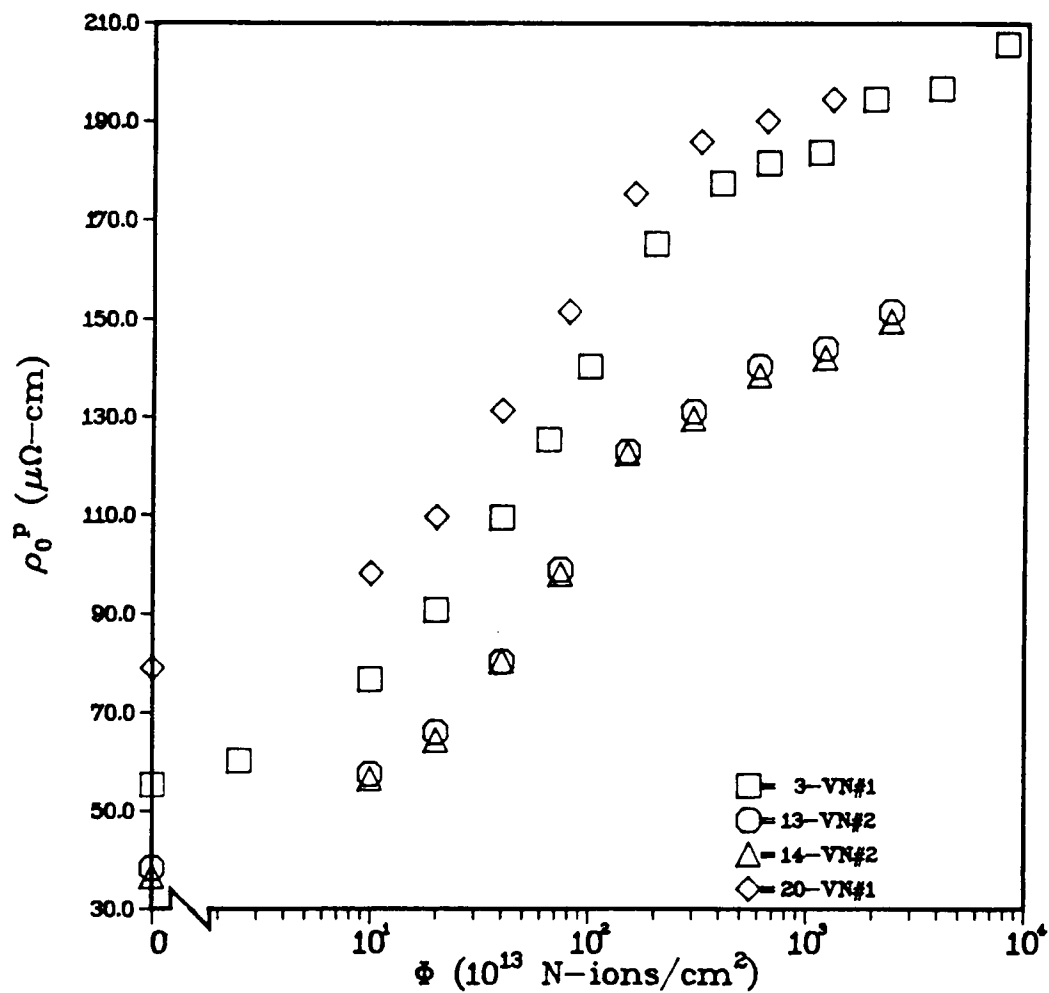


Figure IV.4. The residual resistivity, after the parallel term has been removed, versus the fluence for VN.

samples and had an average value of 8.09×10^{14} N-ions/cm² or 5.06 eV/atom. This corresponds to approximately 0.25 displacements/atom.

As before one needs to separate the impurity term from the defect term. Following the procedure above, we calculated the initial resistivity of the best VN sample by eliminating the parallel resistivity. In the same manner as above the saturated defect resistivity was determined to be $139 \mu\Omega\text{-cm}$ and the other parameters were calculated from this number, the results being given in Table IV.6 and $\rho_D P(\phi)$ vs the fluence is shown in Figure IV.5. As before we see that the impurity term is correlated with T_C .

Therefore we find that the resistivity can be fit to a parallel resistance model just about as well as to a conventional type model. The resulting expression then for the resistivity of VN is

$$\frac{1}{\rho_0(\phi)} = \frac{1}{\rho_0 P(\phi)} + \frac{1}{401 \mu\Omega\text{-cm}},$$

$$\text{where } \rho_0 P(\phi) = \rho_{IP} + \rho_{DPi} + (139 \mu\Omega\text{-cm} - \rho_{DPi}) X,$$

$$X = 1 - \exp(-\phi/b),$$

$$\text{and } b = 8.09 \times 10^{14} \text{ N-ions/cm}^2.$$

Transition Temperature. The transition temperature was found to decrease with increasing ion fluence. The effects of the irradiations on T_C are shown in Figure IV.6, where we have plotted T_C versus the log of the fluence for convenience. Here we see that the transition temperature decreased rapidly at first, then saturated at fluences greater than about 6×10^{15} N-ions/cm² or 37.5 eV/atom. This corresponds to about 1.9 displacements per atom. Similar to the resistivity, above about 1.5×10^{16} N-ions/cm², T_C continued to

Table IV.6. Values of $\rho_0^P(\infty)$, ρ_{IP} , and ρ_{DPI} using $\rho_{DPS} = 139 \mu\Omega\text{-cm}$ for VN.

Sample	$\rho_0^P(\infty)$	ρ_{IP}	ρ_{DPI}
3-VN#1	184	45.0	10.3
13-VN#2	144	5.0	33.3
14-VN#2	142	3.0	33.7
20-VN#1	195	56.0	23.0

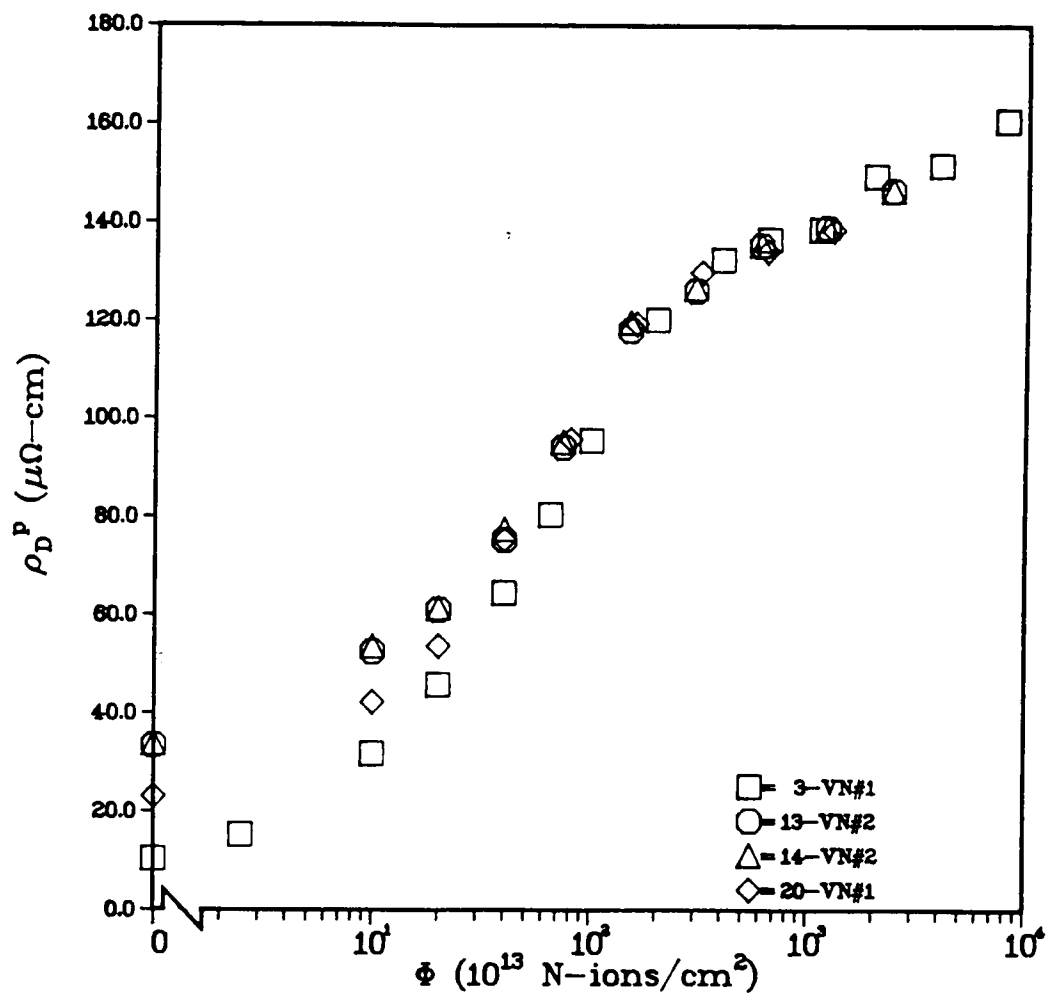


Figure IV.5. The defect part of the residual resistivity, in the parallel resistance model, versus the fluence for VN.

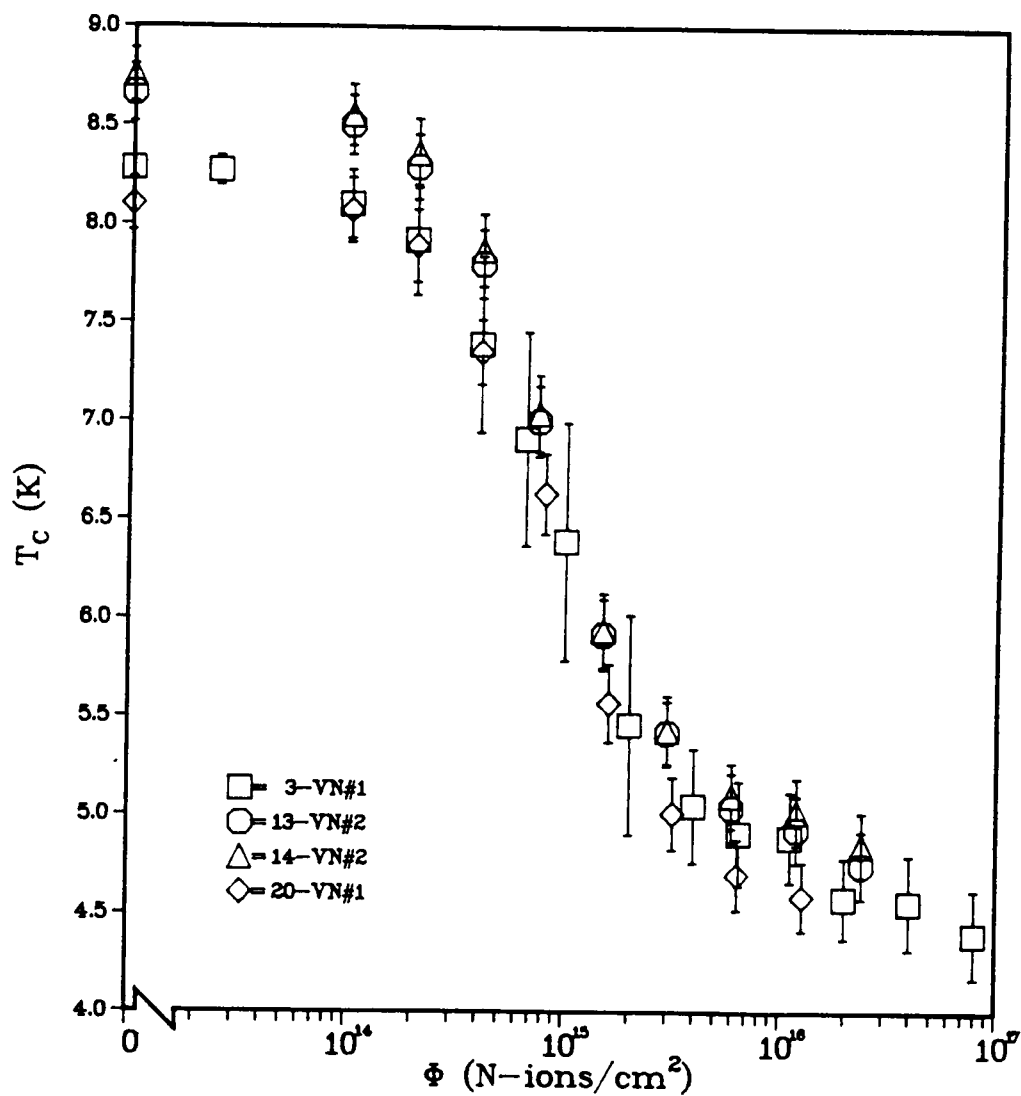


Figure IV.6. The transition temperature T_C versus the incident ion fluence for VN. The error bars indicate the width of the transition.

decrease in small jumps. This was also attributed to ion beam mixing of the sapphire substrate with the sample. The transition width, also shown in Figure IV.6 as error bars, was found to increase with irradiation fluence and, in the case of the sample with the most narrow initial transition, the width reached a maximum at a fluence of $1 \times 10^{15} \text{ N/cm}^2$ and then decreased while the other samples' transition widths only increased slightly and then stayed the same at higher fluences.

The transition temperature was found empirically to follow the behavior of an exponentially decaying function similar to the resistivity. The form of this function is

$$T_C(\phi) = T_C^S + (T_C^i - T_C^S)\exp(-\phi/a), \quad (\text{IV.6})$$

where T_C^S is the saturated value of the transition temperature, T_C^i is the initial value, and a is the decay constant. The initial and saturated transition temperature values were determined experimentally while the data was fit to the above equation to determine the decay constant. These fits were quite good with an RMS standard deviation of $\pm 0.10 \text{ K}$ or about 1.6%. The decay constant was approximately the same for all samples with an average value of $1.31 \times 10^{15} \text{ N-ions/cm}^2 \pm 7.5\%$ which corresponds to 8.20 eV/atom. This is approximately 0.41 displacements per atom. The saturated T_C values were approximately constant for all samples, with an average value of $4.86 \text{ K} \pm 3.8\%$; however, a definite correlation existed between the initial and saturated transition temperatures. These values are shown in Table IV.7.

Table IV.7. Initial and saturated values of T_C along with the decay constants for VN.^a

Sample	T_C^i	T_C^s	a
3-VN#1	8.28	4.89	1.25
13-VN#2	8.66	4.93	1.31
14-VN#2	8.75	5.02	1.24
20-VN#1	8.10	4.59	1.46

^aThe transition temperatures are in units of K and the decay constants are in units of 10^{15} N-ions/cm².

At this point, in an attempt to model this behavior, one would like to divide the change in transition temperature into an impurity term and a defect term as was done with the resistivity. To do this one would write

$$\Delta T_C(\phi) = \Delta T_{CI} + \Delta T_{CD}, \quad (\text{IV.7})$$

where the first term is the change due to impurities and the second is due to other defects. One should then be able to write these changes in terms of absolute transition temperatures:

$$\Delta T_C(\phi) = T_{C\max} - T_C(\phi)$$

$$\Delta T_{CI} = T_{C\max} - T_{CI}$$

$$\Delta T_{CD} = T_{CI} - T_{CD}(\phi),$$

where $T_{C\max}$ is the transition temperature for the material if it existed in a perfect lattice (no defects of any kind), $T_C(\phi)$ is the experimentally measured value of the transition temperature, $T_{CD}(\phi)$ is the transition temperature as a function of fluence due to defects, and T_{CI} is the transition temperature due to impurities (notice that if there were no impurities present then T_{CI} just goes to $T_{C\max}$ and equation IV.7 has only one term on the right hand side). Inserting these terms into equation IV.7 we see that most of them cancel leaving

$$T_C(\phi) = T_{CD}(\phi) .$$

With this in mind a simple defect production and annealing model can also be used to explain the existence of equation IV.6. First, let us assume that the change in the transition temperature with fluence is proportional to a defect density

$$\Delta T_{CD}(\phi) = \ln d, \quad (\text{IV.8})$$

where l is a constant of proportionality and a different symbol for the defect density has been used from the resistivity model so that no equality is implied. As before, let us further assume that the rate of change of the defect density with fluence is given by the expression

$$\frac{dn_d}{d\phi} = A - \frac{n_d}{a},$$

where the first term A is the direct damage rate due to the incoming ions and the second term n_d/a is an annealing or saturating term.

Upon integration we obtain

$$n_d(\phi) = Aa + (n_d^i - Aa)\exp(-\phi/a), \quad (\text{IV.9})$$

where n_d^i is the initial defect density and by observation it is clear that Aa is the saturated defect density. Applying equation IV.8 we see

$$\Delta T_{CD}(\phi) = lAa + (ln_d^i - lAa)\exp(-\phi/a); \quad (\text{IV.10})$$

therefore, lAa is the total change in T_C , ΔT_C^s , and ln_d^i is the change due to initial defects, ΔT_C^i . These changes are defined by

$$\begin{aligned} \Delta T_C^s &= T_{CI} - T_C^s, \\ \Delta T_C^i &= T_{CI} - T_C^i, \end{aligned} \quad (\text{IV.11})$$

and $\Delta T_{CD}(\phi)$ is defined as before. Substituting equations IV.11 into IV.10 and canceling the appropriate terms we obtain equation IV.6.

It is important to note that, in this model, ΔT_C^s is a constant since Aa is a constant. Since, as seen in the section on resistivity, the initial transition temperatures were correlated with the deduced impurity resistivity term, it is expected that T_{CI} , if it could be determined, would be higher for samples with higher T_C^i values. Therefore, since ΔT_C^s is a constant, the saturation transition

temperature values should be correlated with the initial values. On the other hand, ΔT_C^i is not a constant since, as inferred from the resistivity model, the initial defect density is not constant. Thus one should not expect the difference between the initial and saturated transition temperatures to be constant.

Now let us compare the decay constants obtained above for the resistivity, both with and without the parallel resistance model, and for T_C . For the resistivity the decay constants were 4.18 eV/atom for the first model and 5.06 eV/atom in the parallel model while for T_C the decay constant was 8.20 eV/atom. These quantities can be considered a measure of the susceptibility of the relevant parameters to radiation damage since they represent the energy density needed to change the parameter by a factor of $\exp(-1)$; however, it is not to be assumed that these numbers represent the amount of energy needed to displace an atom. Bearing this in mind, these constants indicate that the transition temperature is less sensitive to damage produced by nitrogen ion irradiation than is the resistivity.

From our defect density model it is therefore apparent that the defect densities affecting T_C and ρ_0 are not the same. A possible explanation for this may lie in the displacements of atoms occurring during the irradiation processes. If the transition temperature were more sensitive to vacancies on one of the sublattices than the other (say the metal sublattice) while the resistivity was equally sensitive to vacancies on both lattices and if the irradiations produced more displacements on one sublattice (say, the nitrogen sublattice) than the other the above effect would be observed. This is, of course,

total speculation, and we have no way to prove or disprove this hypothesis.

Lattice Constant. Measurements of the lattice constant a_0 were made at several fluences using thin film x-ray diffraction as described above. The lattice constant was observed not to change, within experimental error (approximately ± 0.0007 nm), with increasing damage up to fluences of 1×10^{15} N/cm². However, with increasing fluence, the higher order peaks in the diffraction pattern were decreasing in intensity and at 1×10^{15} N/cm² all but the two lowest order peaks had vanished, making a lattice constant determination impossible. This indicates that there was considerable disorder in the lattice but the material never became amorphous. This lattice constant behavior is consistent with similar measurements made on MoC irradiated with 300 keV He ions (Ruzicka et al., 1984) and in contrast with measurements on NbN irradiated with 600 keV Ar ions (Jung, 1984) and NbC irradiated with 600 keV Ar ions and 200 keV He ions (Kobayashi et al., 1984 and 1985).

Upper Critical Field. The upper critical field, H_{C2} , of the samples was measured as a function of temperature after each irradiation experiment. The curves obtained were found to fit WHH theory, in the dirty limit, including Pauli paramagnetic limiting. In fitting, the temperature at $H=0$, $T_C(0)$, the slope at $H=0$, H_{C2}' , and the Maki parameter, α , which is a measure of the paramagnetic limiting, were used as fitting parameters. The spin-orbit scattering parameter, λ_{SO} , should also be used; however, there is a strong

interaction in the WHH equation between α and λ_{SO} . Thus one must set one of the parameters to some pre-determined value and determine the other from the fit. We have chosen to set the spin orbit scattering parameter equal to zero; therefore, the Maki parameters determined from the fit are not the real values of the parameter but actually represent some admixture of the two effects, thus one should consider α only as a fitting parameter.

The H_{C2} versus T data for sample 14-VN#2 are shown in Figure IV.7 for several fluences. The curves are from WHH theory and, as one can see, fit the data quite well. From these curves several interesting pieces of information can be extracted. Of particular interest is H_{C2}' and the value of the upper critical field extrapolated to zero temperature $H_{C2}(0)$. A plot of $H_{C2}(0)$ versus the fluence is shown in Figure IV.8. Here we see that $H_{C2}(0)$ initially increased slowly and went through a maximum at 4×10^{14} N/cm², after which it decreased rapidly and saturated. The slope was observed to increase with increasing fluence and saturate similar to the other parameters.

From H_{C2}' and the residual resistivity one can calculate, as discussed in section III,C, the coefficient of the renormalized electronic heat capacity γ^* . This was done for all samples at all levels of damage. The resulting γ^* values are shown, plotted versus the fluence, in Figure IV.9. The electronic heat capacity was found to decrease with damage and to saturate at fluences similar to the other parameters.

Microscopic Properties. Several interesting properties can be deduced from the transition temperature, the resistivity, and the

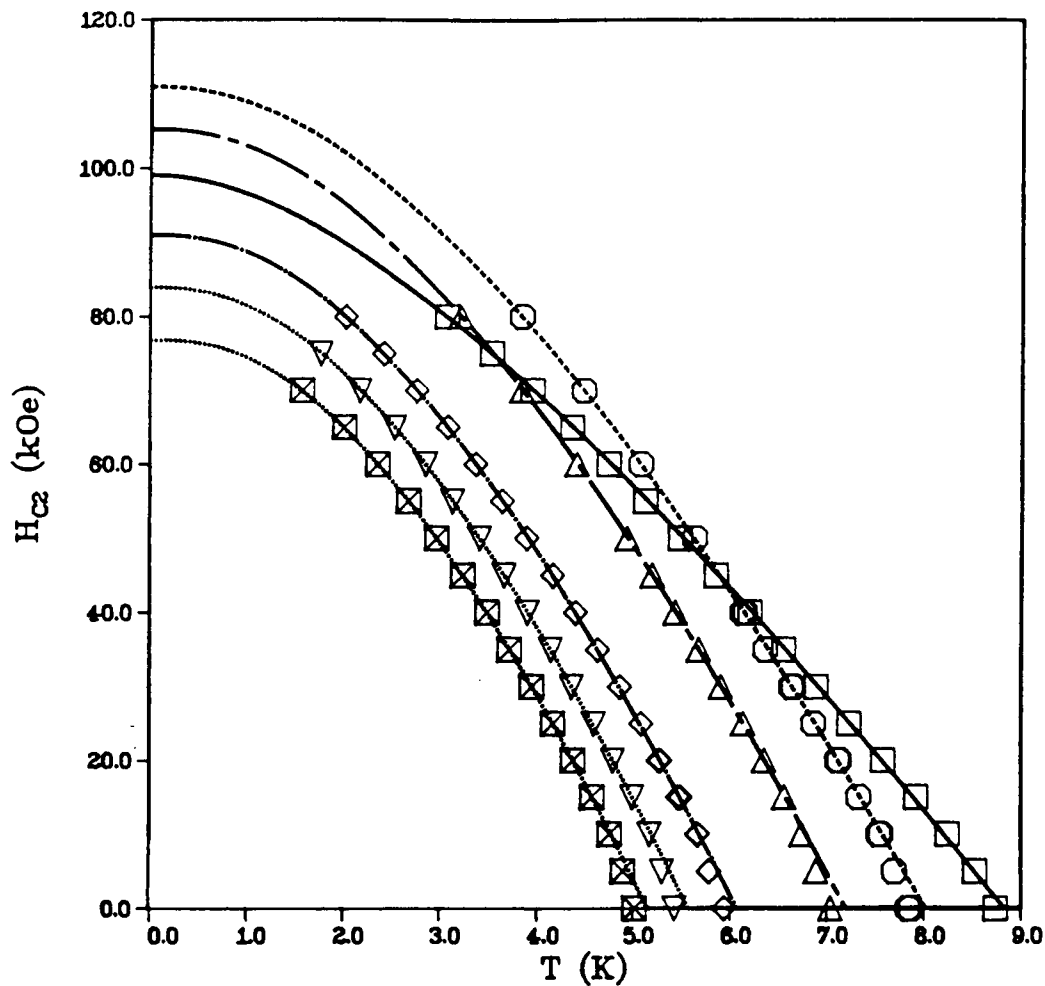


Figure IV.7. The upper critical field H_{C2} as a function of temperature T at several ion fluence for sample 14-VN#2. The symbols for the various fluences are as follows: $\square$, before irradiation; $\circ$, 4×10^{14} N-ions/cm²; $\triangle$, 7.4×10^{14} N-ions/cm²; $\diamond$, 1.5×10^{15} N-ions/cm²; ∇ , 3×10^{15} N-ions/cm²; and $\boxtimes$, 1.2×10^{16} N-ions/cm². The curves were calculated from WHH theory, in the dirty limit (Werthamer et al., 1966).

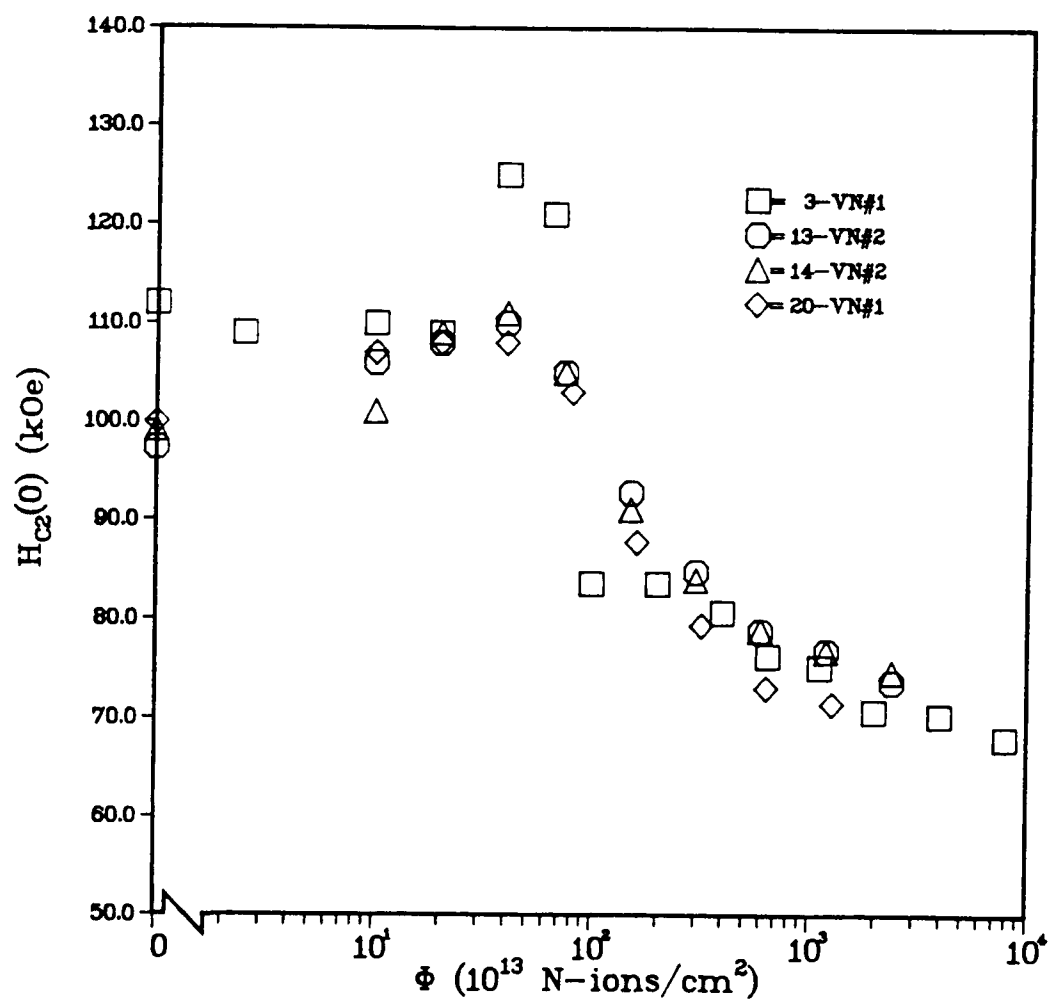


Figure IV.8. The upper critical field extrapolated to zero temperature $H_{C2}(0)$ versus the fluence for VN.

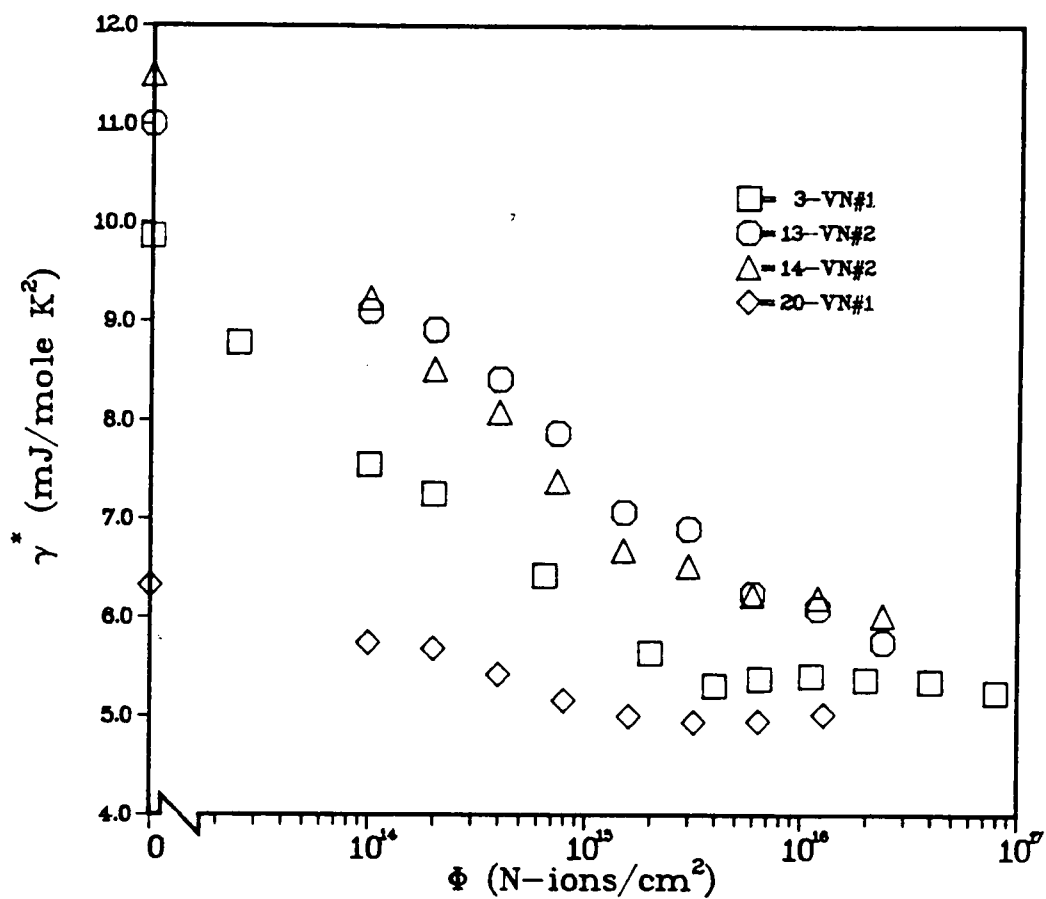


Figure IV.9. The coefficient of the renormalized electronic heat capacity versus the fluence for VN.

upper critical field slope at T_C . From among these we have calculated the zero temperature Ginzburg-Landau coherence length and penetration depth, the renormalized density of electronic states at the Fermi energy, and the electron-phonon coupling parameter as a function of incident ion fluence. In this subsection these deduced values will be presented and an application and discussion of existing theory on the effects of disorder on the density of states will be given.

The zero temperature Ginzburg-Landau coherence length, $\xi_{GL}(0)$, for VN is shown in Figure IV.10. Initially, it decreased slightly with fluence to a minimum at about 4×10^{14} N-ions/cm², after which it increased and saturated at fluences greater than about 6×10^{15} N/cm², similar to the other parameters. The total deviation of the parameter is about 16% before the erratic behavior due to ion-beam mixing of the substrate and sample at fluences above 1.5×10^{16} N/cm². For an individual sample this deviation might be attributed to experimental error; however, since the behavior is systematic for all samples it must be assumed that this is a real effect in the material due to disorder.

The zero temperature penetration depth, $\lambda_{GL}(0)$, is plotted versus the fluence in Figure IV.11. The penetration depth was found to increase with fluence until saturation at the same fluence as the other parameters. Notice that the penetration depth was always greater than the thickness of the films, indicating a complete penetration of the samples by the magnetic field.

The electronic density of states at the Fermi energy (renormalized by many-body corrections), $N^*(0)$, is related to the electronic

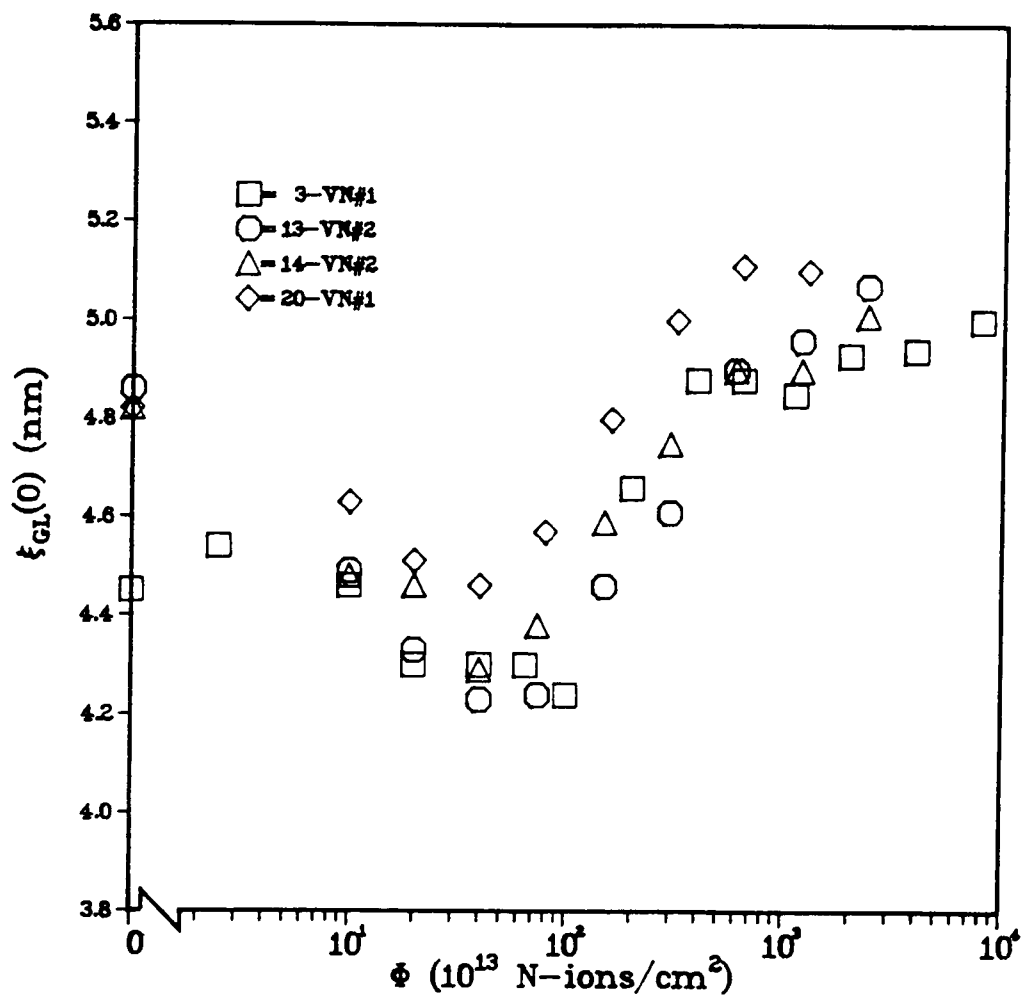


Figure IV.10. The Ginzburg-Landau zero temperature coherence length versus the incident ion fluence for VN.

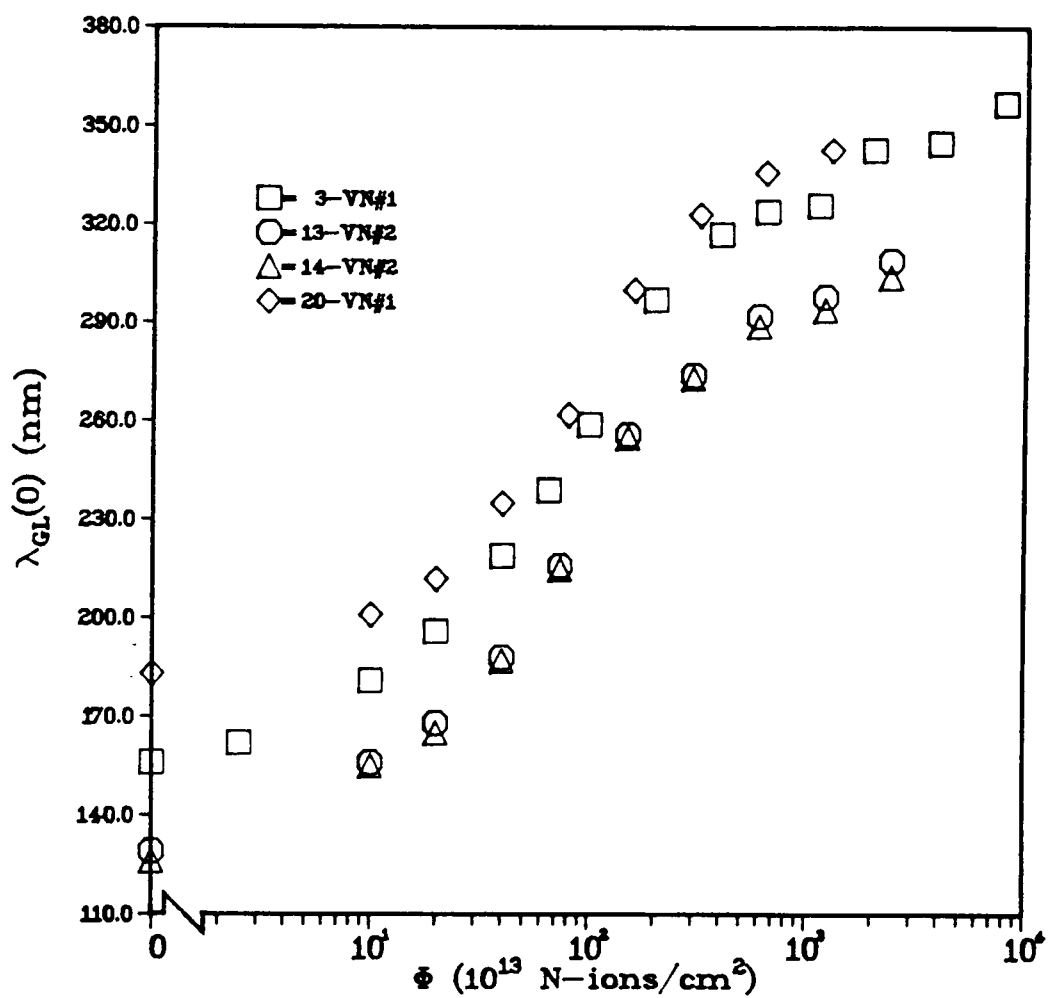


Figure IV.11. The Ginzburg-Landau zero temperature penetration depth versus the fluence for VN.

coefficient to the heat capacity, discussed above, by the formula (Kittel, 1976, p. 165)

$$\gamma^* = 2/3 \pi^2 k_B^2 N^*(0),$$

where k_B is the Boltzmann constant and the 2 appears because the density of states is in units of states/energy-volume-spin. It is related to the band density of states $N^b(0)$ by

$$N^*(0) = (1 + \lambda) N^b(0),$$

where λ is the electronic mass enhancement factor, also called the electron-phonon coupling constant. The renormalized density of states has been calculated from γ^* as a function of fluence and therefore has the same behavior as γ^* in Figure IV.9. The initial values of $N^*(0)$ were correlated with T_C and range, in units of states/eV-V atom-spin, from 1.34 for sample 20-VN#1 to 2.43 for sample 14-VN#2. The values decreased with increasing fluence to saturation. The saturated values of $N^*(0)$ were also correlated with the saturated values of T_C , ranging from 1.06 states/eV-V atom-spin for sample 20-VN#1 to 1.31 states/eV-V atom-spin for 14-VN#2.

To further analyze this data one would like to separate the renormalization factor $(1 + \lambda)$ from the band density of states. We have done this using the electron lifetime model (ELM), discussed in section III,D, to calculate the band density of states as a function of disorder, as measured by the residual resistivity. The results indicate that the band density of states changes very little with disorder, with a total change of about 20% at 200 $\mu\Omega\text{-cm}$. Having determined $N^b(0)$, one may calculate the renormalization λ by

$$\lambda = N^*(0)/N^b(0) - 1.$$

The renormalization may also be calculated from the McMillan equation for T_C , discussed in section III,B. If we assume no spin fluctuations are present we may use equation III.9. Here we also need to know the renormalized coulomb pseudopotential μ^* as well as the prefactor ω_{log} . The coulomb pseudopotential is very difficult to calculate theoretically; therefore, we have used the empirical formula (Bennemann and Garland, 1973; and Papaconstantopoulos et al., 1985)

$$\mu^* = 0.20 \frac{2N^b(0)}{1 + 2N^b(0)},$$

where the density of states was obtained from the ELM. This quantity was found to vary only slightly with damage from an initial value of 0.14 to a value at saturation of 0.13. The phonon frequency ω_{log} for VN, 336 K, was taken from Papaconstantopoulos et al. (1985) and Klein et al. (1974 and 1976), who obtained it in calculations using the phonon spectral function from neutron scattering measurements.

The values of λ determined from γ^* and T_C are both shown in Figure IV.12 as a function of the residual resistivity. The values from T_C decreased from about 0.7 to 0.6; those from γ^* vary much more, even allowing for the sample-to-sample scatter. Several reasons are possible for this disagreement. The most obvious possibility to consider is that spin fluctuations (paramagnons) may be present in this material. Spin fluctuations are conduction electron spin correlations arising from an interaction between their spins which favors parallel alignment. Since the Cooper pair states necessary for superconductivity require the paired electrons to have opposite spin, this clearly is detrimental to the superconducting state. This scheme has been theoretically applied to VN in order to reconcile large

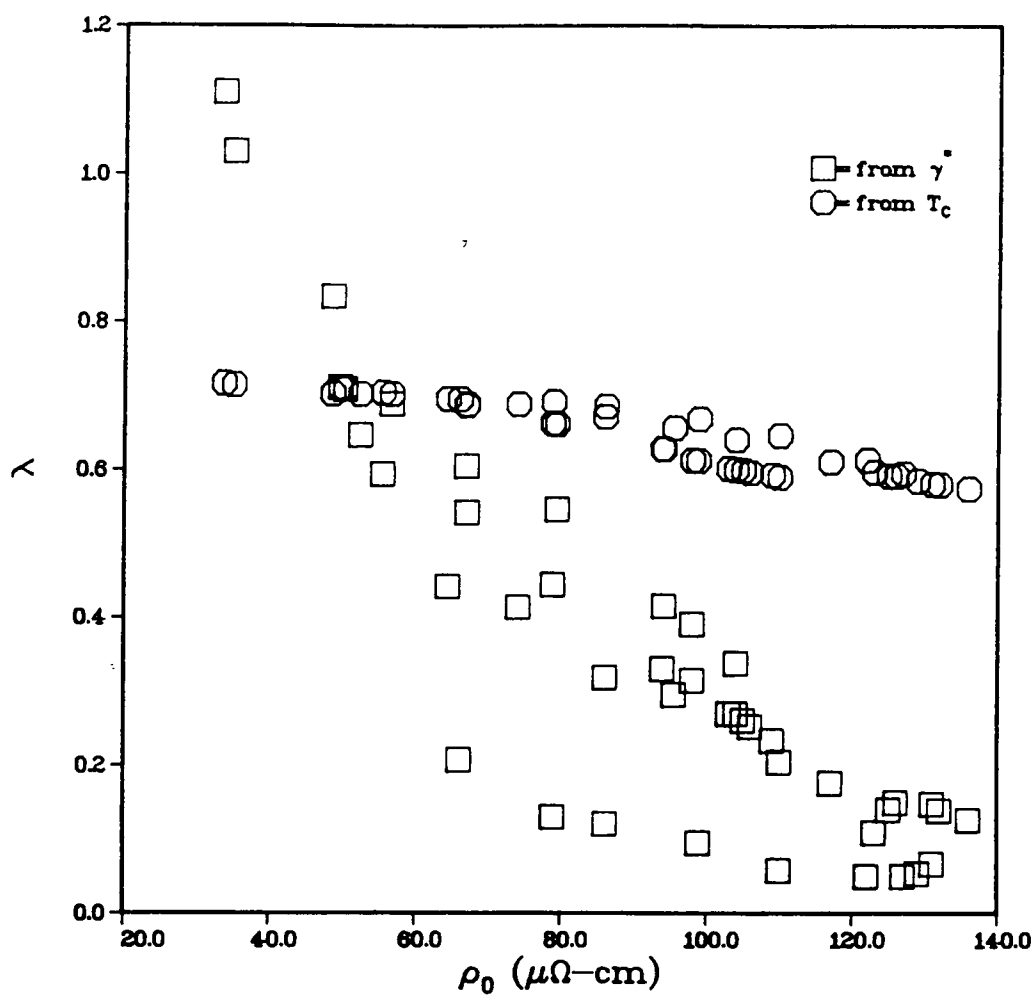


Figure IV.12. Comparison of the mass enhancement factor λ calculated from γ^* and T_c .

differences between calculated and measured values of T_C (Rietschel et al., 1980).

If spin fluctuations do exist, then the McMillan equation must be modified and equation III.10, which includes the spin fluctuation parameter λ_{sf} , must be used. The density of states is also modified:

$$N^*(0) = (1 + \lambda + \lambda_{sf}) N^b(0) = (1 + Z) N^b(0).$$

We can use $N^b(0)$, again determined by using the ELM, to determine the factor Z and along with the modified McMillan equation can obtain two equations involving λ and λ_{sf} which can be solved to determine these parameters. For the unirradiated material reasonable values of λ_{sf} , ≈ 0.2 , were obtained; however, as damage was increased the analysis yielded negative values of λ_{sf} , which is clearly nonphysical since it is a measure of the relative strength of the interaction. Thus we conclude that spin fluctuations do not account for the observed discrepancy.

A second possible explanation for the discrepancy in the two calculations of the electron-phonon coupling constant is that the McMillan equation is not a good approximation to a solution to the Eliashberg equations. This seems very unlikely because it has been used successfully many times to calculate the transition temperature of many superconductors (Allen and Mitrovic', 1982, and references within). Also, in Allen and Mitrovic' (1982, p. 55) a comparison is made between the McMillan equation, numerical solutions of the Eliashberg equations for several different phonon spectra, and experimental results from Allen and Dynes (1975). Here it is shown that the McMillan equation agrees exactly with the numerical solutions

and quite well with the experimental results for λ values up to about 1.2, which is above the range of our highest results. For VN, one can compare the results of Papaconstantopoulos et al. (1985), who calculated T_C and γ^* , from band structure calculations and the McMillan equation, to the results of Geibel et al. (1985), who determined γ^* by direct heat capacity measurements. The former obtained a γ^* value close to the latter but predicted a transition temperature of 19.7 K, thus there exists an apparent inconsistency in the theoretical calculation. The above mentioned theoretical work can also be contrasted to another theoretical calculation of T_C and γ^* where T_C was determined from direct numerical solution of the Eliashberg equations (Rietschel et al., 1980). This also resulted in γ^* values close to the experimental values but yielded a T_C value of 32.3 K. From this evidence it is felt that the McMillan equation is an unlikely culprit for the observed differences in λ .

Another possible problem may lie in the average phonon frequency ω_{log} . Two problems could possibly arise with the use of ω_{log} : (1) ω_{log} could be changing with increasing damage and (2) the value used for ω_{log} could be incorrect. The first possibility is unlikely because the dependence of λ on ω_{log} is logarithmic, thus only large changes would affect it. While there is in principle not a simple relationship between ω_{log} and the Debye temperature Θ_D , it has been found empirically that they are almost proportional in many compounds (Orlando and Beasley, 1981). This is reasonable since both are measures of some average phonon frequency. Unfortunately, no measurements of the heat capacity of B1 materials as a function of

lattice disorder have been made, therefore one cannot directly comment on the behavior of Θ_D ; however, such measurements on A15 compounds (Poate et al., 1975) indicate that Θ_D , and thus probably ω_{log} , changes very little.

An incorrect value for ω_{log} is even less likely. For example, for the best sample ω_{log} would have to be 130 K in order to force the values from T_C and γ^* to agree. Not only is this number itself very small, the resulting dependence on damage is still incorrect. When it is used in the calculation of λ from T_C the resulting resistivity dependence only gives a total change of about 30% while the λ from γ^* changes by 80%; therefore, it is felt that any possible changes in ω_{log} would create only a small change in the λ calculation and definitely could not be the reason for the discrepancy.

The final possibility for the discrepancy is some problem with the electron lifetime model. The parameters that go into this calculation are the resistivity and the Drude plasma frequency. Since the resistivity is an experimentally measured quantity it must be correct; however, the plasma frequency was determined from band structure calculations by D. A. Papaconstantopoulos (private communication). While the accuracy of this number is not questioned (7.1 eV) for a perfectly ordered lattice, we have no way to determine the effect of disorder on the plasma frequency. Calculations of the plasma frequency for A15 materials as a function of disorder (Mattheiss and Testardi, 1979) indicate that it does not change much and the change is not monotonic.

Another possible problem with the ELM is that the form of the broadening function, a Lorentzian in this case, may be inappropriate; however, Testardi and Mattheiss (1978) have compared the results of using two different functions, a Lorentzian and a broadening function obtained by differentiation of the Fermi-Dirac function with respect to energy, and find differences of less than 10% for A15 compounds.

The most obvious problem with the use of the electron lifetime model, however, is that, while it may accurately describe the effects of disorder on the density of states, this may not be the dominant effect on the superconducting properties. The ELM has been shown to work well in describing the effects of ion and neutron damage on the A15 compounds (Testardi and Mattheiss, 1978; Mattheiss and Testardi, 1979; and Soukoulis and Papaconstantopoulos, 1982); in most of these materials however, the Fermi energy lies on a large sharp peak in the density of states so that the ELM predicts a large change in $N_b(0)$ with disorder. This large decrease may therefore overshadow other effects. In VN and many other B1 materials, the Fermi energy is actually on the side of a large peak, so that the ELM predicts instead an initial increase in the density of states and then only a small decrease. Thus the density of states reduction, due to disorder, may be small compared to some other effect.

From the above discussion one must conclude that the damage induced changes in the superconducting properties of VN cannot be accounted for solely by lifetime broadening effects in the density of states. We suggest that some other interaction is taking place, which may be overshadowed in the high temperature A15 superconductors by

large changes in the density of states (since the predicted changes in VN are small). We must also consider the possibility that there is a fundamental problem with the theoretical calculations of the superconducting properties of this material since the calculations yield reasonable values for the normal state properties (for example γ^*) but give gross overestimates of the transition temperature.

3. Annealing Studies

In order to determine whether the damage suffered by the VN samples was reversible, annealing studies were undertaken on the irradiated samples. Sample 13-VN#2 was annealed in vacuum while sample 14-VN#2 was annealed in a nitrogen atmosphere. The measured quantities are presented in the same order as above and then discussed so that comparison is made straightforward.

Resistivity. Figure IV.13 shows the effect of annealing in nitrogen and vacuum on the residual resistance ratio R , plotted versus the annealing temperature T_A . R increased very little, by 0.03, up to annealing temperatures of about 500°C. Above 500°C it increased rapidly to a maximum at 900°C. The maximum value for the nitrogen annealed sample was 1.73, while for the vacuum annealed sample the maximum was 1.69, which are both equal to the their initial predamaged values within experimental error. Up to this temperature the vacuum and nitrogen anneal data were very similar; however, at higher temperatures the vacuum annealed sample showed a much faster decrease in R than did the N₂-annealed sample.

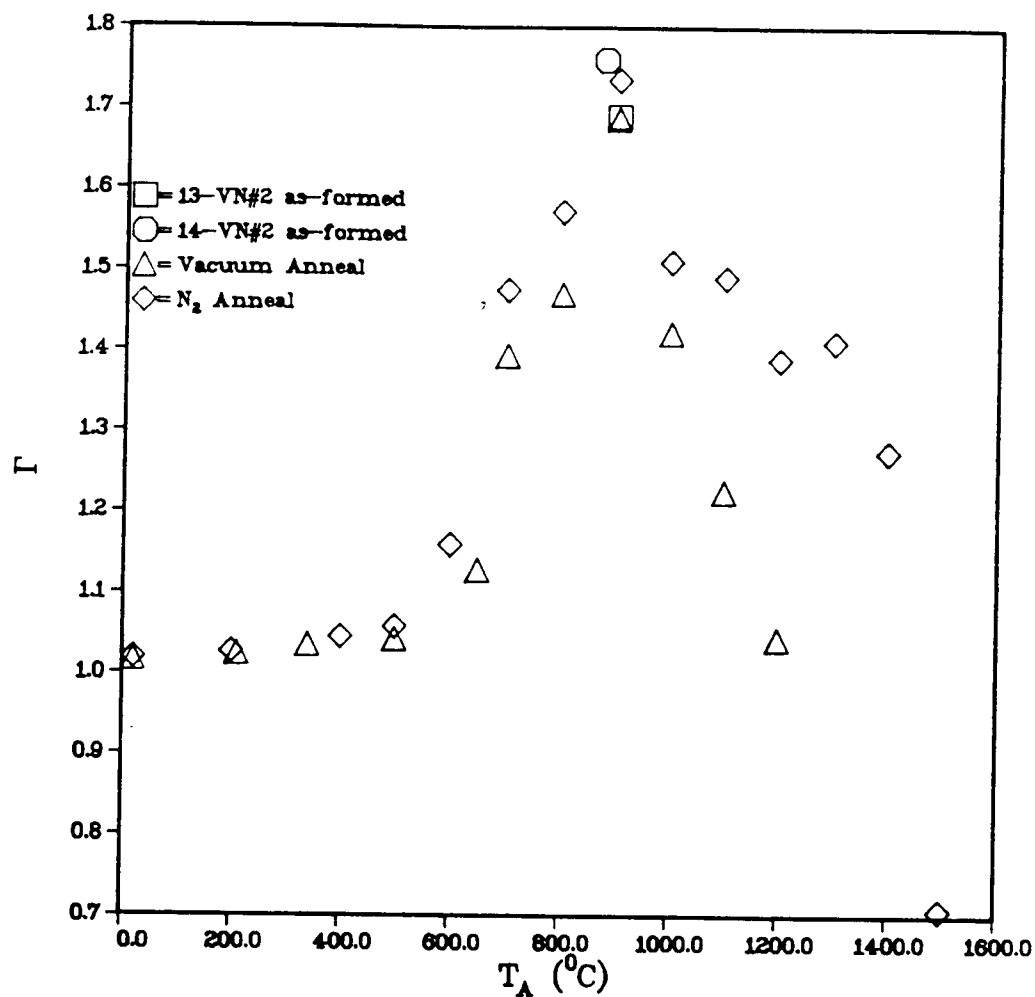


Figure IV.13. The residual resistance ratio versus the annealing temperature T_A . Sample 13-VN#2 was annealed in vacuum while sample 14-VN#2 was annealed in a nitrogen atmosphere. The values for the samples prior to ion irradiation are shown at their formation temperature.

The effect of annealing in nitrogen and vacuum on the residual resistivity is shown in Figure IV.14. As with the resistance ratio, the resistivity of both samples behaved similarly up to 900°C. The resistivity decreased slowly to a temperature of 500°C after which it decreased much more rapidly to a minimum at 900°C. The minimum values were 34.6 $\mu\Omega$ -cm for the nitrogen annealed sample and 36.6 $\mu\Omega$ -cm for the vacuum annealed sample, both just slightly above their original values. Above this temperature the resistivity of the nitrogen annealed sample increased slowly while the resistivity of the vacuum annealed sample increased very rapidly.

Transition Temperature. The transition temperature in Figure IV.15 followed a somewhat different recovery behavior than the resistance ratio and resistivity. As with the previous parameters T_C slowly increased with increasing annealing temperatures up to $T_A = 500^\circ\text{C}$, where T_C for both samples had increased by about 0.7 K. From 500 to 700°C T_C quickly jumped up to a value of 8.63 K for the nitrogen annealed sample and 8.47 K for the vacuum annealed sample. From 700 to 1000°C T_C remained approximately constant, reaching maxima of 8.64 K in N_2 and 8.55 in vacuo at $T_A = 800^\circ\text{C}$. These values are slightly lower than the initial ones, which is probably due to some extra impurities in the samples arising from ion mixing with the substrate at high radiation doses. Above 1000°C the T_C of the N_2 -annealed sample slowly decreased to 8.34 K at 1300°C and dropped quickly above this temperature. The transition temperature of the vacuum annealed sample dropped rapidly above 1000°C and was reduced to 4.90 K at 1200°C.

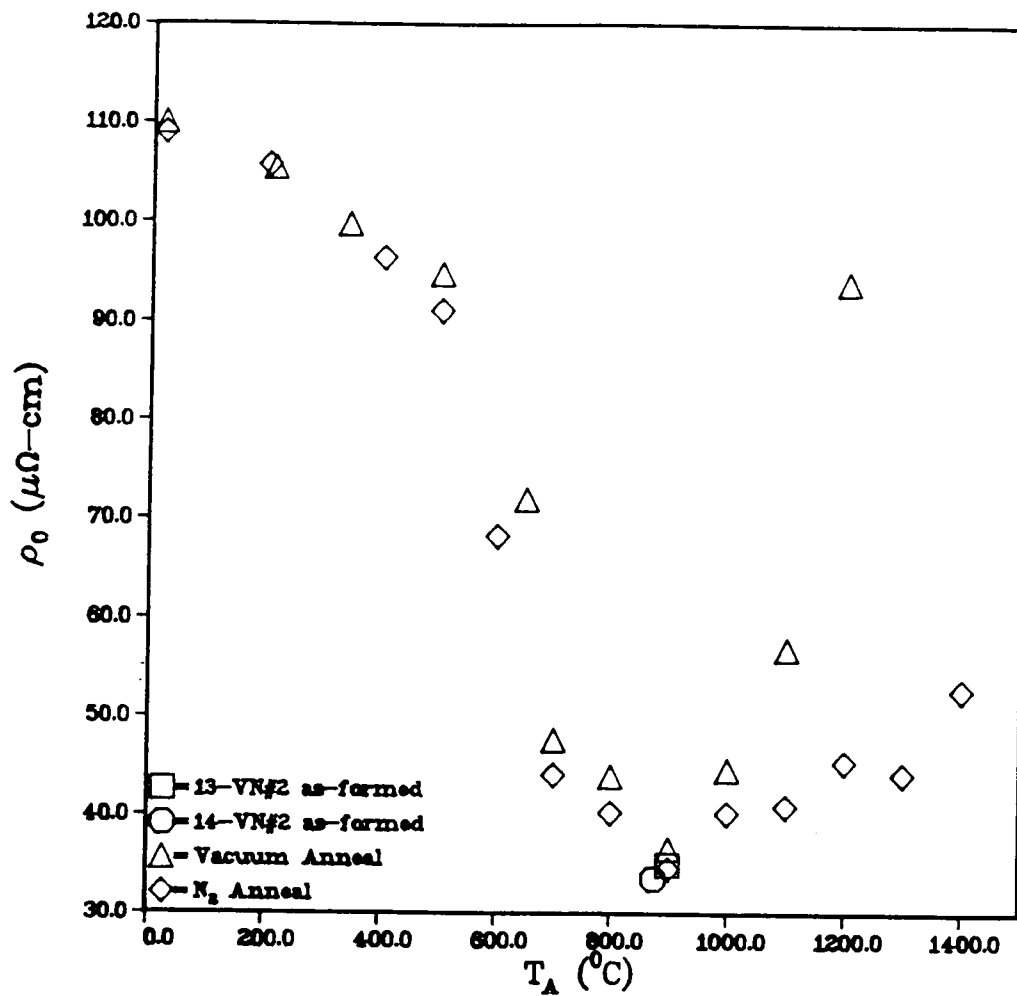


Figure IV.14. The residual resistivity versus the annealing temperature for VN.

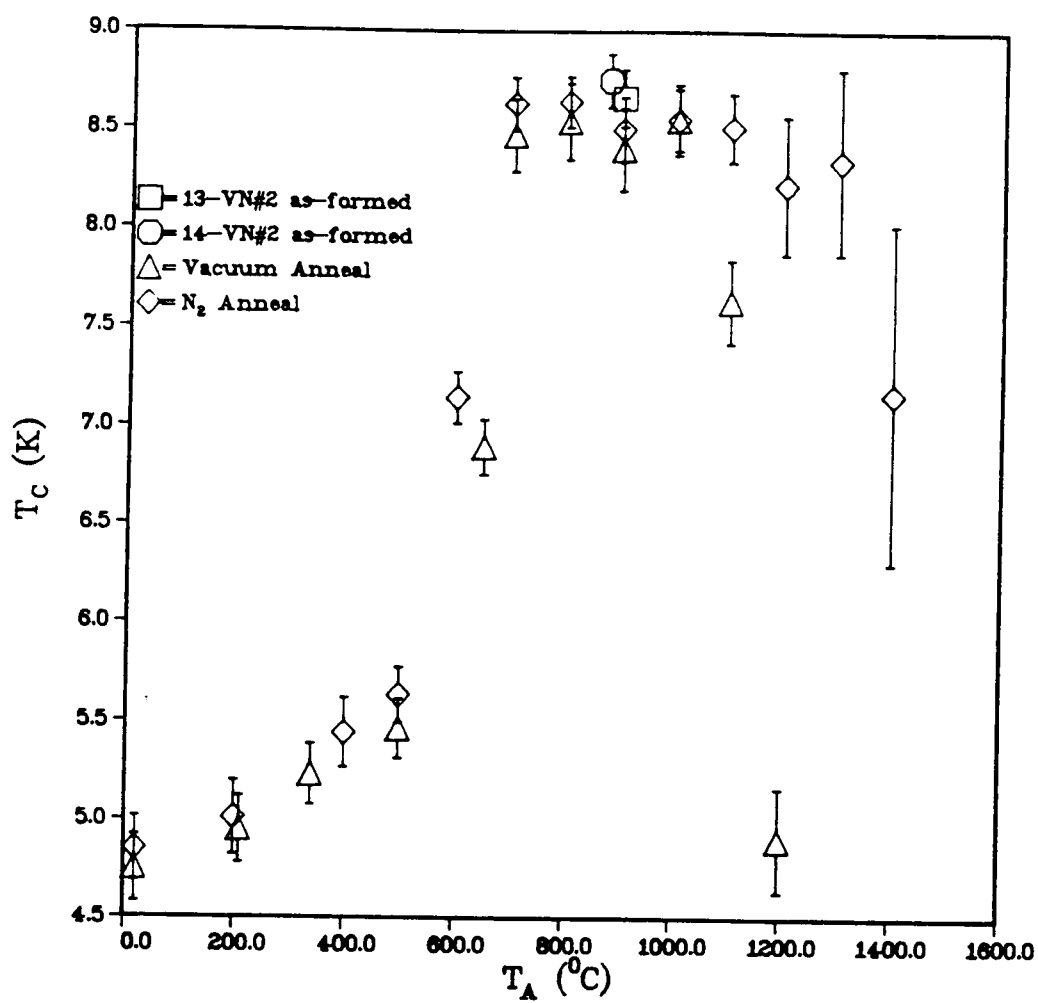


Figure IV.15. The transition temperature versus the annealing temperature for VN. The error bars indicate the width of the transition.

The transition widths, shown in Figure IV.15 as error bars, of both samples initially increased slightly and then decreased to a minimum at about 650°C. From there the width of the vacuum annealed sample continuously increased with annealing temperature to a value of 0.53 K at 1200°C. The transition widths of the N₂-annealed sample remained constant up to 800°C where they rapidly increased with annealing temperature to a value of 2.66 K at 1500°C.

Lattice Constant. The lattice constant a_0 was determined at several annealing temperatures using X-ray diffraction. For the N₂-annealed sample a_0 remained constant at 0.4144 nm, within experimental error, throughout the annealing sequence. The lattice constant of the vacuum annealed sample remained constant for annealing temperatures up to 1100°C with an average value of 0.4143 nm. At 1200°C the lattice constant dropped to 0.4115 nm, indicating a loss of nitrogen from the VN lattice. This corresponds to a nitrogen concentration of $x = 0.906$ (Brauer and Schnell, 1964) where x is given by VN _{x} .

For both samples, after annealing at 700°C, the higher order peaks in the X-ray diffraction pattern began to reappear, and by 900°C most of the higher order peaks had returned. At 1200°C the higher order peaks had sharpened and all the appropriate peaks were visible. At 1500°C, the vacuum annealed sample's pattern showed all of the expected peaks; however, two extra peaks appeared which could not be identified.

Upper Critical Field. The upper critical field of each sample was measured, as a function of temperature, after each anneal. In both

the N₂-anneals and the vacuum anneals the upper critical field curves were found to fit the WHH theory, in the dirty limit, including Pauli paramagnetic limiting. The H_{C2}' values measured as a function of annealing temperature were found to behave very similar to the resistivity. For both samples, H_{C2}' reached a minimum at an annealing temperature of 900°C, which in both cases was actually below the initial value. Above this temperature H_{C2}' of the N₂-annealed sample increased slowly up to 1400°C where it jumped up rapidly, while the slope for the vacuum annealed sample increased rapidly above 900°C.

The γ^* values for the N₂-annealed sample increased slowly from 6.02 mJ/mole-K² to 6.81 mJ/mole-K² at an annealing temperature of 500°C. Above this temperature it increased rapidly to 10.5 mJ/mole-K² at 900°C. From 900 to 1200°C γ^* slowly decreased and dropped sharply at 1300°C. At 1400°C γ^* jumped up again to a maximum of 10.7 mJ/mole-K². The γ^* values for the vacuum annealed sample followed those for the nitrogen annealed sample very closely for temperatures less than and equal to 500°C. Above this temperature γ^* for the vacuum annealed sample increased rapidly and continuously to a maximum of 10.4 mJ/mole-K² at 1100°C. At 1200°C γ^* dropped to a value of 6.93 mJ/mole-K².

Microscopic Properties. As in the ion irradiation studies, we have calculated the zero temperature Ginzburg-Landau coherence length and penetration depth as a function of the annealing temperature. The coherence lengths for the vacuum and nitrogen annealed samples are shown in Figure IV.16. Here we see that the coherence length initially decreased slowly with increasing temperature to about 500°C.

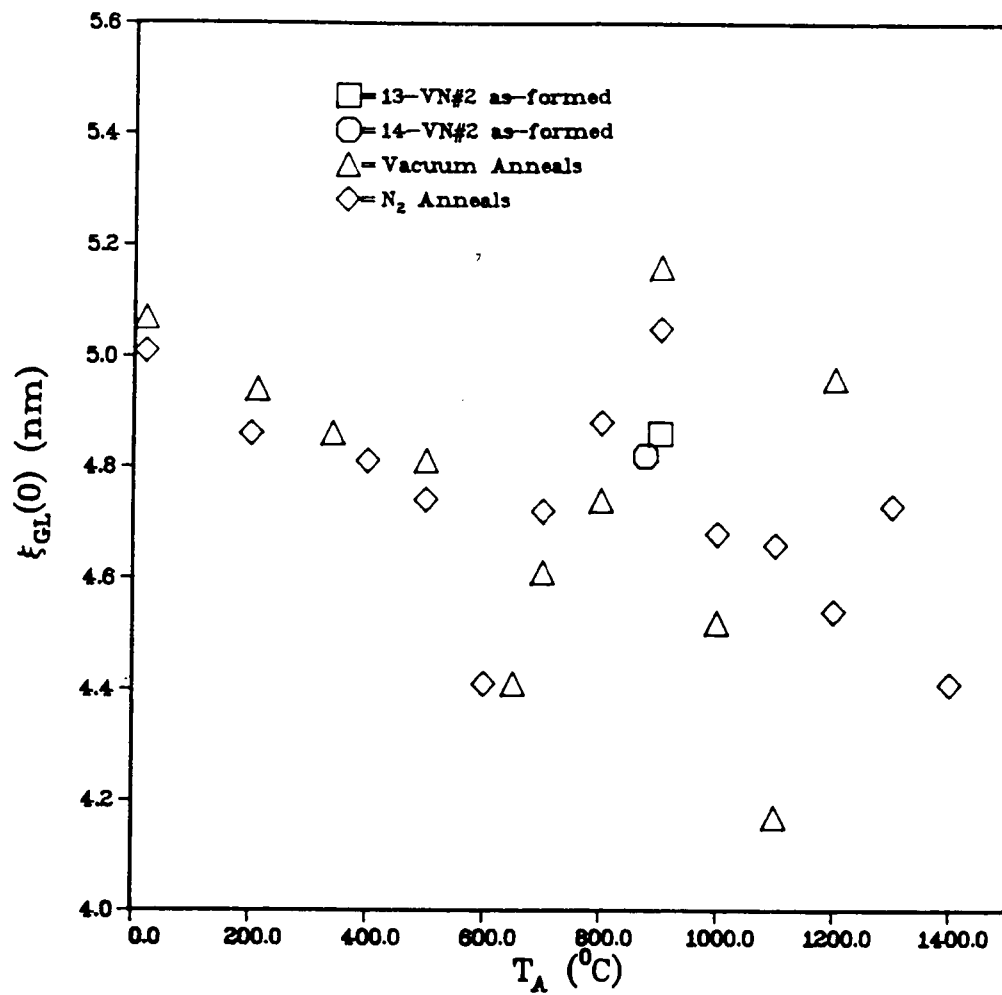


Figure IV.16. The Ginzburg-Landau zero temperature coherence length versus the annealing temperature of VN.

Above this temperature it dropped quickly then rapidly increased to a maximum at 900°C. Above 900°C the vacuum annealed sample's coherence length dropped drastically, while the N₂-annealed sample's coherence length only gradually decreased. The overall change was actually quite small.

The Ginzburg-Landau penetration depth is shown in Figure IV.17. The penetration depth behaved very similarly to the resistivity. It decreased rapidly to a minimum at 900°C. At higher temperatures the penetration depth for the nitrogen annealed sample only gradually increased while for the vacuum annealed sample it increased rapidly.

The renormalized density of states at the Fermi energy $N^*(0)$ for both samples is shown in Figure IV.18. It was observed to increase slowly at first, then rapidly to a plateau region between 900 and 1100°C for the N₂-annealed sample and to a sharp maximum at 1100°C for the vacuum annealed sample. Above this temperature $N^*(0)$ decreased rapidly for the vacuum annealed sample and slowly for the nitrogen annealed sample.

Discussion of Annealing Behavior. At this point some remarks are needed as to the interpretation of the annealing results. From the X-ray analysis it is obvious that annealing the VN films in vacuum at temperatures above 1100°C caused some loss of nitrogen in the samples since the lattice constant was observed to decrease. This is not unexpected when one considers the nitrogen partial pressure work of Kieda et al. (1984). In this work the equilibrium nitrogen partial pressure was measured for VN bulk samples as a function of temperature. They found that at 1107°C and at a nitrogen pressure of

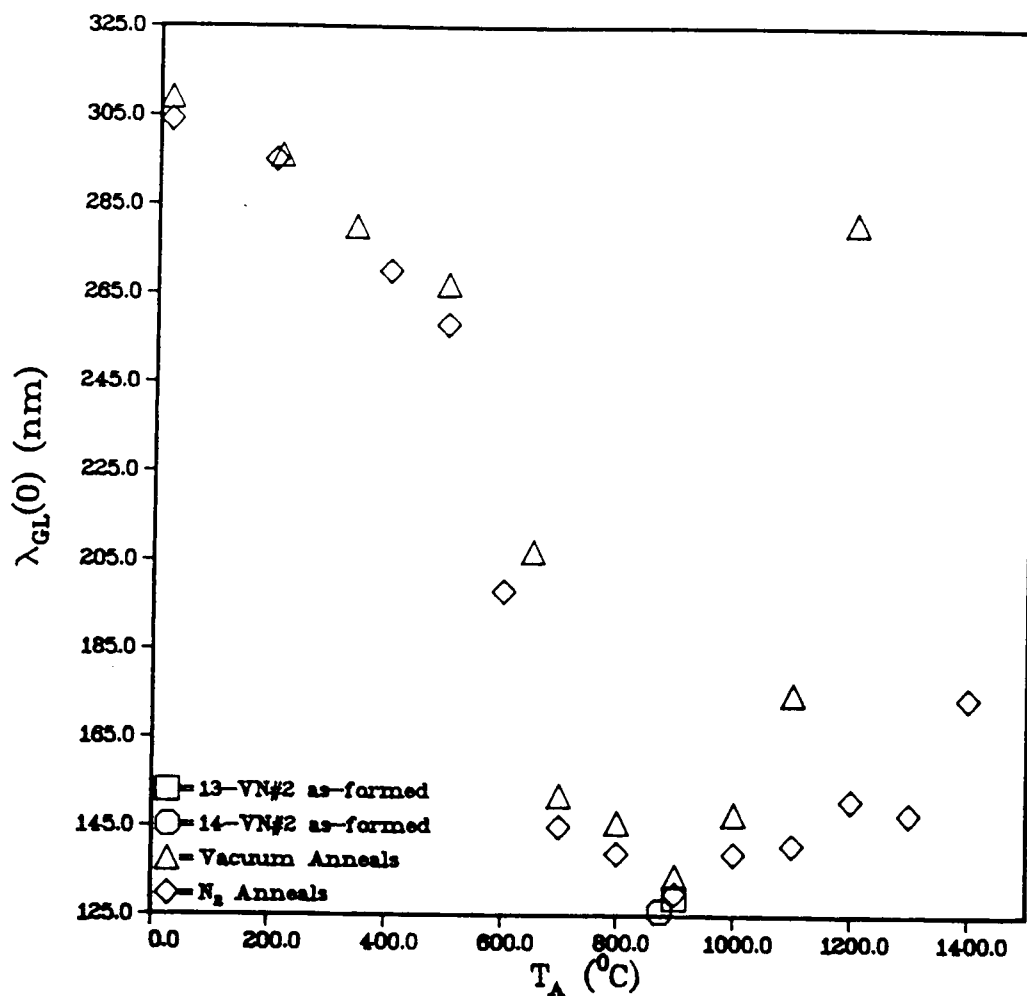


Figure IV.17. The Ginzburg-Landau zero temperature penetration depth versus the annealing temperature for VN.

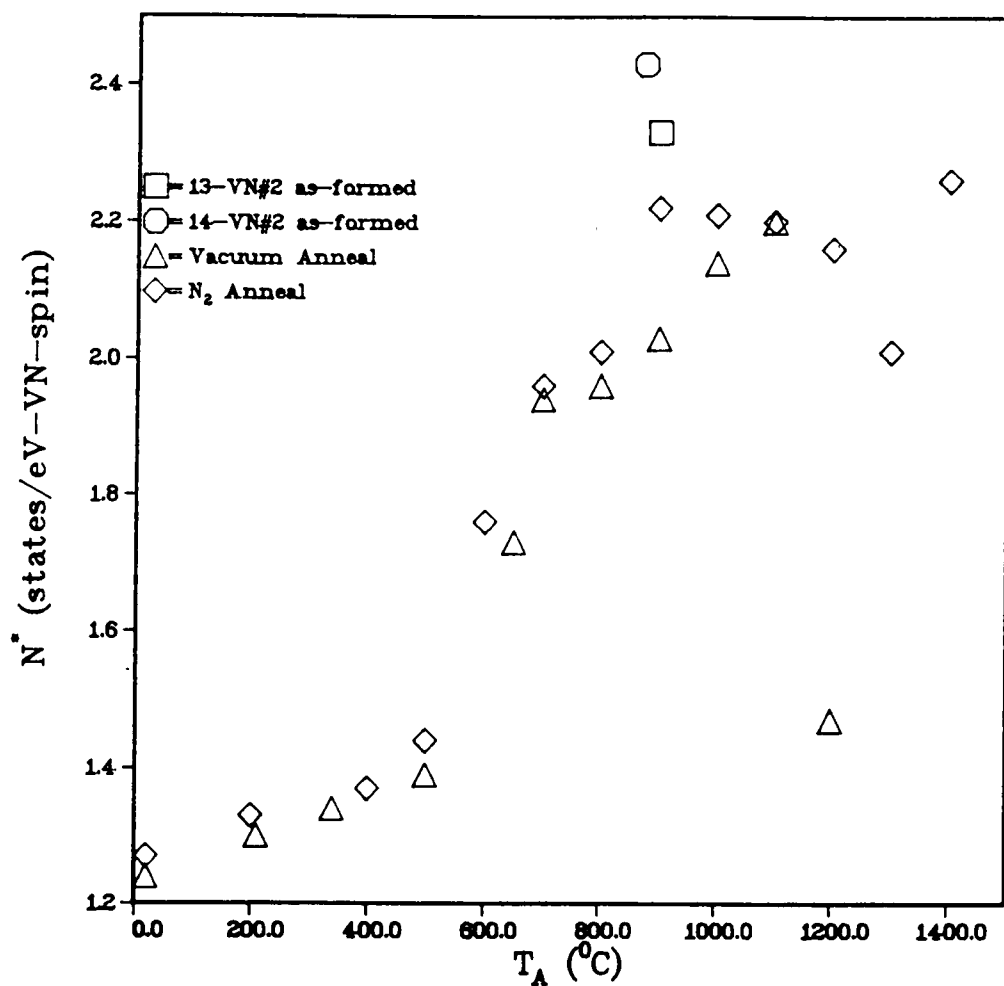


Figure IV.18. The renormalized density of electronic states at the Fermi energy versus the annealing temperature for VN.

1×10^{-2} atmospheres the equilibrium nitrogen concentration was $x = 0.89$ in VN_x . From the lattice constant of the vacuum annealed film we calculate, using the data of Brauer and Schnell (1964), the nitrogen concentration has dropped to 0.906. This decrease in nitrogen explains the difference in behavior between the vacuum and nitrogen annealed samples at temperatures above about 1000°C .

Since X-rays are more strongly scattered by V atoms than nitrogen atoms, the X-ray diffraction analysis of VN was much more sensitive to the metal sublattice than to the non-metal sublattice. The recovery of higher order B1 peaks after annealing at 700°C indicates that this is an annealing stage for the metal sublattice. (This has also been noted in annealing of ion damaged NbC by Kobayashi et al., 1985.) The simultaneous recovery of T_C at this temperature further indicates that T_C is more sensitive to metal sublattice vacancies than is the resistivity since it was still decreasing at this temperature. This seems to support our supposition (first stated in section IV, A, 2) that T_C is more sensitive to defects on one sublattice than the other; however, one must carefully note that we still can make no statement about defects on the nitrogen sublattice at annealing temperatures below 1100°C . Both theoretical (Marksteiner et al., 1986; and Papaconstantopoulos and Pickett, 1985) and experimental (Ajami and MacCrone, 1975; Toth et al., 1966; and Pessall et al., 1976 and 1968) investigations of the sensitivity of properties of B1 superconductors to vacancies on the non-metal sublattice indicate that they are indeed very sensitive to these vacancies; however, no work has been done on the sensitivity of properties to metal sublattice vacancies.

B. TITANIUM NITRIDE

In order to determine if the effects of nitrogen ion irradiation and thermal annealing observed in vanadium nitride are exclusive to this material or if these are general characteristics of B1 phase, superconducting compounds we have performed similar experiments using the B1 phase superconductor titanium nitride. The results of these experiments are presented and discussed in this section. It is organized in the same manner as with VN for ease of comparison.

1. As-Formed Samples

In this section the properties of the titanium nitride films prior to ion irradiation will be discussed. In the process of optimizing the properties of the TiN films many samples were produced; however, only four optimized films were used in the subsequent irradiation and annealing experiments, the following discussion will be restricted to these films. First the initially measured quantities will be discussed, followed by a discussion of the parameters obtained from them.

The initially measured parameters are summarized in Table IV.8. The first parameter of interest is the transition temperature, which ranged from 4.22 to 4.48 K. The transition widths ranged from 0.07 to 0.15 K and were not correlated with T_C . The residual resistivity ranged from 16.4 $\mu\Omega$ -cm for the sample with the highest T_C to 44.9 $\mu\Omega$ -cm for the sample with the lowest T_C . The residual resistivities were correlated with the transition temperature in this manner, but as with VN, not so that a maximum T_C could be deduced. The residual

Table IV.8. Initial parameters of the TiN samples.^a

Sample	T_C	ΔT_C	ρ_0	Γ	H_{C2}'	a_0
8-TiN#1	4.44	0.07	18.3	1.84	2.42	.4243
9-TiN#1	4.22	0.10	44.9	1.31	4.25	.4244
19-TiN#1	4.34	0.15	18.9	1.68	2.73	.4239
20-TiN#1	4.48	0.10	16.4	1.78	2.50	.4243

^aThe units are T_C in K, ΔT_C in K, ρ_0 in $\mu\Omega\text{-cm}$, H_{C2} in kOe/K, and a_0 in nm.

resistance ratio ranged from 1.31 to 1.84 and was correlated with the transition temperature except for sample 8-TiN#1 which had the second highest T_C but the highest resistance ratio.

The upper critical field data as a function of temperature was found to fit the WHH theory in the dirty limit, without including paramagnetic limiting or spin orbit scattering; however, in two of the films positive curvature near T_C was observed. This has also been observed in other materials and has been attributed to inhomogeneities but no evidence of inhomogeneity was seen in these samples. The slope of the upper critical field at T_C , H_{C2}' , varied from 2.42 to 4.25 kOe/K and was not correlated with the transition temperature in general. The three samples with the highest T_C values had very similar H_{C2}' values but the lowest T_C sample had a slope almost twice as large as the others.

The lattice constant, a_0 , determined from X-ray diffraction ranged from 0.4239 to 0.4244 nm. Measurements on bulk TiN samples have found lattice constants of 0.4239 to 0.4241 nm (Toth, 1971, p. 220) with a_0 decreasing as the nitrogen concentration varies from the stoichiometric composition. The lattice parameters of the TiN films were closer to the bulk values than those of the VN films. This is probably due to the fact that there is only an 8.1% volume increase when transforming from the h.c.p Ti metal to the f.c.c. space lattice TiN, as compared to 27.5% for VN, therefore the stresses in the film are likely to be less. As with VN, the transition temperature has been observed to depend strongly on stoichiometry (Toth et al., 1966). Since our samples all have the same lattice constant, any deficiency

in nitrogen is probably due to the occupation of nitrogen sites by oxygen and/or carbon impurities as discussed in the vanadium nitride section. The X-ray diffraction patterns showed only peaks associated with B1 phase of TiN except for the peaks from the sapphire substrate.

The upper critical field extrapolated to zero temperature, $H_{C2}(0)$, was found to range from 7.41 to 13.2 kOe and was not correlated with the initial parameters. The renormalized electronic heat capacity coefficient γ^* , calculated from H_{C2}' and ρ_0 , ranged from 2.42 to 3.79 mJ/mole-K². These were correlated with T_C and were close to the values 2.5 mJ/mole-K² (Costa, 1968) and 3.3 mJ/mole-K² (Pessall et al., 1967) reported from direct heat capacity measurements. A value of 2.7 mJ/mole-K² has also been obtained in band structure calculations (Rietschel et al., 1980).

The renormalized electronic density of states at the Fermi energy $N^*(0)$, calculated from γ^* , varied from 0.513 to 0.803 states/eV-Ti atom-spin and was also correlated with the transition temperature. The zero temperature Ginzburg-Landau coherence length $\xi_{GL}(0)$ was nearly constant for the three best samples, with an average value of 17.1 nm, and was not correlated with T_C ; however, the sample with the lowest T_C had a coherence length of 13.5 nm. The zero temperature Ginzburg-Landau penetration depth $\lambda_{GL}(0)$ ranged from 125 to 209 nm and was correlated with the resistivity as would be expected from the equation used to calculate it. These values are shown in Table IV.9.

Table IV.9. Superconducting properties calculated from the initial parameters for TiN.^a

Sample	$H_{C2}(0)$	γ^*	$N^*(0)$	$\xi_{GL}(0)$	$\lambda_{GL}(0)$
8-TiN#1	7.41	3.38	0.716	17.5	130
9-TiN#1	13.2	2.42	0.513	13.5	209
19-TiN#1	8.18	3.12	0.667	16.8	146
20-TiN#1	7.73	3.79	0.803	17.1	125

^aThe units are $H_{C2}(0)$ in kOe, γ^* in mJ/mole-K², $N^*(0)$ in states/eV-metal atom-spin, $\xi_{GL}(0)$ in nm, and $\lambda_{GL}(0)$ in nm.

2. Irradiation Studies

The N-ion irradiation experiments on the TiN films were done exactly like those on the VN films reported above. The same empirical models were found to apply equally well to this system so any discussion of their origin will be omitted; the results will then be discussed.

Resistivity. The effect of nitrogen ion irradiation on the residual resistance ratio R is shown in Figure IV.19. The resistance ratio of TiN was found to decrease with increasing fluence as with the VN samples; however, R saturated to a value of about 1.1 rather than 1.0. This means that there was still some temperature dependence to the resistivity even at high radiation doses.

The residual resistivity ρ_0 was observed to initially increase rapidly then saturate at fluences greater than about 1×10^{16} N-ions/cm² or about 60 eV/atom. This corresponds to approximately 3 displacements per atom. At fluences greater than 1.5×10^{16} N/cm² the resistivity behaved erratically indicating again ion beam mixing. This is the same fluence at which this effect occurred for VN indicating that it is related to the sapphire substrate rather than the film material deposited on it. The initial and saturated resistivities were found to be sample dependent. The residual resistivity as a function of fluence is plotted in Figure IV.20 (note: the erratic behavior at high fluences has been omitted from the figure).

The residual resistivity was also found to fit an exponentially saturating function of the same form as vanadium nitride. The fits to

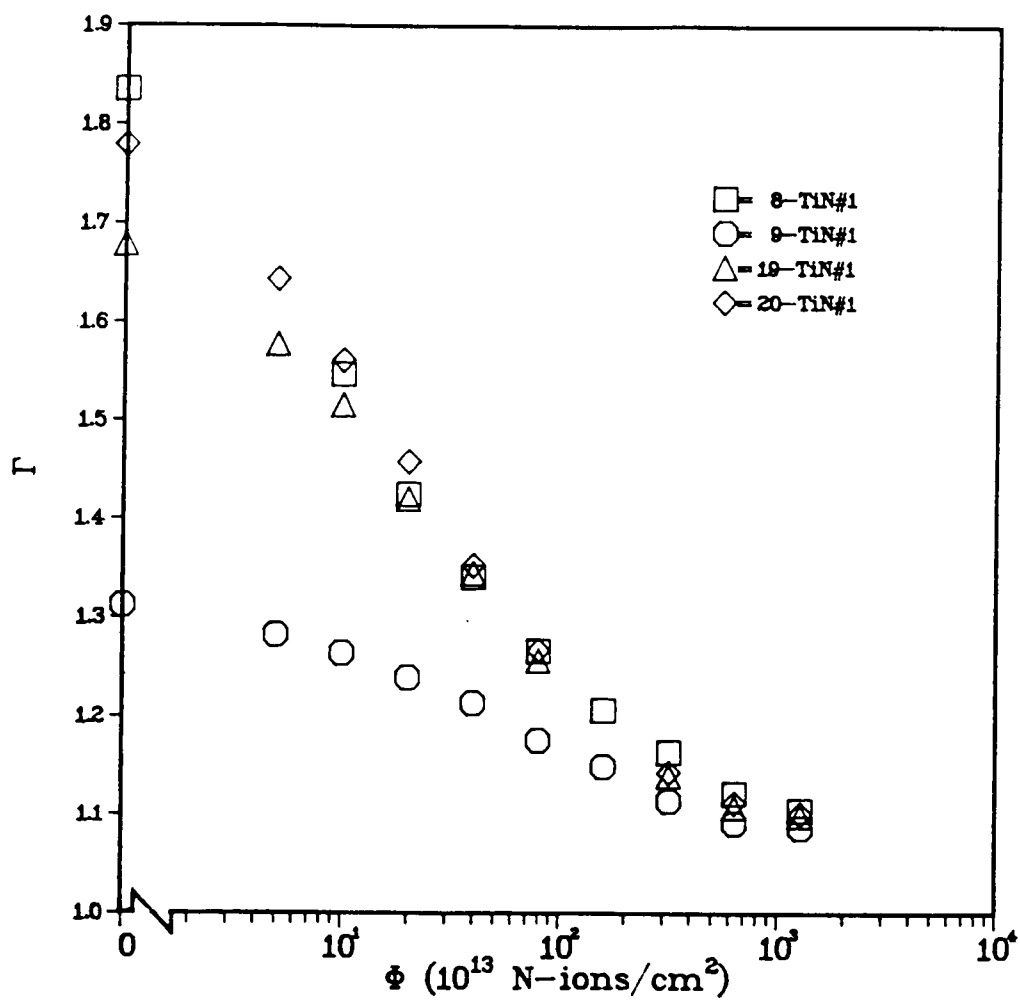


Figure IV.19. The residual resistance ratio versus the incident ion fluence for TiN.

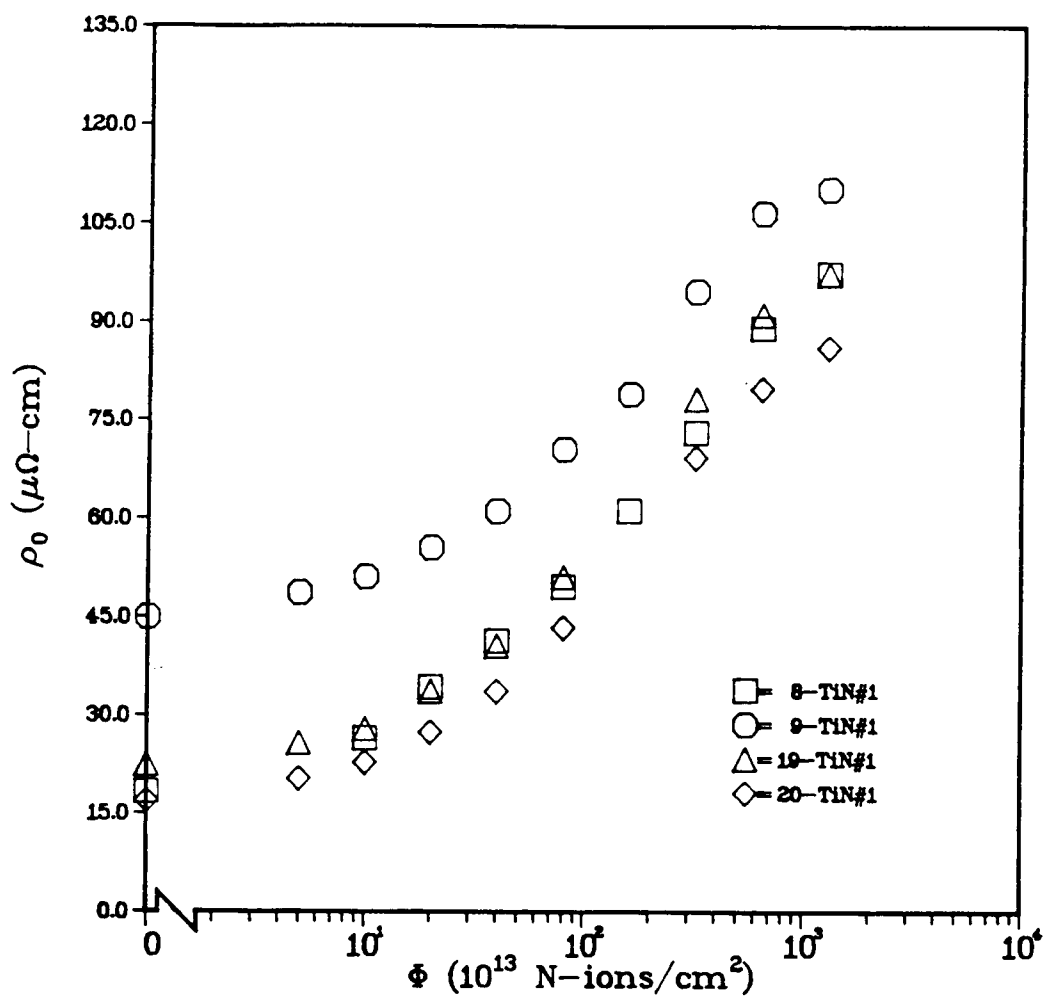


Figure IV.20. The residual resistivity versus the fluence for TiN.

this function were good with a average RMS deviation of $3.8 \mu\Omega\text{-cm}$ (6.0%). The initial and saturated resistivities, $\rho_0(0)$ and $\rho_0(\infty)$, respectively, are shown in Table IV.10. The decay constant was approximately sample independent and had an average value of $1.92 \times 10^{15} \text{ N-ions/cm}^2 \pm 2.5\%$ or equivalently 11.6 eV/atom. This corresponds to about 0.6 displacements per atom.

We can now apply our defect production and annealing model to the TiN system. Following the same procedure as with VN we define the sample with the highest transition temperature and lowest initial residual resistivity to have a zero impurity resistivity term. Please note that, as with VN, this method is used only to set some relative value to the associated parameters; that is, it gives us a quantity relating the relative impurity contributions of the samples studied. This is stated here rather than in the VN section because it is felt the assumption that the best VN film has no impurities may have been proper since it possessed a transition temperature close to the bulk value for VN (about 4% below the highest reported value); however, this assumption is probably not as close to reality for the TiN films since the best sample's T_C was about 18% below the bulk value of 5.5 K.

Applying this model the defect and impurity terms in the resistivity can be separated as before. The results of this are shown in Table IV.10 along with the measured initial and saturated resistivity values. We see that the impurity term is correlated with the transition temperature while the defect term is not correlated

Table IV.10. The values of ρ_I and ρ_D^i for TiN using $\rho_D^S = 86.0 \mu\Omega\text{-cm}$.^a

Sample	$\rho_0(0)$	$\rho_0(\infty)$	ρ_I	ρ_D^i
8-TiN#1	18.3	97.4	11.4	6.90
9-TiN#1	44.9	110	24.0	20.9
19-TiN#1	22.4	97.2	11.2	11.2
20-TiN#1	16.9	86.0	0	16.9

^aAll units are in $\mu\Omega\text{-cm}$.

with T_C at all. The resistivity can now be completely described by the equation

$$\rho_0(\Phi) = \rho_I + \rho_D^i + (86.0 \mu\Omega\text{-cm} - \rho_D^i) [1 - \exp(-\Phi/b)],$$

where $b = 1.92 \times 10^{15}$ N-ions/cm². The defect part of the resistivity is plotted versus the fluence in Figure IV.21.

It is now interesting to see if the parallel resistance model can be applied to the TiN system. Fitting the data to the model in the same manner as before, the parallel resistance was determined to be $\rho_{\max} = 383 \mu\Omega\text{-cm} \pm 6.2\%$. This parallel resistivity can now be removed so the "ideal" resistivity ρ_P can be inspected. This is plotted versus the fluence in Figure IV.22 and the associated parameters are shown in Table IV.11.

The resistivity with the parallel term removed may now be fitted to the defect production and annealing model as before. The fit was fairly good with an average RMS deviation of 5.2%, better than the fit found without applying the parallel resistance model. This yielded a decay constant of 2.36×10^{15} N-ions/cm² or 14.4 eV/atom. This is equivalent to approximately 0.72 displacements per atom. The saturation defect resistivity was determined to be $111 \mu\Omega\text{-cm}$ and the resulting impurity and defect resistivity terms are shown in Table IV.12. The residual resistivity can then be written, in the parallel resistance model, as

$$\begin{aligned} \frac{1}{\rho_0(\Phi)} &= \frac{1}{\rho_I^P + \rho_D^P(\Phi)} + \frac{1}{\rho_{\max}}, \\ \rho_D^P(\Phi) &= \rho_D^P i + (\rho_D^P s - \rho_D^P i) X, \\ X &= 1 - \exp(-\Phi/b), \\ \text{and } b &= 2.36 \times 10^{15} \text{ N-ions/cm}^2. \end{aligned}$$

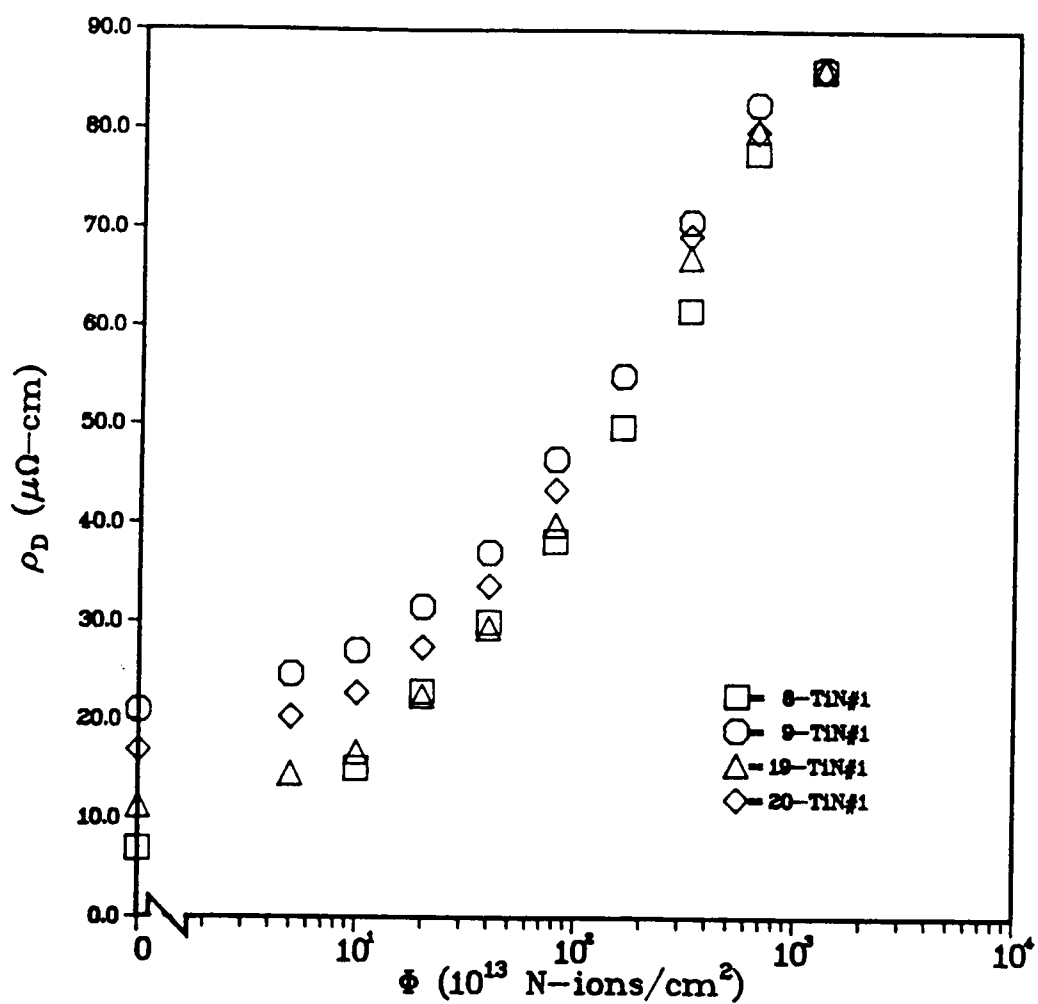


Figure IV.21. The defect part of the residual resistivity versus the fluence for TiN.

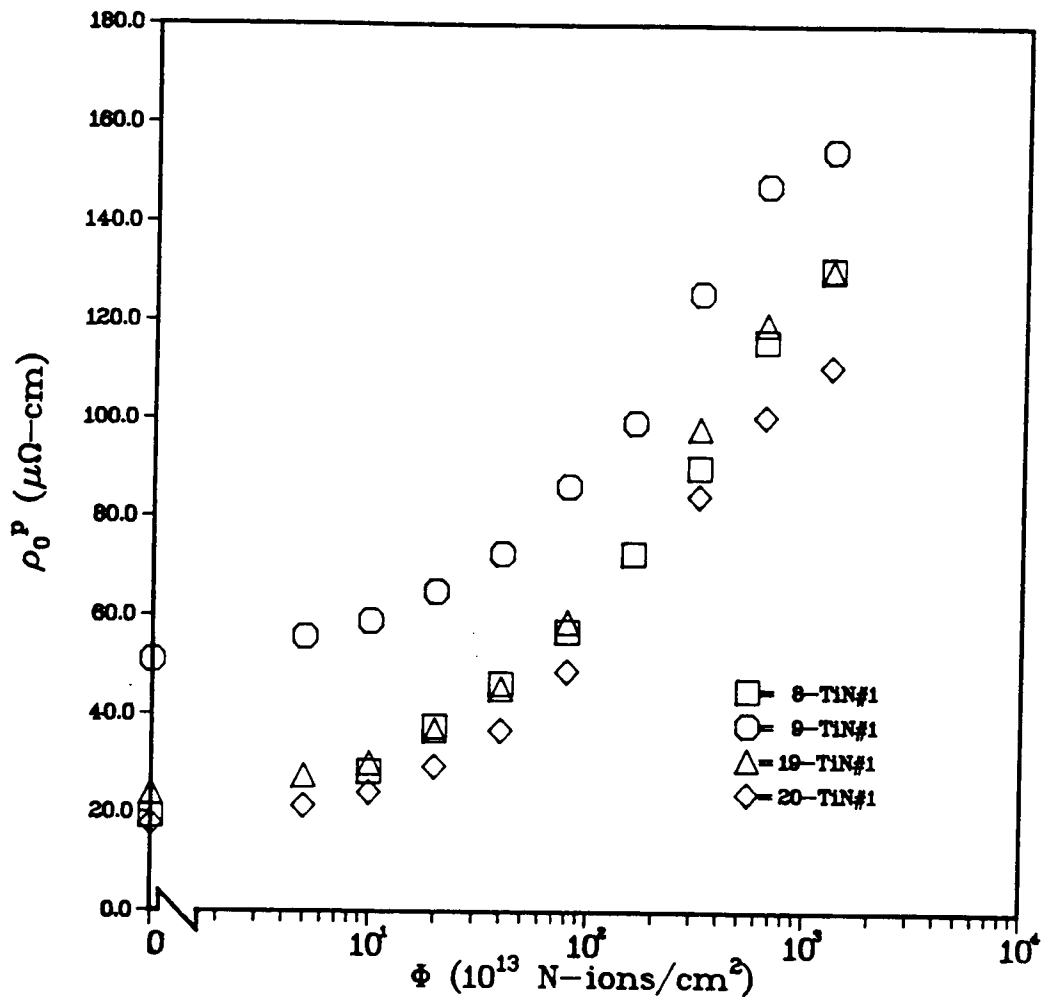


Figure IV.22. The residual resistivity, in the parallel resistance model, versus the fluence for TiN.

Table IV.11. The resistivity values with the parallel resistivity removed for TiN.^a

Sample	$\rho_{0P}(0)$	$\Delta\rho_P$	$\rho_{0P}(\infty)$
8-TiN#1	19.2	112	131
9-TiN#1	50.9	103	154
19-TiN#1	23.8	106	130
20-TiN#1	17.7	93.3	111

^aThese are calculated using $\rho_{\max} = 383 \mu\Omega\text{-cm}$ as described in the text.

Table IV.12. Values of $\rho_{0P}(\infty)$, ρ_{IP} , and ρ_{DPI} using $\rho_{DPS} = 111 \mu\Omega\text{-cm}$ in the parallel resistance model for TiN.

Sample	$\rho_{0P}(\infty)$	ρ_{IP}	ρ_{DPI}
8-TiN#1	131	19.0	0.2
9-TiN#1	154	43.0	7.9
19-TiN#1	130	19.0	4.8
20-TiN#1	111	0	17.7

The defect resistivity, in the parallel resistance model, is shown in Figure IV.23 plotted versus the fluence.

Transition Temperature. The transition temperature was found to decrease with increasing fluence, rapidly at first then to saturate at fluences greater than 1×10^{16} N-ions/cm². The total percent decrease of T_C was approximately 62%, although the saturation T_C values varied some what from sample to sample. The effect of ion irradiation on the transition temperature is shown in Figure IV.24. The transition temperature was also found to fit an exponential decay function, similar to that of T_C for VN, with average RMS deviations of 0.15 K (or 4.9%). The initial and saturated values of T_C , T_C^i and T_C^s , respectively, along with the decay constants are shown in Table IV.13. The decay constant was approximately sample independent and had an average value of 2.30×10^{15} N-ions/cm². This corresponds to 13.9 eV/atom or about 0.7 displacements per atom.

The transition widths were found to remain approximately constant for all samples up to fluences of 3.2×10^{15} ions/cm² where all widths increased; however, they all decreased with further damage. The transition widths are shown in Figure IV.24 as error bars. Transition widths have been included in this Figure for all samples and at all radiation doses; however, in some cases the widths were more narrow than the symbol size so they do not appear in the figure.

Comparing the decay constants for T_C , ρ_0 , and ρ_{0P} we see that they are quite similar. The decay constant for T_C was 2.30×10^{15} N-ions/cm² or 13.9 eV per atom while the decay constant for ρ_0 was 1.92×10^{15} N-ions/cm² or 11.6 eV per atom and for ρ_{0P} it was 2.36×10^{15}

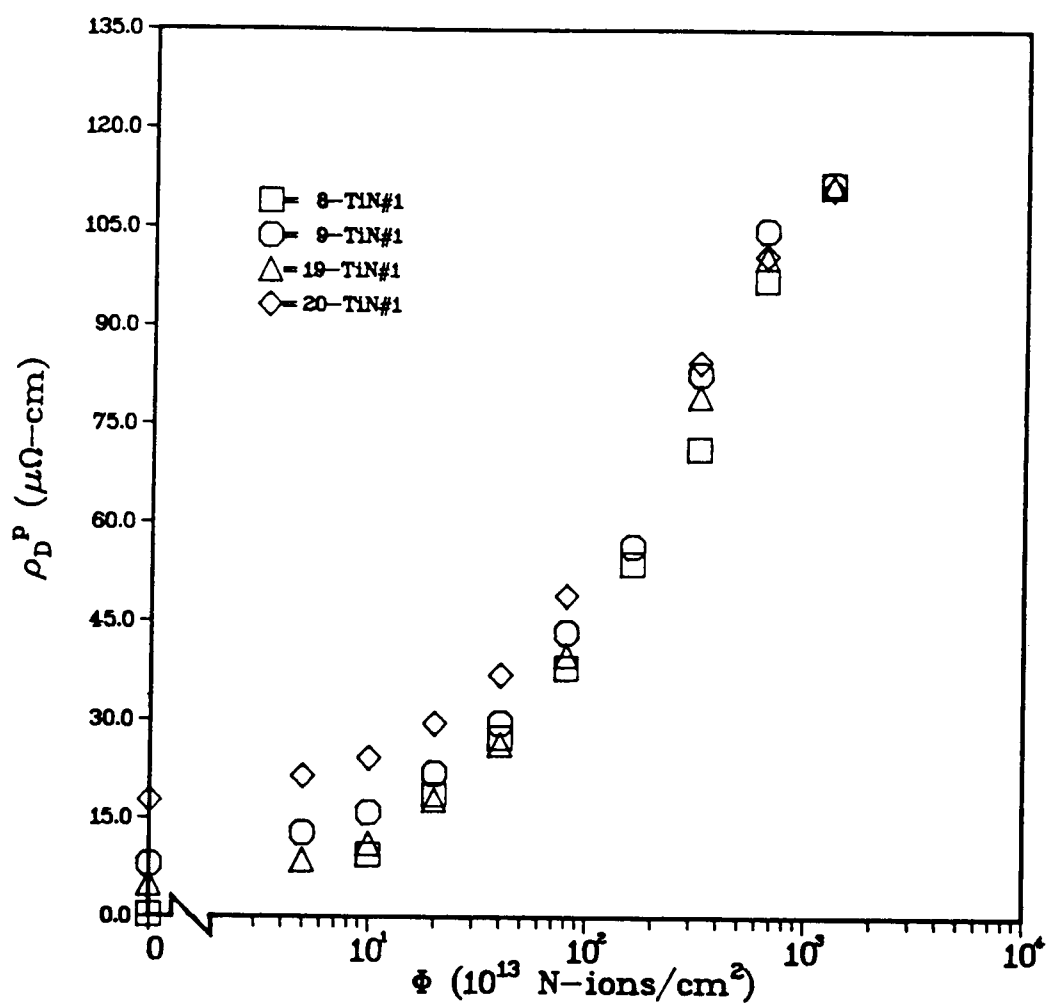


Figure IV.23. The defect part of the residual resistivity, in the parallel resistance model, versus the fluence for TiN.

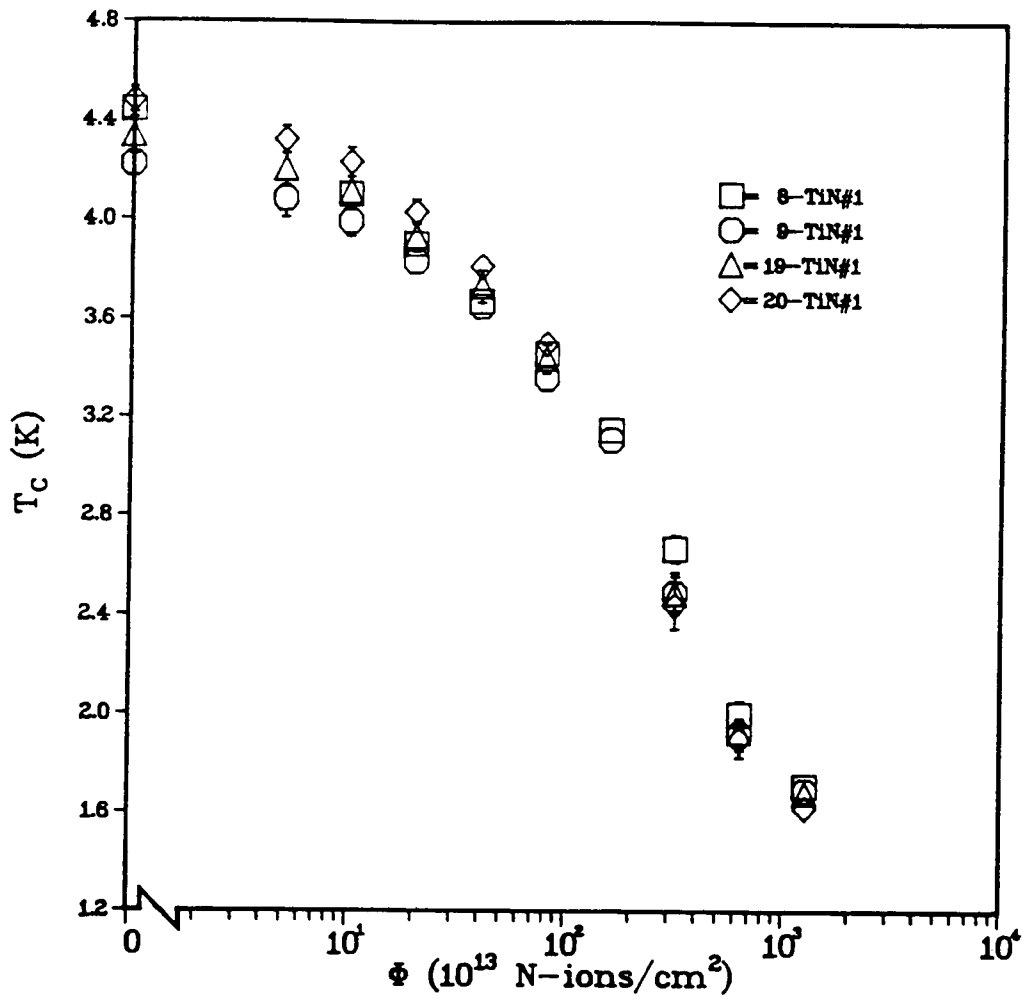


Figure IV.24. The transition temperature versus the incident ion fluence for TiN. The error bars indicate the width of the transition. At several points the transition width is less than the size of the symbol.

Table IV.13. Initial and saturated values of T_C along with the decay constants for TiN.^a

Sample	T_C^i	T_C^s	a
8-TiN#1	4.44	1.71	2.35
9-TiN#1	4.22	1.69	2.45
19-TiN#1	4.335	1.68	2.25
20-TiN#1	4.48	1.62	2.16

^aThe transition temperatures are in units of K and the decay constants are in units of 10^{15} N-ions/cm².

N-ions/cm² or 14.4 eV per atom. The decay constants for T_C and the resistivities only differ by a few eV in the worst case; therefore, it appears that the transition temperature and the resistivity in TiN are equally susceptible to lattice damage by nitrogen ion irradiation.

Lattice Constant. The lattice constants of the titanium nitride films were measured at several fluences. Within experimental error they did not change throughout the entire experiment; in fact, the average lattice constant for all samples at all fluences was 0.4241 ± 0.0003 nm. This value is exactly that given by Toth (1971, p. 220) for measurements on bulk TiN. The peaks in the X-ray diffraction spectrum were decreasing in magnitude with increasing damage, indicating that the lattice was becoming disordered; however, even at the highest fluence (1.28×10^{16} N-ions/cm²) the four lowest order peaks could be seen. This implies that the TiN is still in the B1 phase, the same as the result for VN, but that the lattice is, in general, less disordered than in the case of VN.

Upper Critical Field. After each irradiation the upper critical field H_{C2} of the samples was measured as a function of temperature. At all fluences the H_{C2} data was found to fit the WHH theory, in the dirty limit, without including Pauli paramagnetic limiting or spin orbit scattering; however, some samples, as formed and at very low fluences, exhibited a positive curvature in the $H_{C2}(T)$ curves near T_C . Typically this is attributed to inhomogeneity in a given sample, but there was no evidence for this in the X-ray measurements. The H_{C2} versus T data for sample 8-TiN#1 at several fluences is shown in

Figure IV.25 along with curves calculated from WHH theory. Notice that the zero fluence curve exhibits the positive curvature mentioned above and that it disappears as the fluence is increased.

The upper critical field extrapolated to zero temperature $H_{C2}(0)$ is shown in Figure IV.26, plotted versus the fluence. It was found to increase with increasing damage to a maximum at a fluence of about 1.5×10^{15} N-ions/cm². Above this fluence $H_{C2}(0)$ decreased and saturated at a level above its initial value. The slope of the upper critical field curve at T_C exhibited a monotonic increase with fluence except for sample 9-TiN#1 which appeared to saturate.

In Figure IV.27 we see the renormalized coefficient of the electronic heat capacity γ^* plotted as a function of the fluence. In this figure the lines are included as a guide to the eye so that one can see the behavior of the individual samples. Generally, the γ^* values decrease with increasing fluence to a minimum of 2.2 to 2.4 mJ/mole-K² at a fluence of about 3 to 6 $\times 10^{15}$ N-ions/cm² and above this fluence γ^* increases. The exception is sample 9-TiN#1 which had an initial γ^* value somewhat less than the others and which increased with fluence up to 3.26 mJ/mole-K² at 4×10^{14} N-ions/cm². Above this fluence γ^* for 9-TiN#1 then followed the same trend as the other samples.

Microscopic Properties. The zero temperature Ginzburg-Landau coherence length and penetration depth were calculated from the measured parameters after each irradiation. The coherence length is shown in Figure IV.28 plotted versus the fluence. As with vanadium nitride, the coherence length decreased initially, reached a minimum

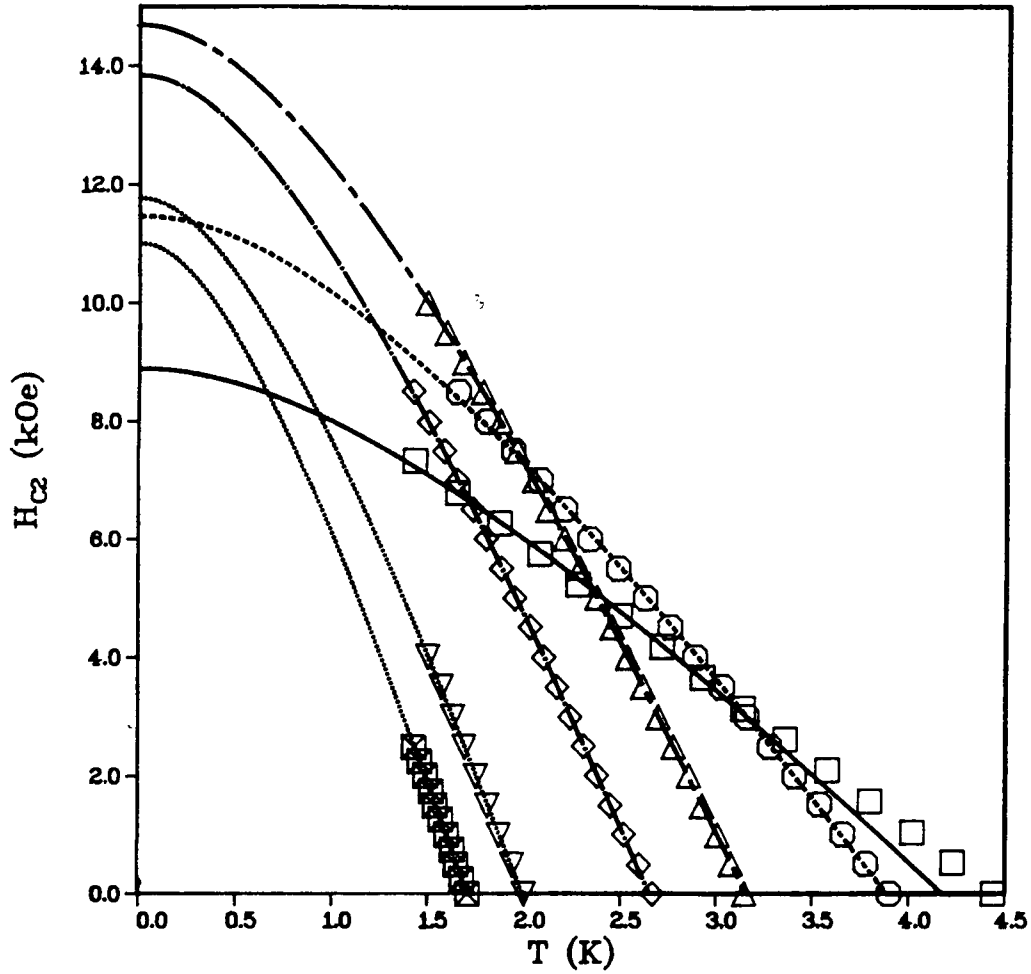


Figure IV.25. The upper critical field versus the temperature for The sample 8-TiN#1 at several ion fluences. The symbols are defined as follows: $\square$, before irradiation; $\circ$, 2×10^{14} N-ions/cm²; $\triangle$, 1.6×10^{15} N-ions/cm²; $\diamond$, 3.2×10^{15} N-ions/cm²; ∇ , 6.4×10^{15} N-ions/cm²; and $\boxtimes$, 1.28×10^{16} N-ions/cm². The curves are calculated from WHH theory in the dirty limit.

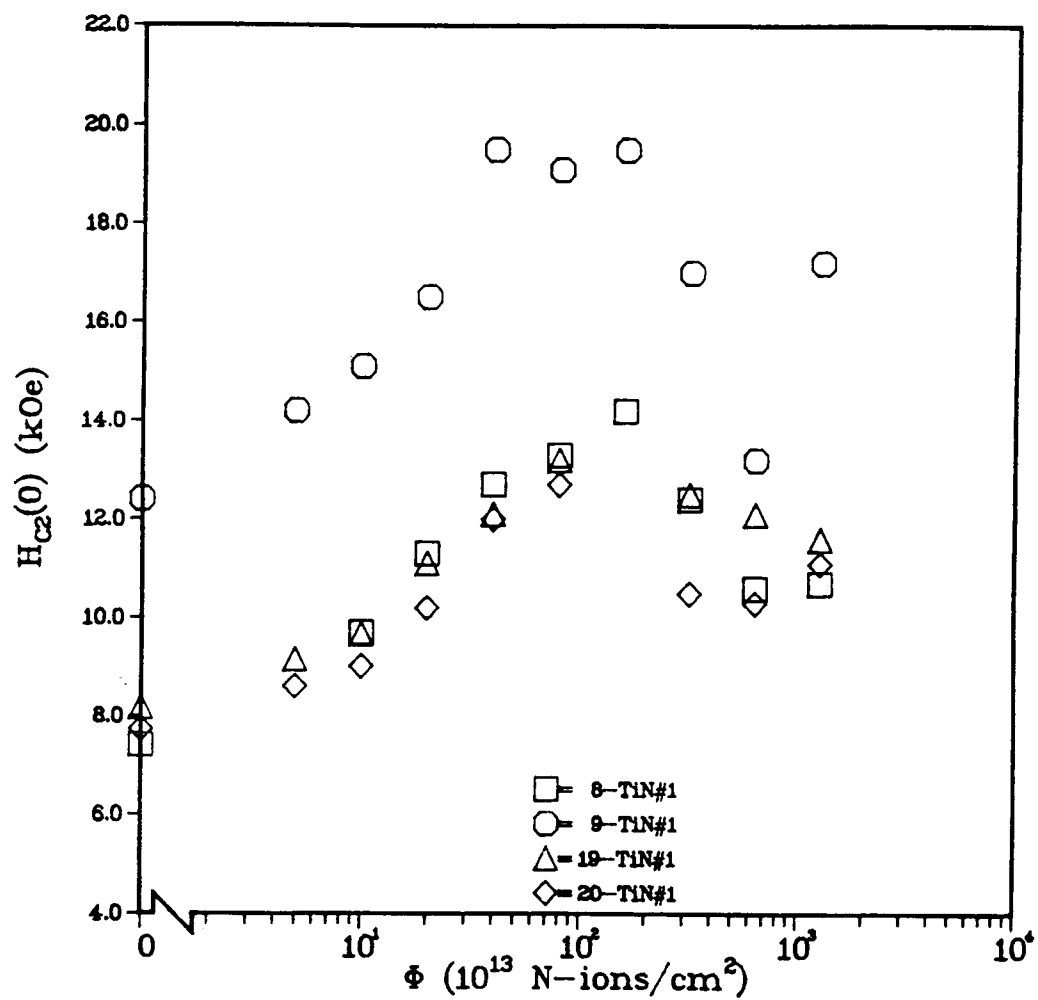


Figure IV.26. The upper critical field at zero temperature versus the ion fluence for TiN.

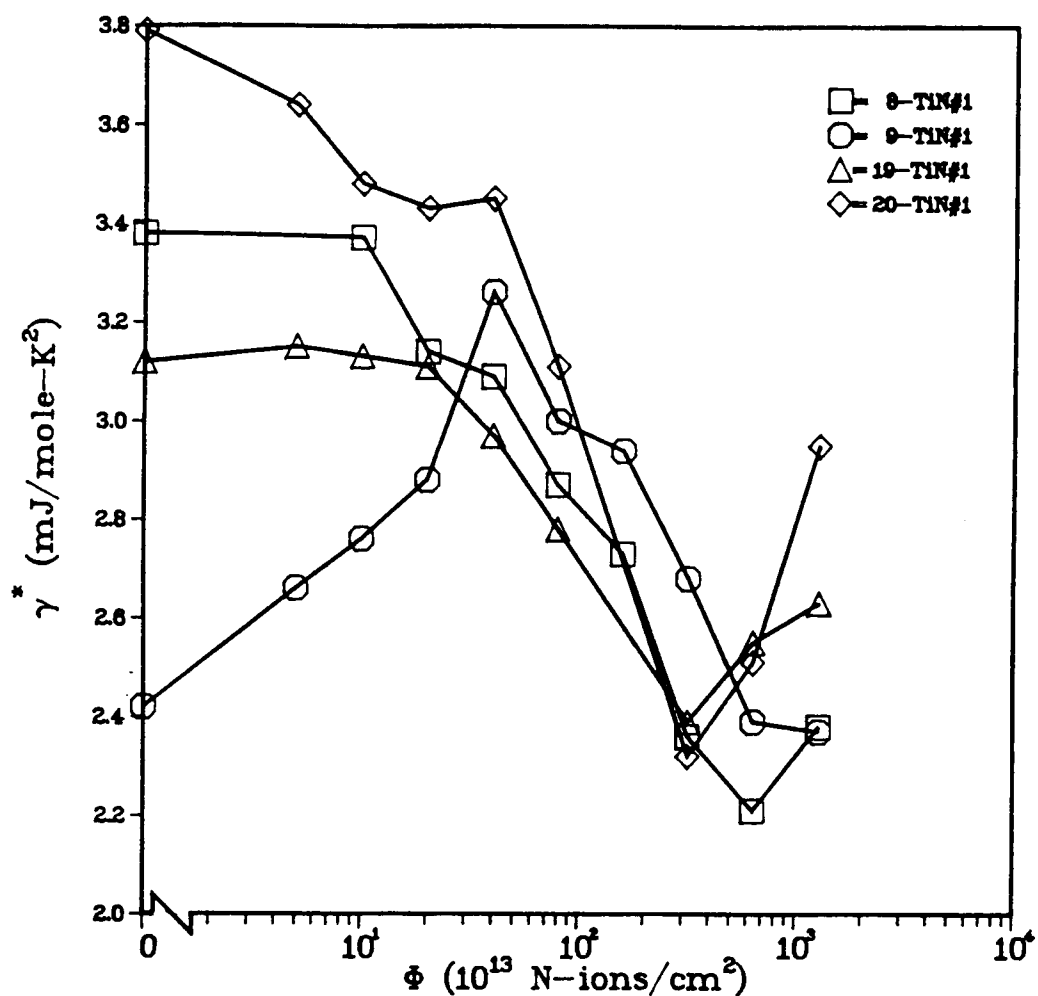


Figure IV.27. The coefficient of the renormalized electronic heat capacity versus the fluence for TiN. The lines are included only as a guide to the eye.

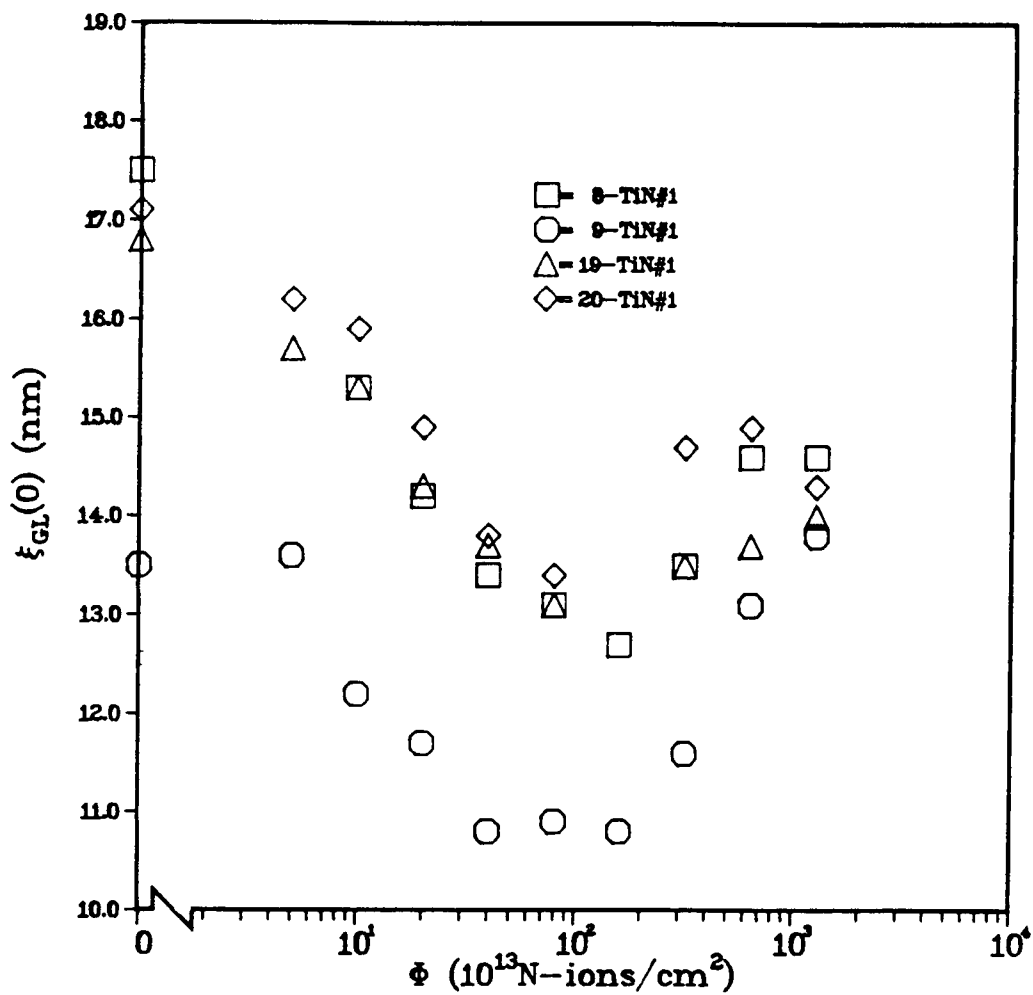


Figure IV.28. The Ginzburg-Landau zero temperature coherence length versus the fluence for TiN.

around 1.5×10^{15} N-ions/cm² and increased afterward, but never regained its initial value. Figure IV.29 shows the penetration depth as a function of fluence. It increased monotonically with damage and was always greater than the thickness of the film.

The renormalized electronic density of states at the Fermi energy $N^*(0)$ was calculated from γ^* ; therefore, the behavior of $N^*(0)$ is the same as γ^* in Figure IV.27. The initial density of states values were correlated with the initial T_C values, just as with VN; however, the saturated values were not correlated with T_C at all.

In order to separate the electron-phonon coupling constant from the band density of states at the Fermi energy, $N_b(0)$ has been calculated using the electron lifetime model as before. The resulting density of states changes little with disorder, changing only about 10% at 200 $\mu\Omega$ -cm. The electron-phonon coupling constant can now be calculated as before from $N^*(0)$ and $N_b(0)$.

The electron-phonon coupling constant can also be calculated from the transition temperature using the McMillan equation. The Coulomb pseudopotential, calculated from the empirical equation as described in the VN section, was equal to 0.09 and did not change throughout. The average phonon frequency ω_{log} was not as easy to determine.

No determination of ω_{log} could be found in the literature. In one case where TiN was considered theoretically, (Rietschel et al., 1980) T_C was calculated directly from numerical solution of the Eliashberg equations, therefore ω_{log} must be estimated. It has been noted that the Debye temperature Θ_D and ω_{log} must be related in some fashion since they are both measures of an average phonon frequency.

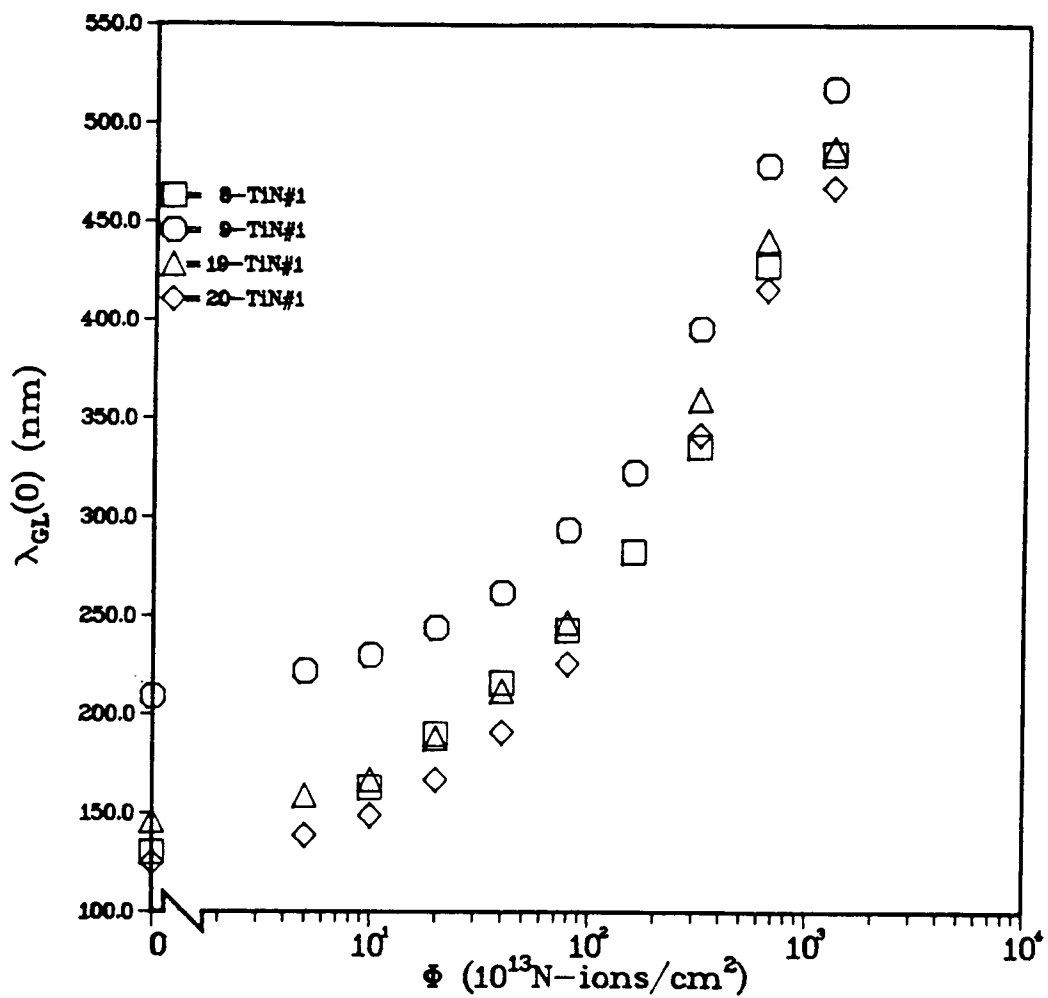


Figure IV.29. The Ginzburg-Landau zero temperature penetration depth versus the fluence for TiN.

In the literature it has been assumed that these two quantities are proportional for a given crystal structure when $\omega_{\log}$ was not known (Orlando and Beasley, 1981); thus we have used this method to determine $\omega_{\log}$ for TiN from $\omega_{\log}$ and Θ_D for VN.

The Debye temperature for VN is 420 K as determined from heat capacity measurements (Pessall et al., 1967) and, as mentioned above, $\omega_{\log}$ is 336 K. This yields a constant of proportionality of 0.800 ($\omega_{\log}/\Theta_D$). Titanium nitride has a Debye temperature of 636 K (Pessall et al., 1967) thus this proportionality gives an $\omega_{\log}$ of 509 K. This is the value used in the calculation of λ from T_C . As described in the VN section on ion irradiation, the dependence of λ on $\omega_{\log}$ is weak, so small errors in this value will be of no consequence.

The values of λ calculated from γ^* and T_C are both plotted in Figure IV.30 versus the resistivity. Here we see, as with VN, that the two do not agree. The relative behavior of λ is generally the same as that observed in VN. The same problems would therefore seem to exist in this system as with the VN system. As before with VN, spin fluctuation are unlikely since the spin fluctuation parameter must become negative, which is non-physical, in order to describe the behavior. Furthermore, in the case of TiN spin fluctuation are even less likely.

The spin fluctuation parameter λ_{sf} , as discussed by Allen and Mitrovic' (1982, p. 83 through 88), is approximately proportional to the electronic density of states at the Fermi energy. The band density of states, calculated from band structure calculations, for TiN is 0.432 states/eV-Ti atom-spin (Marksteiner et al., 1986) while

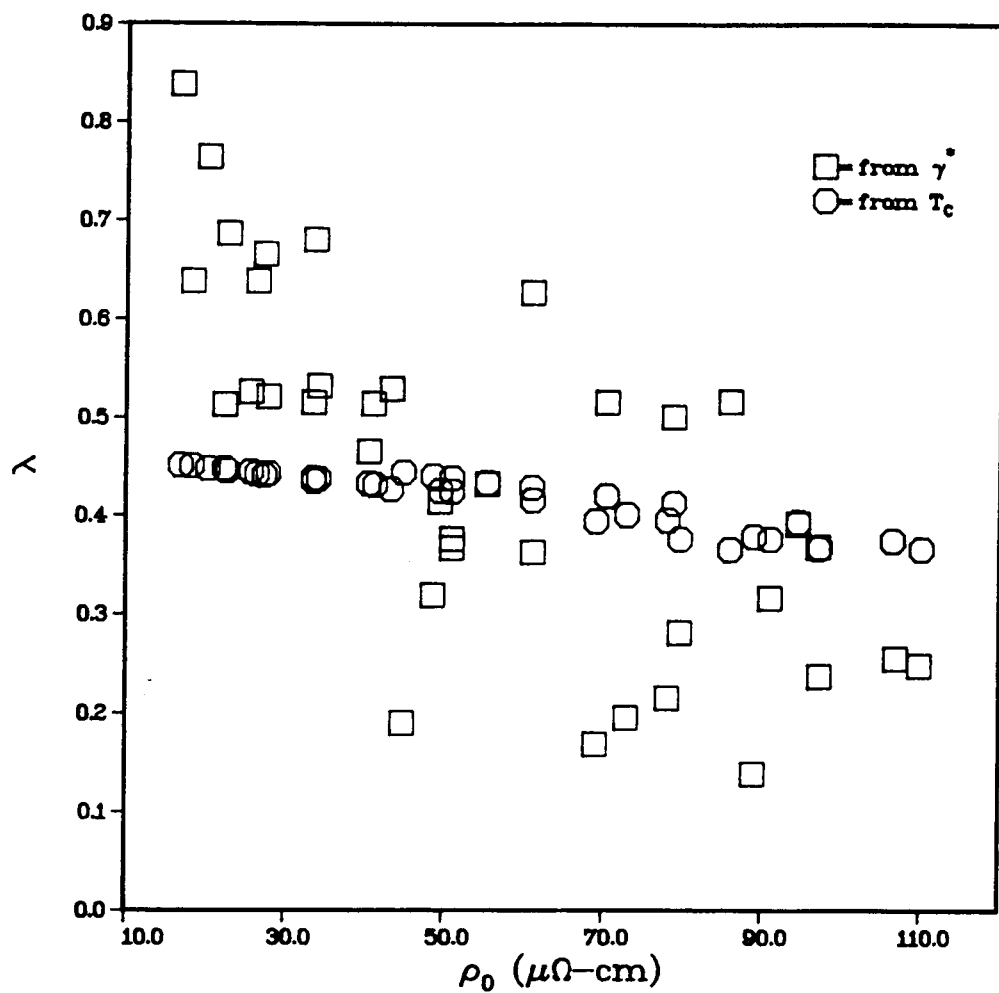


Figure IV.30. Comparison of the electron-phonon coupling constant calculated from γ^* and T_c , for TiN, plotted versus the residual resistivity.

for VN this quantity is 1.12 states/eV-V atom-spin (Papaconstantopoulos et al., 1985). Since the TiN density of states is more than 60% less than that of VN, and since the spin fluctuation argument was apparently incorrect for VN, this argument must be even less likely for TiN.

The arguments presented for the validity of $\omega_{\log}$ and the McMillan equation in the analogous subsection in the vanadium nitride section hold equally well for titanium nitride. It should be noted, however, that a calculation of T_C and γ^* has been carried out for TiN where the Eliashberg equations were solved numerically (Rietschel et al., 1980). This calculation found $T_C = 2.8$ K and $\gamma^* = 2.7$ mJ/mole-K². While the γ^* value is not far from the experimental value, T_C is too low. This indicates that there is also a problem with the theoretical treatments of this system just as with vanadium nitride.

While the discussion of the electron lifetime model in the VN section still holds for titanium nitride, some additional comments are appropriate. As with VN, the resistivity entering the ELM is measured so it cannot be considered as uncertain. The Drude plasma frequency, on the other hand, is a calculated parameter. No value for this parameter could be found in the literature for TiN so some method had to be found to determine it. As previously stated, the plasma frequency for VN was calculated by D. A. Papaconstantopoulos (private communication) and found to be 7.1 eV. Through electron-energy-loss spectroscopy measurements on TiN and VN Pfluger et al. (1984) determined the complex dielectric function for both VN and TiN. They found that an interband transition, represented by a strong oscillator

at 7 eV, could be used to model their results for both VN and TiN. Since the experiment agrees so well with the theoretical result for VN, we have assumed that the Drude plasma frequency for TiN is also 7.1 eV. The dependence of the plasma frequency on disorder, discussed above, is still uncertain and cannot be resolved.

With titanium nitride, as with vanadium nitride, the Fermi energy lies on the side of a peak in the density of states. For this reason the density of states at the Fermi energy is little affected by disorder (only a 10% decrease at 200 $\mu\Omega\text{-cm}$), thus, as discussed in the VN section, other effects may be observed. Thus we think that this is the prime reason for the discrepancy between the λ values calculated from T_C and γ^* .

3. Annealing Studies

To determine if the damage induced in the lattice of the titanium nitride samples could be removed through thermal annealing, titanium nitride samples were annealed in vacuum (sample 8-TiN#1) and a nitrogen (20-TiN#1) atmosphere, simultaneously with the vanadium nitride samples. The results of these studies will be given, followed by a discussion of the annealing behavior.

Resistivity. After each anneal, the room temperature and low temperature resistivities were measured and the residual resistance ratio was determined. The resistance ratio R as a function of the annealing temperature T_A is shown in Figure IV.31. R changed little for anneals up to about 800°C for both vacuum and nitrogen anneals. Above this temperature R for both samples increased rapidly until a

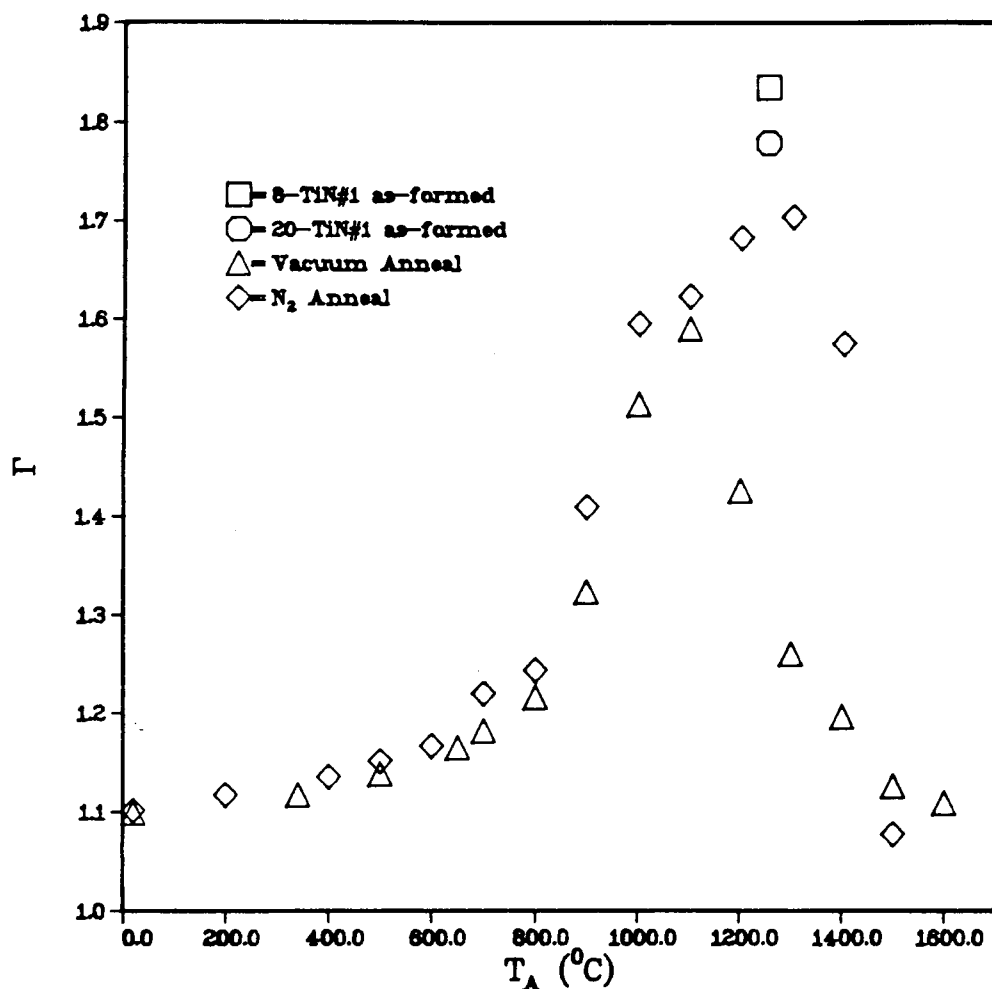


Figure IV.31. The residual resistance ratio versus the annealing temperature for TiN. Sample 8-TiN#1 was annealed in vacuum while sample 20-TiN#1 was annealed in a nitrogen atmosphere. The values for the samples prior to irradiation are shown at their formation temperatures.

temperature of 1100°C was reached. At this temperature the resistance ratio of the vacuum annealed sample reached a maximum and rapidly decreased after subsequent higher temperature anneals. The r value for the N₂-annealed sample on the other hand, continued to increase, though at a slower rate, to a maximum at 1300°C, above which it also fell rapidly. Neither sample regained its pre-irradiation resistance ratio value.

The effect of annealing on the residual resistivity is shown in Figure IV.32. In both cases the resistivity decreased rapidly with increasing annealing temperature up to a temperature of 1000°C. Above this temperature the residual resistivity of the N₂-annealed sample continued to decrease slightly to a minimum of 19.4 $\mu\Omega$ -cm at 1200°C, after which it increased slowly with continued anneals up to 1400°C. Above 1400°C, the resistivity of the N₂-annealed sample jumped up rapidly. The residual resistivity of the vacuum annealed sample reached a minimum of 26 $\mu\Omega$ -cm at 1100°C, after which it increased rapidly with increasing annealing temperature. The residual resistivity of the N₂-annealed sample practically reached its initial value, at approximately the temperature where it was formed, while the resistivity of the vacuum annealed sample never was reduced to its initial value.

Transition Temperature. The effect of annealing on the transition temperature is shown in Figure IV.33. For both cases the transition temperature increased only slightly for annealing temperatures less than about 600°C. From 600 to 1000°C T_C increased rapidly. Above 1000°C the transition temperature of the N₂-annealed

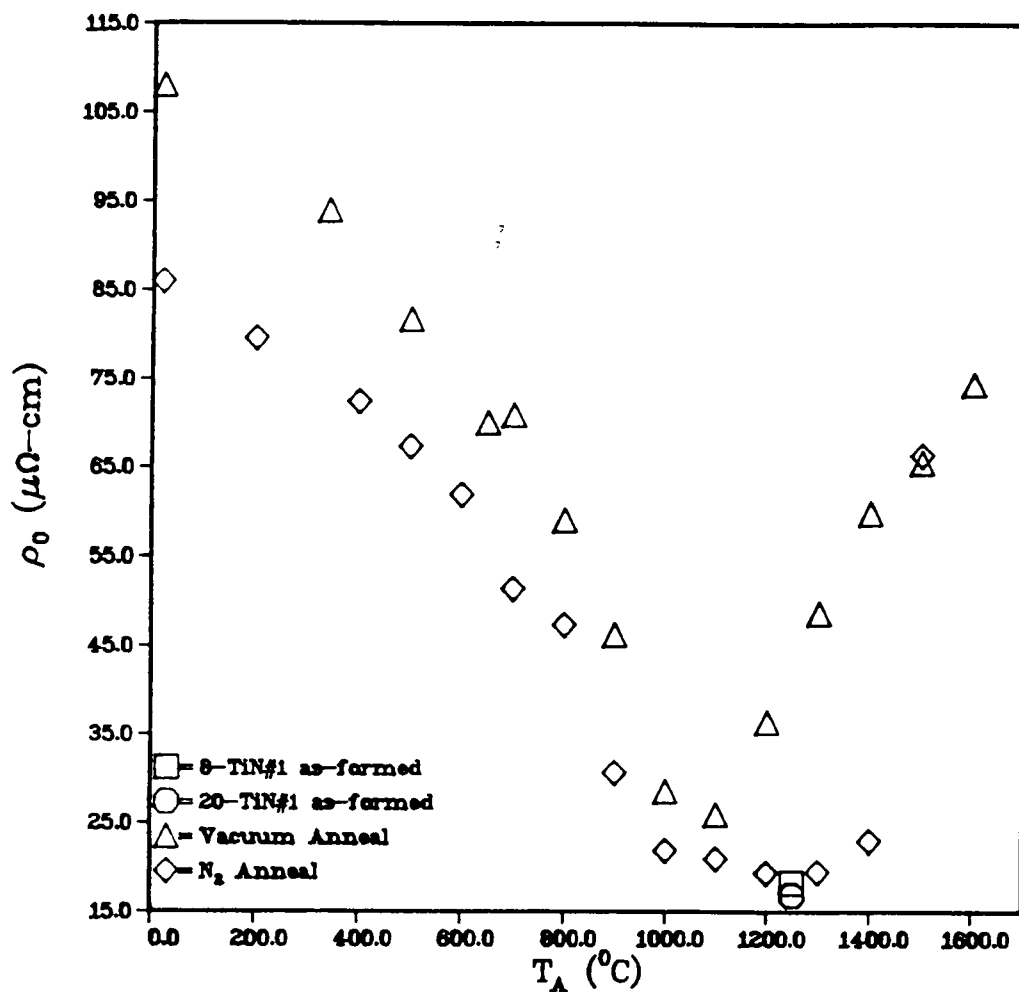


Figure IV.32. The residual resistivity versus the annealing temperature for TiN.

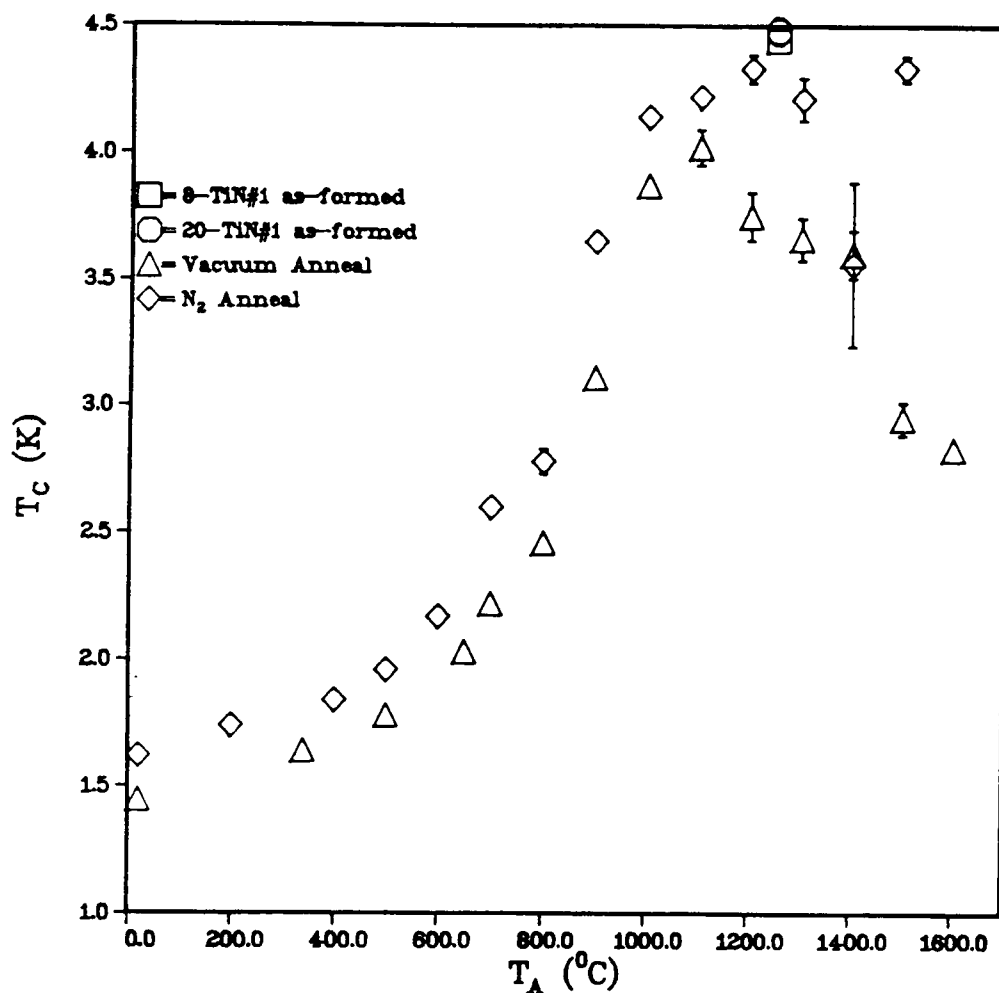


Figure IV.33. The transition temperature versus the annealing temperature for TiN. The error bars indicate the width of the transition. Notice that in most cases the widths are less than the size of the symbols.

sample remained approximately unchanged until 1400°C where T_C dropped considerably. At 1500°C, T_C for the N₂-annealed sample increased again to 4.33 K.

The transition temperature of the vacuum annealed sample behaved similar to the N₂-annealed sample for temperatures less than or equal to 1100°C; however, T_C for the vacuum annealed sample reached a maximum at 1100°C. At 1200°C T_C had decreased slightly and continued to decrease slowly for annealing temperatures up to 1400°C. Above 1400°C the transition temperature decreased more rapidly for the remainder of the experiment.

The transition widths are also shown in Figure IV.33, being represented by error bars. The transition widths for both samples were unchanged for anneals at less than 1100°C, in fact, in the Figure, the transition widths shown are actually less than the size of the symbols. From 1100 to 1400°C the widths became noticeably larger with a maximum width occurring at 1400°C. Above this temperature the transition widths decreased considerably.

Lattice Constant. X-ray diffraction measurements were taken after several of the anneals. The lattice constant was determined from these measurements and was found to remain constant within the experimental error. The average lattice constant was 0.4240 ± 0.0005 nm for the vacuum annealed sample and 0.4239 ± 0.0005 nm for the N₂-annealed sample. These values are the same as those reported in bulk stoichiometric TiN, 0.4239 nm and 0.4241 nm (see Toth, 1971).

The higher order peaks of both samples behaved very much the same. After being annealed at 700°C a few of the higher order peaks

had reappeared and at 900°C they were beginning to sharpen. There was little change at 1100°C; however, at 1200°C the peaks had become much sharper and distinct, especially the (333) peak. At 1500 and 1600°C the peaks were even sharper indicating that the metal sublattice was much more ordered at this point.

Upper Critical Field. The upper critical field of the samples was measured as a function of temperature after each anneal. The resulting H_{C2} versus T curves were found to fit the WHH theory, in the dirty limit, excluding paramagnetic limiting and spin-orbit scattering. The behavior of H_{C2}' was very similar to that of the residual resistivity. In both the N_2 -annealed and vacuum annealed cases the slope decreased rapidly for anneals up to 1100°C. Above this temperature H_{C2}' of the N_2 -annealed sample remained about the same up to a temperature of 1400°C and at 1500°C the slope increased substantially. For the vacuum annealed sample H_{C2}' increased continuously above 1100°C.

The coefficient of the renormalized electronic heat capacity γ^* was calculated from the residual resistivity and H_{C2}' for each anneal. This quantity was found, in both cases, to increase with increasing annealing temperature up to 1000°C. From 1000 to 1300°C γ^* of the N_2 -annealed sample remained approximately unchanged and dropped drastically at temperatures above 1300°C. The γ^* values for the vacuum annealed sample reached a maximum at 1000°C, changed only slightly at 1100°C, and decreased rapidly at higher temperatures.

Microscopic Properties. The Ginzburg-Landau zero temperature coherence length and penetration depth were calculated for each anneal. The coherence length is plotted versus the annealing temperature in Figure IV.34. Here we see that the coherence length for the vacuum annealed sample changed little during the annealing experiment, decreasing gradually with increasing annealing temperature. On the other hand, the coherence length of the N_2 -annealed sample increased with increasing annealing temperature for temperatures greater than about 800°C and then dropped drastically after being annealed at 1500°C .

The penetration depth of both samples is shown in Figure IV.35. It was found to decrease rapidly with increasing annealing temperature up to 1000°C . Above this temperature the penetration depth of the vacuum annealed sample increased rapidly while for the N_2 -annealed sample it remained approximately constant, increasing slightly for temperatures greater than about 1300°C .

The effect of annealing on the renormalized density of electronic states at the Fermi energy $N^*(0)$ is shown in Figure IV.36. In this figure we see that the density of states of the N_2 -annealed sample increased with annealing temperature up to 1000°C , where it reached a plateau which persisted up to about 1300°C . Above this temperature the density of states decreased rapidly. The density of states of the vacuum annealed sample reached a maximum at 1000°C and then dropped rapidly when annealed at temperatures greater than 1100°C . Both samples regained or exceeded their original values.

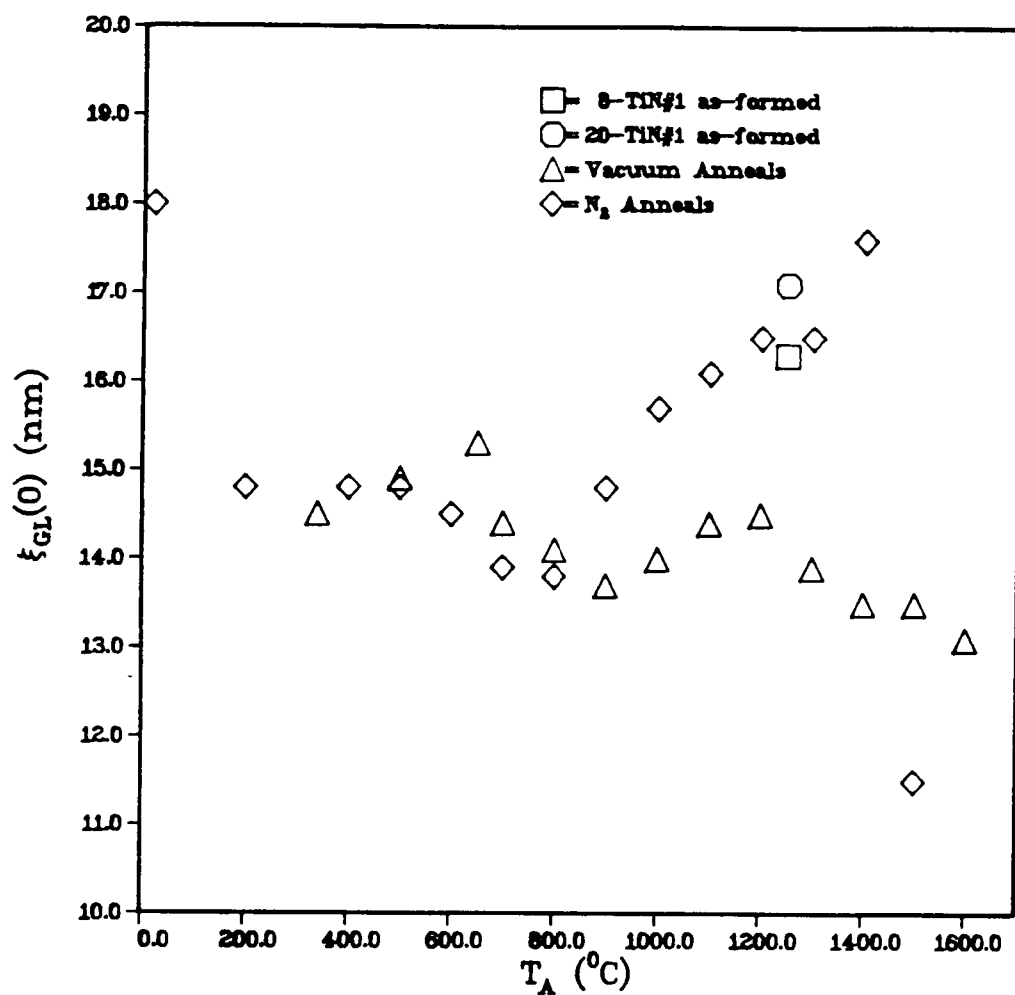


Figure IV.34. The Ginzburg-Landau zero temperature coherence length versus the annealing temperature for TiN.

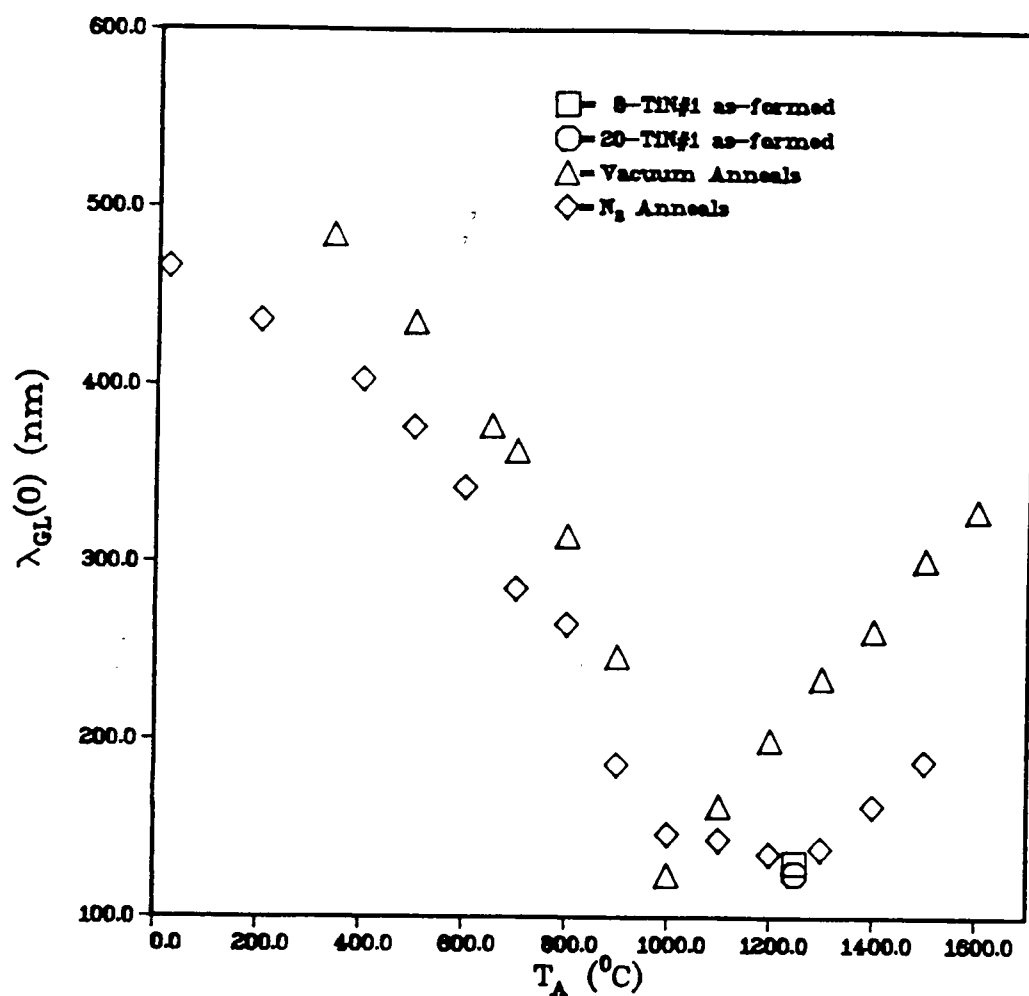


Figure IV.35. The Ginzburg-Landau zero temperature penetration depth versus the annealing temperature for TiN.

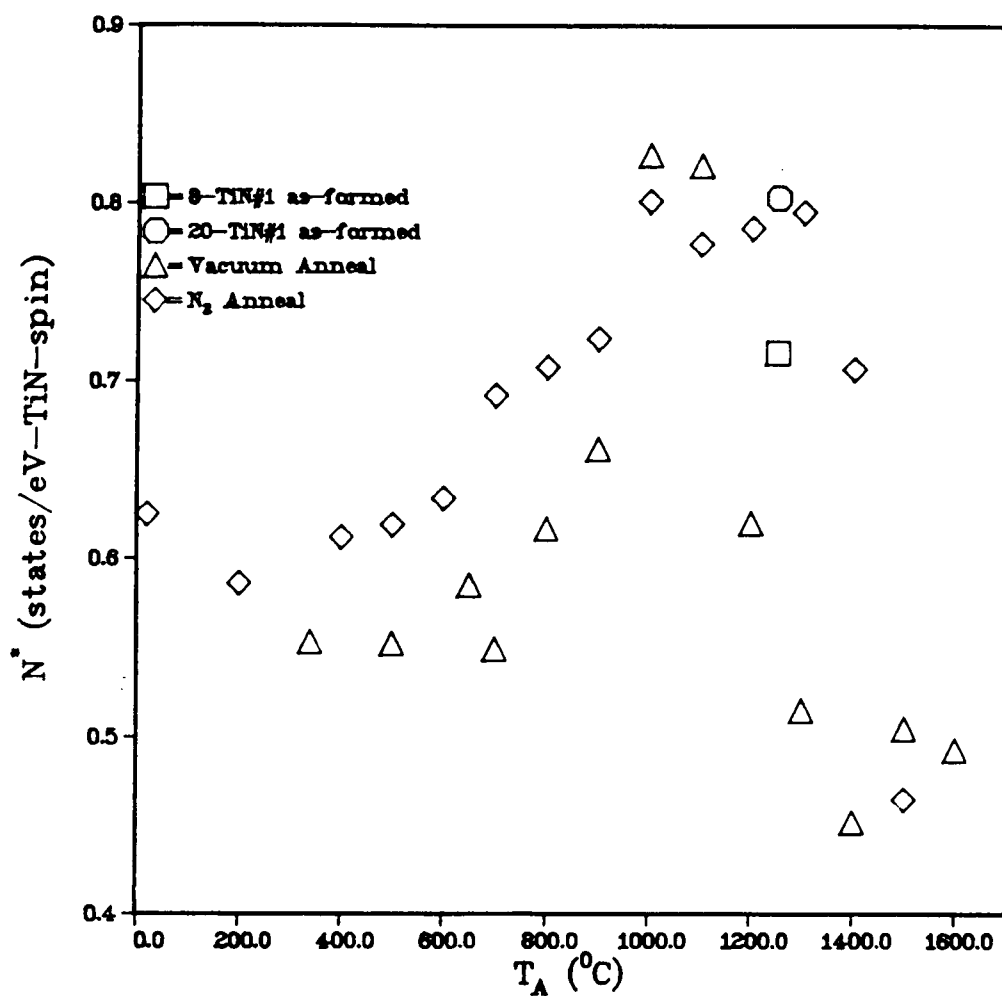


Figure IV.36. The renormalized electronic density of states at the Fermi energy versus the annealing temperature for TiN.

Discussion of Annealing Behavior. From the X-ray studies of these samples we see that there is an annealing stage of the metal sublattice at 900°C. This continues up to 1200°C where the diffraction peaks become even sharper, indicating possibly another annealing stage; however, the other properties do not confirm this. The initial annealing stage does, however, correspond to the rapid change in the measured parameters between 800 and 1100°C.

The transition temperature and the residual resistivity, unlike the vanadium nitride system, recover at about the same temperature. This is not surprising when one considers the decay constants which were used to describe the behavior of the resistivity and the transition temperature as a function of ion damage. For VN these decay constants are quite different while they are very similar for TiN. Thus, if one refers to the arguments on the difference in susceptibility of these two parameters to the type of defect, one must conclude that, in the TiN system, T_C and ρ_0 are equally affected by defects.

As with VN, the behavior of the properties of TiN annealed at high temperature in nitrogen and vacuum are quite different. The most obvious explanation for this difference is that at high temperatures in vacuum the nitrogen sublattice is decomposing and the sample is losing nitrogen. This is not, however, confirmed by the X-ray diffraction results. A theoretical study of the effects of vacancies on nitrogen sites on the band structure of TiN indicates that the density of states actually increases as x decreases in TiN_x (Marksteiner et al., 1986); however, experimental results show that

the transition temperature decreases as x decreases (Toth et al., 1966). Our opinion remains that the high temperature differences are due to loss of nitrogen from the samples.

C. COMPARATIVE DISCUSSION

To conclude this section we will discuss the similarities and differences between the vanadium nitride and the titanium nitride systems. We will also draw some conclusions concerning the behavior of B1 phase superconductors by comparing the present work with other studies performed on other B1 phase compounds as well as with ion damage experiments performed on the A15 phase superconductors.

We shall begin our comparison of the two systems with a discussion of the decay constants determined from analysis of the ion irradiation experiments. A summary of these constants is given in Table IV.14. The decay constants represent a measure of the susceptibility of a given property of a given material to radiation damage by nitrogen ions since they are the amount of energy per atom of the compound required to reduce that property by the factor $\exp(-1)$; thus a larger decay constant indicates less susceptibility to radiation damage.

A discussion of the difference in the decay constants for the transition temperature and resistivity of each individual compound is given above; however, the interesting feature here is the difference in the decay constants for a given property between the two systems. In the table we see that the decay constants for TiN are considerably larger than the corresponding constants for VN. This indicates that more energy per atom of the TiN compound is required to reduce a given

Table IV.14. Comparison of the results of the ion damage and annealing experiments on the vanadium nitride and titanium nitride systems.

property	VN	TiN	Rd
decay constants:			
T_C	8.20 eV/atom	13.9 eV/atom	1.70
ρ_0	4.18 eV/atom	11.6 eV/atom	2.78
ρ_0^D	5.06 eV/atom	14.4 eV/atom	2.85
annealing results: ^a			
T_C plateau onset	700°C	1000°C	1.3
T_C plateau end	1300°C	none	none
ρ_0 minimum	900°C	1100-1300°C	1.25-1.33
Γ peak	900°C	1300°C	1.33
θ_D^b	420 K	636 K	$R^2 = 2.29^e$
ΔG_f^0 at 1000 K ^c	-44.0 kCal/mole N ₂	-118 kCal/mole N ₂	2.68

^aThe values presented in the table are for the nitrogen anneals.

^bThe Debye temperatures are from N. Pessall, J.K. Hulm, and M.S. Walker, Final Rep., Westinghouse Research Laboratories, AF 33 (615)-2729, 1967.

^cThe free energies of formation of the compound are from T.B. Reed, Free Energy of Formation of Binary Compounds (MIT Press, Cambridge, Mass., 1971) p. 6.

^d R is the ratio of the given parameter for TiN to that parameter for VN.

^e R^2 is given here since it is proportional to the ratio of the spring constants.

parameter than is required for VN. This suggests that the strength of the bonds in TiN is greater than in VN.

Now consider the annealing results also shown in Table IV.14. Here we see in the table that the temperatures at which the features in the annealing results occur are consistently 200 to 400°C higher for titanium nitride. This means that more thermal energy is needed for the defects (vacancies and interstitial atoms) in the TiN system to become mobile than in the VN system. That is, the atoms in TiN are sitting in a deeper potential well than the atoms in VN. This gives further evidence that the bonding is stronger in TiN than in VN.

To further reinforce this hypothesis we now turn to the literature. The Debye temperature for each compound, as measured from heat capacity measurements, is shown in Table IV.14. The Debye temperature is considerably higher for TiN. If, for the sake of discussion, we consider the bonds between the atoms in the lattice as springs, a measure of the strength of the spring (or bond) is the spring constant k . Since the Debye temperature (or equivalently the Debye frequency $\omega_D = \Theta_D k_B / \hbar$) represents a cutoff in the phonon spectrum, and since the masses of titanium and vanadium are only different by two parts in fifty, it can be considered as an approximation to the square root of the spring constant, that is $k \approx M\omega_D^2$. Thus from the Debye temperature we see that the "spring constant" for TiN is larger than VN; therefore, this also suggests the bonds are stronger in TiN than in VN.

As a last piece of evidence in our discussion we have included values of the free energy of formation of the compounds at 1000 K,

this temperature being chosen arbitrarily for comparison. The free energy can be considered the driving force for the reaction of the gas with the metal. If the free energy of formation is negative the reaction will proceed and the compound will form. At a given temperature a free energy of formation for a compound that is large and negative indicates that it is more stable than a compound whose free energy of formation is not as negative. Therefore, TiN is much more stable than VN since the ratio of the TiN free energy of formation to the VN free energy of formation is about 2.7. This implies that the potential well representing the compound relative to the free elements (metal and nitrogen atoms) is almost three times deeper for TiN than for VN, thus again we reach the conclusion that the bonds between atoms in TiN are stronger than in VN.

The ratio of the parameters for TiN to the same parameter for VN are also given in Table IV.14. Here we see that the ratio for both the resistivity decay constants, the free energy of formation, and the square of the ratio for the Debye temperature (since the square is proportional to the "spring constant") are all very similar; the average value being 2.65. This indicates that not only are the above qualitative arguments valid but there is a systematic behavior between the relative values. Since these parameters are all dependent, directly or indirectly, on the energy of the bonds, one can then conclude that the average bonding in TiN is about 2.7 times stronger than in VN.

Now we shall compare the electron-phonon coupling constant as calculated from the transition temperature and the electronic heat

capacity coefficient for each compound. Consider Figure IV.12, page 121, which shows λ for VN and Figure IV.30, page 165, which shows λ for TiN. From these figures we observe that, not only do the two calculated λ values disagree for a given compound, the relative behavior of λ from γ^* and from T_C is quite similar for VN and TiN. This suggests that the reason for the discrepancy in the two λ values is the same for both systems. This also suggests that if, as we believe, some mechanism other than electron lifetime reduction of the density of states is responsible for the observed effects of disorder on the properties of these compounds, then the mechanism must be the same for both compounds.

We shall conclude this discussion with a comparison of the behavior of the transition temperatures with ion damage of TiN and VN to each other and to other typical high T_C superconducting compounds. Figure IV.37 shows a plot of the reduced transition temperature, T_C/T_{C0} , where T_{C0} is the value of T_C prior to irradiation, versus the log of the deposited energy per atom for titanium nitride and vanadium nitride. Here we see, as expected, the two systems saturate at different reduced T_C values; however, the behavior of the reduced T_C is very similar in the region prior to saturation. In Figure IV.38 the reduced transition temperature (T_C/T_{C0}) is plotted versus deposited energy per atom for several other superconducting compounds. In addition to the present work this figure includes Nb_3Sn , a typical A15 phase superconductor, irradiated with 25 MeV oxygen atoms (Besslein et al., 1975) and with 2 MeV helium atoms (Poate et al., 1976) and the B1 phase superconductors MoC irradiated with 300 keV

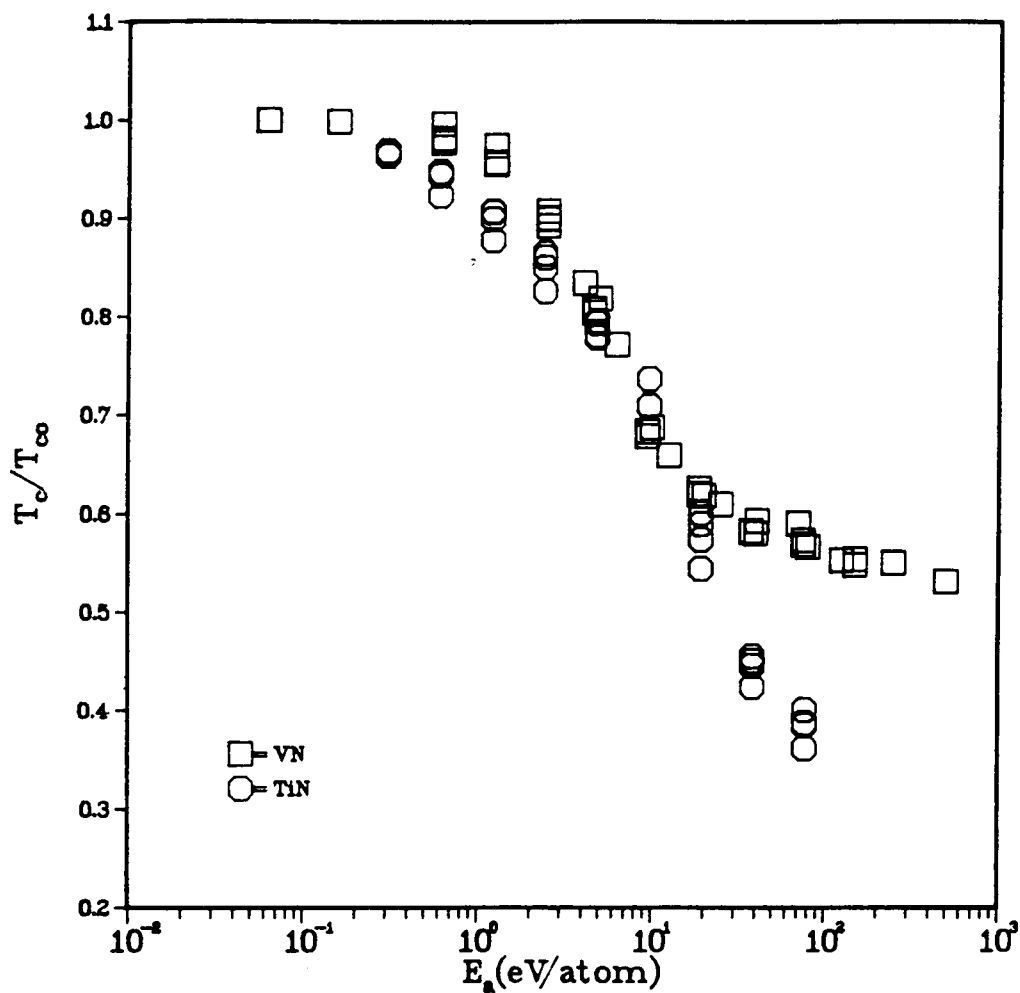


Figure IV.37. The reduced transition temperature T_c/T_{c0} versus the deposited energy per atom for VN and TiN. Notice that they both follow the same curve before VN saturates.

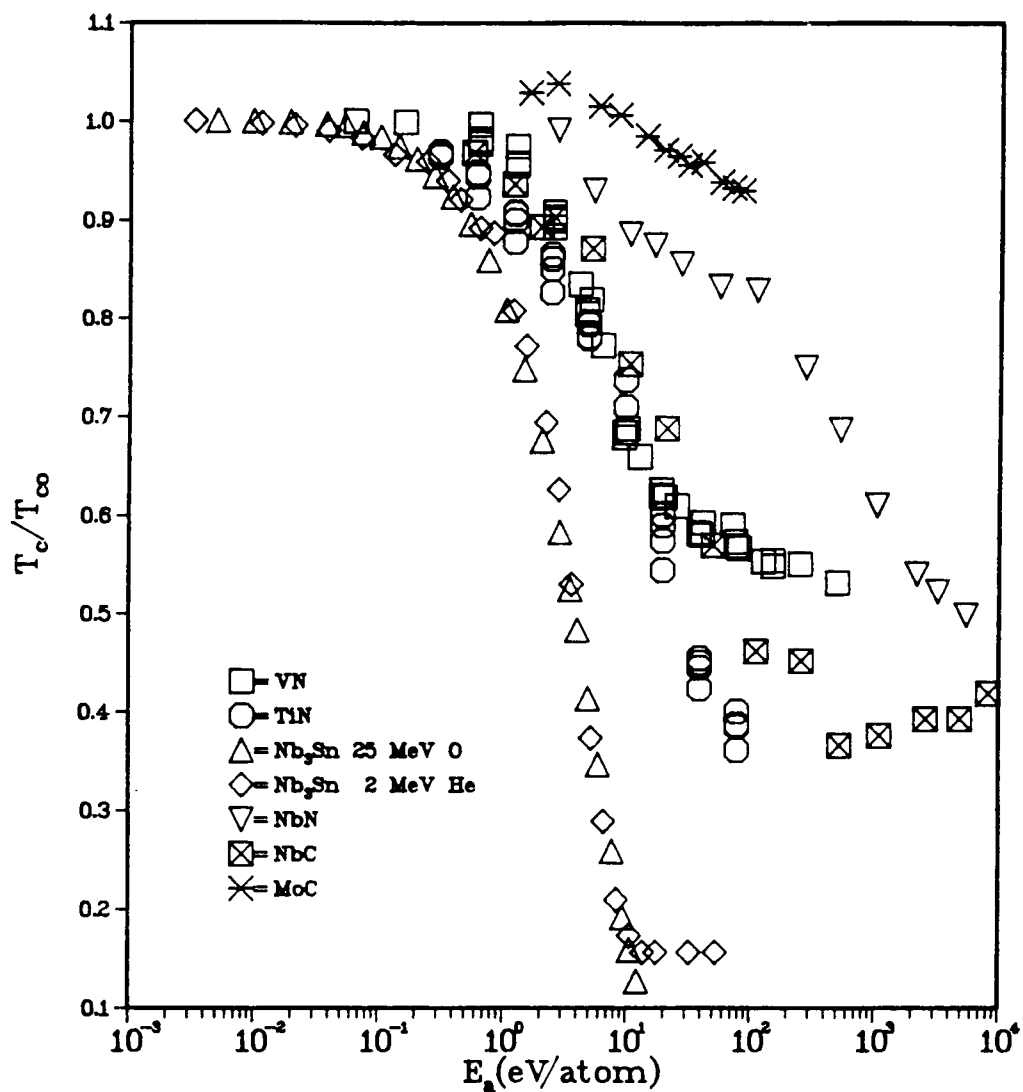


Figure IV.38. Comparison of the reduced transition temperatures versus the deposited energy per atom for a typical A15 compound and several B1 compounds.

helium ions (Ruzicka et al., 1984), NbC irradiated with 600 keV argon ions (Kobayashi et al., 1984) and NbN irradiated with 600 keV argon ions (Jung, 1984). The deposited energy per atom for all samples was calculated using the computer program E-DEP-1, as described above, and the ion fluences given in the respective publications.

Notice that the data for Nb₃Sn falls off faster than the others and that the relative reduction in T_C is greater. This behavior is typical of the A15 compounds (Sweedler et al., 1979). The data for TiN, VN, and NbC all lie on the same curve above saturation, while the data for NbN lie above the present work. The data for MoC also lie above our data. This B1 compound is known to be a metastable compound, stable only above 1960°C, while a hexagonal phase exists above 1655°C (Toth, 1971, p. 83; and Krauss and Politis, 1982). The B1 phase has been found with a T_C of 12 to 13 K (Krauss and Politis, 1982; Toth et al., 1965; and Willens and Buehler, 1965) while the hexagonal phase has a T_C of 8 to 9 K (Roberts, 1976), thus one can speculate as to whether or not the ion irradiation is inducing a phase transition to some more stable phase. We conclude that the B1 phase superconducting compounds are, therefore, less susceptible to radiation damage than the A15 compounds and that a general pattern of behavior of the transition temperature with damage, characterized by the reduced transition temperature, is observed in many of the B1 phase compounds prior to saturation.

V. SUMMARY AND CONCLUSION

Thin films have been formed of the B1 phase, superconducting compounds vanadium nitride and titanium nitride. These films were prepared by heating films of the pure metal, which were previously electron-beam evaporated, in very pure nitrogen gas. The appropriate temperature for forming these nitrides was determined by trial and error, resulting in optimum nitriding temperatures of 850°C for VN and 1250°C for TiN. The optimized films were characterized and found to have superconducting and normal state properties similar to those reported in the literature for bulk and thin film samples of these materials. The coefficients of the renormalized electronic heat capacity, calculated from the upper critical field slope at T_C and the residual resistivity, were very close to values obtained from direct heat capacity measurements and calculated from band structure calculations. The Ginzburg-Landau zero temperature coherence length and penetration depth were calculated for these samples from measured parameters. For VN the average coherence length was 4.85 nm and the sample with the highest transition temperature had a penetration depth of 120 nm. The TiN samples had an average coherence length of 17.1 nm and the TiN sample with highest T_C had a penetration depth of 125 nm.

The VN and TiN samples were irradiated at room temperature with nitrogen ions in order to study the effects of lattice damage on the superconducting and normal state properties. For both materials the residual resistivity was found to increase with increasing damage until reaching saturation at higher ion doses. This behavior could be described by a saturating exponential function with a decay constant

of 4.18 eV/atom for VN and 11.6 eV/atom for TiN. This exponential behavior was derived from a simple defect production and annealing model in which the residual resistivity was proportional to a defect density. In the model the resistivity was separated into a defect contribution, dependent on ion induced damage, and an impurity contribution, constant for a given sample. The transition temperature, before irradiation, was found to be correlated with the impurity term.

A parallel resistor type model, incorporating the defect production and annealing model, was applied to the irradiation data. The resulting parallel term was found to be 401 $\mu\Omega\text{-cm}$ for VN and 383 $\mu\Omega\text{-cm}$ for TiN. Considering the similarity of these numbers we wonder if this is a constant for all B1 superconductors; however, experiments on others would be necessary to support or disprove this conjecture. The decay constants determined from this model were 5.05 eV/atom and 14.4 eV/atom for VN and TiN, respectively.

The transition temperature T_C was found to decrease with increasing damage to saturation. It also could be described by a saturating exponential function, with decay constants of 8.20 eV/atom for VN and 13.9 eV/atom for TiN. This behavior was modeled by a defect production and annealing model similar to the one used for the resistivity. In the T_C model, the change in the transition temperature was proportional to a defect density. The impurity and defect contributions to the reduction of T_C could not be determined since they cancel in the resulting equation.

The lattice constant was measured by X-ray diffraction as a function of ion damage. It was found to remain unchanged in both samples within the experimental error. However, the peaks in the diffraction patterns were observed to decrease in intensity with increasing damage. In the case of VN, all but the two lower peaks had vanished after a total dose of 6.25 eV/atom (1×10^{15} N-ions/cm²) making a lattice constant determination impossible. For TiN, the four lowest order peaks remained through the experiment. No peaks other than from the B1 material or the sapphire substrate were observed during the ion irradiation experiments.

The upper critical magnetic field, measured as a function of temperature, was found to fit WHH theory at all ion fluences. In the case of VN paramagnetic effects had to be included for the theory to fit the data, while the TiN data could be fit without this inclusion. The upper critical field extrapolated to zero temperature was found to increase with irradiation in both materials; however, in VN $H_{C2}(0)$ reached a maximum and then decreased with further damage.

The coefficient of the renormalized electronic heat capacity was determined from the upper critical field slope at T_C and the residual resistivity. In both materials it was found to decrease with ion damage. The Ginzburg-Landau zero temperature coherence lengths of VN and TiN were calculated and found to decrease with damage to a minimum, then increase with further irradiation. The total change in this parameter was not large but the changes were systematic. The Ginzburg-Landau zero temperature penetration depth was found to increase with damage and saturate.

The band density of states at the Fermi energy was calculated as a function of resistivity using the electron lifetime model. Using this band density of states and the renormalized density of states determined from the electronic heat capacity, the electron-phonon coupling constant was determined. This parameter was also calculated from the transition temperature and the two were compared. The two determinations did not agree at all. Spin fluctuations were ruled out as possible reasons for the discrepancy as well as problems with the McMillan equation and the phonon frequency $\omega_{\log}$.

It was concluded that the most likely reason for the difference in λ calculated by the two methods is that the electron lifetime reduction of the density of states with disorder is not the only mechanism at work in this system. While the ELM seems to work well in predicting the changes in the properties of the A15 compounds, it must be noted that the Fermi energy of most of these materials lies on a large peak in the density of states, thus the ELM results in large reductions in the density of states with increasing disorder. It is felt that if another mechanism is at work in the A15 materials it must be overshadowed by this large reduction. On the other hand, the B1 materials' Fermi energy lies on the side of a large peak, therefore the ELM reduction is actually quite small.

Annealing experiments were performed on the ion damaged samples in vacuum and nitrogen atmospheres. The parameters of the VN samples generally recovered fully by temperatures of about 900°C, except for T_C which recovered at 700°C, while the parameters of TiN recovered at 1100°C. The transition temperature of both materials recovered to a

plateau while the other parameters reached maxima or minima at a definite temperature. The samples annealed in nitrogen retained there recovered values at higher temperatures than the vacuum annealed samples.

X-ray diffraction measurements at several annealing temperatures indicate that, in VN, the metal sublattice anneals at 700°C. This corresponds to the recovery of T_C at this temperature. In TiN, the metal sublattice appears to have an annealing stage at 900°C which roughly corresponds with the recovery of the other parameters.

From the decay constants determined from the ion damage experiments and the annealing results several conclusions can be drawn. Comparing the decay constants for the resistivity and the transition temperature of VN, one can see that T_C is less sensitive to damage than ρ_0 . This indicates that the transition temperature is less sensitive to certain types of defects than others while the resistivity is equally sensitive to all defects. From the annealing studies it is inferred that the transition temperature is more sensitive to defects on the metal sublattice than the nitrogen sublattice since it has recovered at 700°C, where the metal lattice anneals, while the resistivity is still recovering at this temperature.

The decay constants of the resistivity and transition temperature for TiN, on the other hand, are very similar. This would indicate that both T_C and ρ_0 are equally influenced by defects. This supposition is also indicated by the annealing results where the

transition temperature and resistivity both recovered at about the same temperature.

Comparing the magnitude of the decay constants for VN and TiN one can see that, for a given parameter, more energy per atom is necessary to make changes in TiN than in VN, thus indicating that the bonding in TiN is stronger than VN. This is also confirmed by the annealing results as well as measurements of the Debye temperature and the free energy of formation of the compounds. From the ratios of the decay constants for a given parameter, the free energies of formation, and the square of the Debye temperatures for TiN and VN, we conclude that the average bonding energy in TiN is about 2.7 times larger than in VN.

Finally, we find that the compounds VN and TiN are less sensitive to ion damage than the A15, superconducting compounds as confirmed by comparing the reduced transition temperature after ion irradiation. We also find that above saturation the reduced T_C values for VN and TiN lie on the same curve. Comparison of these compounds with other B1 compounds indicates that some of the others lie on the same curve of reduced T_C while others lie above it. Thus, in conclusion, we find that the behavior of the residual resistivity and transition temperature of VN and TiN can be modeled by a simple defect production and annealing model, the bonding in TiN is almost three times stronger than in VN, the reduction of T_C with ion damage is less for these materials than for the A15 materials, and the reduced T_C values for TiN, VN, and some other B1 compounds lie on the same curve.

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APPENDIX

THE PARALLEL RESISTANCE MODEL

In section IV the parallel resistance model was applied to the resistivity data, as a function of ion damage, for VN and TiN. In this appendix the algebraic details of applying this model to the data will be presented. In section IV the parallel resistance model use was applied in the form

$$\frac{1}{\rho_0(\phi)} = \frac{1}{\rho_0^P(\phi)} + \frac{1}{\rho_{\max}},$$

where the subscripts and superscripts have the same meanings as in the text. The defect production and annealing model is then applied to the "ideal" term, thus

$$\rho_0^P(\phi) = \rho_I^P + \rho_D^P i + \Delta \rho^P X,$$

$$\text{where } X = 1 - \exp(-\phi/b),$$

$$\Delta \rho^P = \rho_D^P s - \rho_D^P i_{\infty}.$$

Upon substitution and rearrangement we have

$$\rho_0(\phi) = \frac{\rho_{\max} \rho_0^P(0) + \rho_{\max} \Delta \rho^P X}{\rho_{\max} + \rho_0^P(0) + \Delta \rho^P X},$$

where $\rho_0^P(0) = \rho_I^P + \rho_D^P i$.

This equation may be expanded to obtain a more convenient form

$$\rho_0(\phi) = P_1 + P_2 X - P_3 X^2,$$

where the coefficients are

$$P_1 = \rho_{\max} \rho_0^P(0) / y,$$

$$P_2 = \rho_{\max}^2 \Delta \rho^P / y^2,$$

$$P_3 = \rho_{\max} \Delta \rho^P^2 / y^2, \text{ and}$$

$$y = \rho_{\max} + \rho_0^P(0).$$

This form still contains many undetermined variables thus the experimentally determined values of the resistivity at zero fluence

and the total change in the resistivity can be introduced by making the following substitutions:

$$P_1 = \rho_0(0) \text{ and } P_2 = \Delta\rho + P_3.$$

With these substitutions one can then fit to the data as before and determine the decay constant b and the constant P_3 . By inverting the above equations the value of the parallel resistance is determined.

VITA

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