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I am submitting herewith a dissertation written by James Reese Moore entitled "Magnetism in Californium." 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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MAGNETISM IN CALIFORNIUM

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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James Reese Moore

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ABSTRACT

A SQUID-based magnetic susceptometer has been constructed for studying small radioactive samples at temperatures below 350 K and in magnetic fields up to 50 kilogauss. The device has been used to study californium (element 98) in a number of solid-state forms: the dhcp metal, several oxides (Cf_2O_3 in both the bcc and monoclinic structures, Cf_7O_{12} , CfO_2 and BaCfO_3), several mononictides (CfN , CfAs and CfSb) and the trichloride (in both the hexagonal and orthorhombic structures). All of these materials were studied in polycrystalline form, and hexagonal CfCl_3 was studied in single-crystal form as well. The susceptometer has the sensitivity to measure samples containing less than 10 micrograms of californium.

The magnetic susceptibilities of all of the californium materials at temperatures above about 100 K are described well by the Curie-Weiss relationship

$$\chi_M(T) = \frac{N_A \mu_{\text{eff}}^2}{3k_B(T - \theta_P)}.$$

This behavior is consistent with the assumption that the magnetic 5*f* electrons are localized and that the paramagnetic behavior can be interpreted in terms of the properties of the free ion. The measured values of the effective paramagnetic moment, μ_{eff} , for all the californium materials that were studied are reasonably consistent with theoretical values based on intermediate coupling models. All of the californium materials showed some indications of cooperative magnetic effects. The dhcp metal was observed to order ferromagnetically at 52 K, and all of the californium compounds studied showed signs of antiferromagnetic ordering, mostly at temperatures below 25 K.

Although the $5f$ electrons of californium are not severely influenced by the solid state environment, crystal field effects are evident in the magnetic properties. For the metal, oxides and monopnictides, estimates of the crystal field strengths have been made based on extrapolations from the known crystal fields of analogous lanthanide and light actinide materials. For hexagonal CfCl_3 , where single-crystal samples are available, anisotropy in the magnetic susceptibility allows a direct determination of the crystal field parameters.

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CHAPTER I

INTRODUCTION

Californium, which has an atomic number of 98, is a member of the actinide series of elements.¹ The actinides are the fourteen elements that are characterized by the filling of the 5*f*-electron shell while having nearly the same 6*d* and 7*s* valence electron structure. The actinides are in many ways chemically and physically similar to the lanthanide elements, which are characterized by the filling of the 4*f* shell.

Californium does not occur in nature and must be created artificially in nuclear reactors or accelerators. The most readily available isotope is californium-252 which is produced in sub-gram quantities on a yearly basis in the United States. ²⁵²Cf is a strong emitter of spontaneous fission neutrons and is therefore unsuitable for solid state chemical and physical research, but it is used as a neutron source in medical and industrial applications. Californium-249, an alpha-emitter with a half-life of 351 years, is the isotope that is most commonly used for research purposes. It is obtained in an isotopically pure form from the beta-decay of berkelium-249 and is produced in quantities of up to 60 milligrams per year in the U. S. These quantities provide the capability of working with samples containing multi-milligram quantities of californium. However, due to the desirability of limiting the specific activity of individual samples and the necessity of distributing the available materials among a number of research organizations, it is important to be able to perform experiments using as little californium as possible. In the experiments described in

¹For a general review of californium see R. G. Haire, in *Chemistry of the Actinide Elements*, edited by J. J. Katz *et al.*, (Chapman and Hall, New York, 1986), Vol. 2, p. 1025.

this work, the solid state samples contain quantities of californium ranging from several micrograms to several hundred micrograms.

Actinide Magnetism

Because the 5*f*-electron shell in the actinide elements is only partially filled, some of the *f* electrons are unpaired and the actinides, like the lanthanides, exhibit paramagnetism. In all of the lanthanides except cerium (which has one *f* electron in the trivalent state) the solid state magnetic behavior can be reasonably well explained by assuming that the *f* electrons are localized at each atom and that there is little overlap of the *f*-electron wavefunctions between atoms. The radial extension of the 4*f*-electron wavefunctions is less than that of the 5*p*, 5*d* and 6*s* electrons. In the actinides, the 5*f* electrons extend relatively farther radially than the 4*f* electrons of the lanthanides and are consequently less localized. The absence of magnetic behavior in the metallic forms of the elements at the beginning of the actinide series has been interpreted as an indication that the 5*f* electrons for those elements are not in strictly atomic states, but participate significantly in the band structure of the solid.² The metals of the transamericium elements are, however, magnetic, and localization of the 5*f* electrons is usually assumed to begin with americium (element 95).

The paramagnetic behavior of many materials can be described in terms of the Curie-Weiss relationship

$$\chi_M(T) = \frac{N_A \mu_{eff}^2}{3k_B (T - \theta_P)} , \quad (I-1)$$

²J.-M. Fournier and L. Manes, in *Actinides - Chemistry and Physical Properties*, edited by L. Manes (Springer-Verlag, Berlin, 1985), p. 24.

where χ_M is the molar susceptibility, N_A is Avogadro's number, k_B is Boltzmann's constant, μ_{eff} is the effective paramagnetic moment and θ_P is the Weiss constant. In this work, electromagnetic units (emu) will be used, and the molar susceptibility has units of cm^3/mol . Molar units in this work will always refer to a mole of californium ions. Magnetic moment per californium ion will be given in units of the Bohr magneton,

$$\mu_B = \frac{e\hbar}{2mc} = 0.927 \times 10^{-20} \text{ erg/gauss.} \quad (\text{I-2})$$

Since the f electrons are localized, they are not severely influenced by the crystalline electric field in the solid state and the total angular momentum J is a "reasonably good" quantum number. The effective paramagnetic moment can therefore be calculated from

$$\mu_{\text{eff}}^2 = J(J+1)g_J^2\mu_B^2, \quad (\text{I-3})$$

where g_J is the Landé g -factor (see Chapter III). The paramagnetic measurements on californium show that this relationship holds quite well provided that intermediate coupling wavefunctions are used in calculating g_J . The Weiss constant, θ_P , is influenced principally by the effects of cooperative magnetic behavior and the effects of the crystalline electric field.

Another consequence of the localization of the f electrons and their isolation from solid state environmental effects is the presence of well-defined peaks in the optical spectra, as shown in Figure I-1. Transitions between energy levels of the f^n ground configuration, which are forbidden by parity considerations, can occur because of configuration mixing³ and can be observed in many compounds. In cases where both magnetic measurements and

³S. Hufner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic, New York, 1978), p. 6.

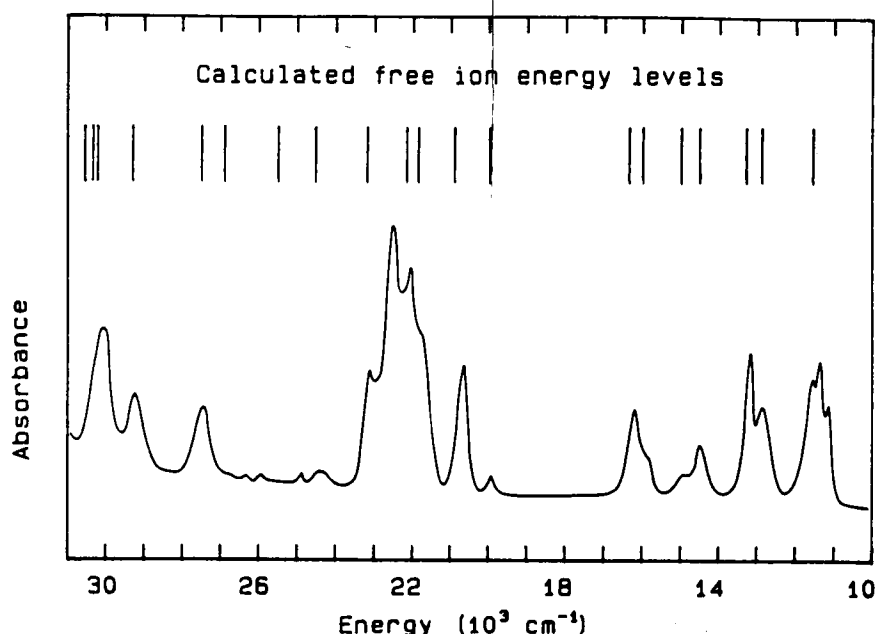


Figure I-1. Optical absorption spectrum of hexagonal CfCl_3 . Adapted from the room temperature spectrum of J. R. Peterson *et al.*, *Inorg. Chem.* 25, 3779 (1986). The calculation of the free ion energies is described in Chapter III.

spectroscopic measurements can be made, the two techniques complement each other and provide a self-consistent test of models of the electronic structure. When detailed spectra are not available, as is the case for most of the materials studied in this work, the magnetic measurements by themselves contribute significantly to the understanding of the electronic structure.

Magnetic susceptibility and magnetization measurements can provide the following types of information:

- Information on the charge state of the californium ion from the measurement of the effective paramagnetic moment at temperatures that are high compared to the crystal field splitting of the ground state (typically above 100 K);
- Information on the splitting of the ground state by the crystalline

electric field from susceptibility and magnetization measurements at lower temperatures (typically below 100 K);

- Information on cooperative magnetic effects from measurements of magnetic ordering temperatures and saturation magnetic moments (typically below 25 K).

Historical Perspective

The first magnetic measurements of californium were made by Cunningham⁴ in the late 1950's. Using a sensitive Faraday balance, he measured the magnetic susceptibility of 0.056 μg of Cf^{3+} absorbed on a bead of ion exchange resin. His result of $\mu_{\text{eff}} = 9.2 \pm 0.9 \mu_{\text{B}}$, when compared with his measurement of $\mu_{\text{eff}} = 8.7 \pm 0.9 \mu_{\text{B}}$ for Bk^{3+} , indicated that the ground state of Cf^{3+} has the f^9 configuration. Fujita⁵ in the late 1960's made measurements on resin beads containing approximately one microgram of californium with similar results.

The first reported susceptibility measurements of a bulk solid sample of californium is that of Fujita *et al.*⁶ in 1975 on samples of several micrograms of californium metal. Electron paramagnetic resonance measurements on cubic californium compounds were performed at about the same time.⁷ Nave⁸ and Huray,⁹ in the late 1970's, began a systematic study of the magnetic properties of the transplutonium elements through einsteinium (element 99). The

⁴B. B. Cunningham, J. Chem. Ed. **36**, 32 (1959).

⁵D. K. Fujita, University of California Radiation Laboratory Report No. UCRL-19507, 1969 (unpublished), p. 25.

⁶D. K. Fujita *et al.*, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 173.

⁷N. Edelstein and D. G. Karraker, J. Chem. Phys. **62**, 938 (1975).

⁸S. E. Nave *et al.*, Phys. Rev. B **28**, 2317 (1983).

⁹P. G. Huray *et al.*, J. Less-Common Met. **93**, 293 (1983).

californium measurements described herein are a part of that work.

Materials Investigated

The four types of californium materials that are investigated in this work are the metal, the oxides, the mononictides (compounds with the group VA elements) and the trichloride. The californium ion occurs in a variety of different solid state environments in these materials. The oxides and the trichloride are ionic compounds, but the mononictides are semi-metallic. The conduction electrons in the mononictides and in the pure metal play an important role in the collective magnetic behavior in those materials. The relationship between the spacing of the californium ions and the magnetic ordering temperatures in the mononictides sheds some light on the mechanisms of magnetic ordering in those compounds.

The pure oxides Cf_2O_3 , Cf_7O_{12} and CfO_2 make up a series of compounds in which the californium is found in the 3+ and 4+ charge state. Measurements of the effective paramagnetic moments of these compounds is one way to confirm the charge states. BaCfO_3 is another ionic compound in which the californium ion is in the less common 4+ charge state. Measurements on the two crystal forms of Cf_2O_3 (bcc and monoclinic) allow a comparison of the magnetic ordering and crystalline electric field splitting in the two different crystal environments.

Californium trichloride is of interest for a number of reasons. It has both a hexagonal and an orthorhombic crystal form, which provides two different symmetries for investigating crystal field effects and magnetic ordering. Single crystals of the hexagonal structure can be grown and the anisotropy of the magnetic properties can be measured. CfCl_3 is also optically

transparent and the optical spectrum of the hexagonal form has been well characterized. The splitting of energy levels by the crystal field as determined from the optical spectrum can be directly compared with the effects of that splitting on the magnetic properties. None of the other californium materials studied in this work have been so well characterized by optical absorption measurements and allow such a comparison.

CHAPTER II

THE MAGNETIC SUSCEPTOMETER

The magnetic measurements described in this work were performed on a magnetic susceptometer that was constructed specifically for studying small samples. It is patterned after a device built by Nave and Huray,¹ but with modifications to allow measurements on somewhat larger samples and measurements at higher magnetic fields. The description of the susceptometer in this chapter applies to the device as it is presently operating. For measurements made during the initial operations of the device, some mechanical features were different. The significant differences will be noted when the actual measurements are discussed in later chapters.

Overall Mechanical Features

An overall schematic diagram of the susceptometer is shown in Figure II-1. The sample, temperature sensors and a sample heater are suspended by wires in an evacuated space inside a liquid helium cryostat. The wires are pulled up and down from outside the cryostat causing the sample to move up and down through a pair of sensing coils that are part of a superconducting loop. The superconducting loop is connected to a Superconducting QUantum Interference Device (SQUID) which acts as a current-to-voltage converter and gives a signal directly proportional to the magnetic moment of the sample.

Sample changing is accomplished by the use of an airlock at the top of the cryostat. The sample can be pulled up into the sample tube by pulling

¹S. E. Nave and P. G. Huray, Rev. Sci. Inst. **51**, 591 (1980).

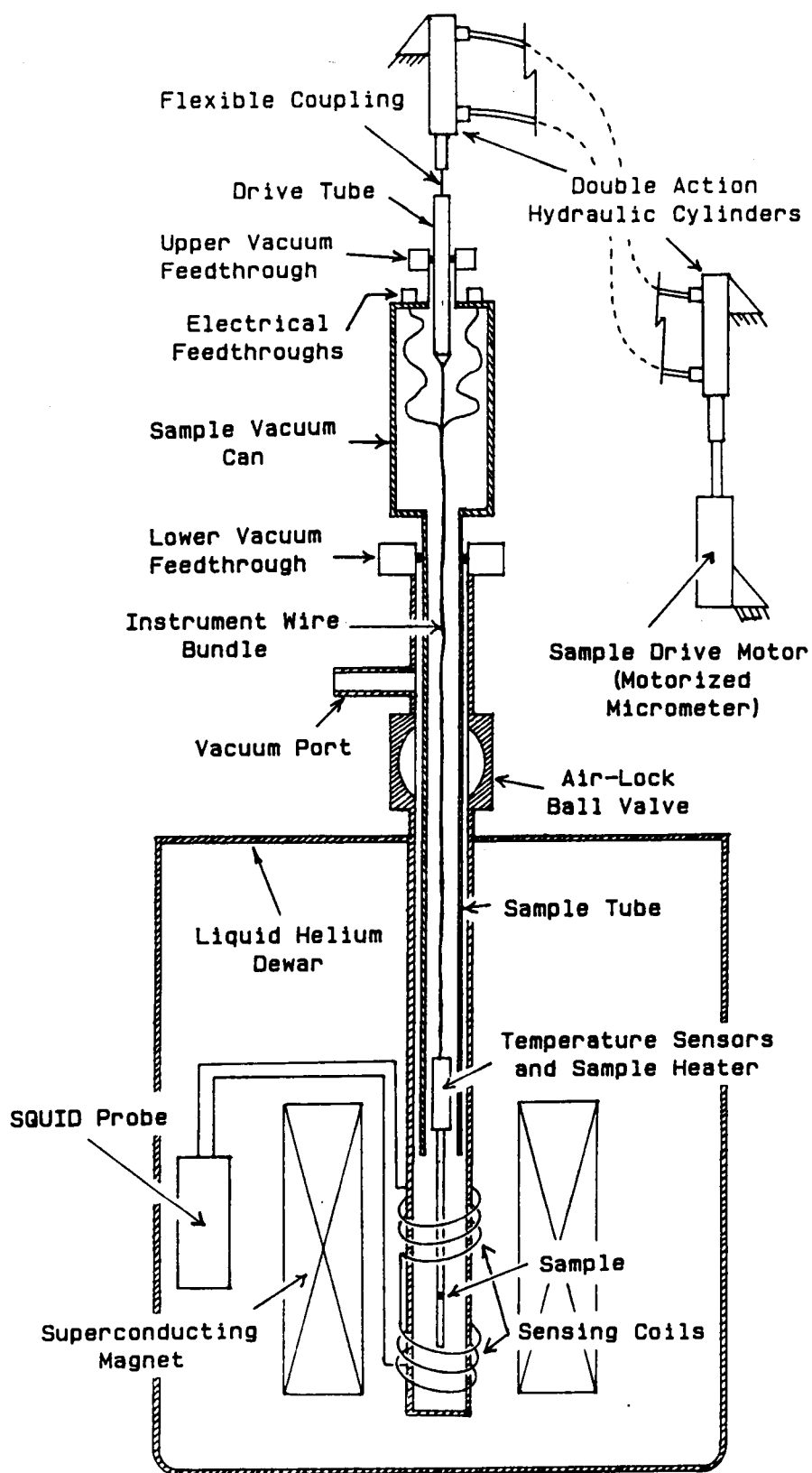


Figure II-1. Schematic diagram of the magnetic susceptometer.

the drive tube partially out of the sample vacuum can. The sample tube can then be withdrawn through the lower vacuum feedthrough until the air-lock ball valve can be closed, isolating the vacuum below it. The sample tube can then be removed entirely and the sample can be changed.

Experimental Control and Data Acquisition

A 16-bit micro-computer (IBM PC/XT) is used for both experimental control and data acquisition. Figure II-2 is a block diagram of the system. The computer is connected to the susceptometer and other peripheral devices through an IEEE 488 instrument buss and through a bank of digital I/O lines. Both of these computer interface capabilities are provided by special hardware mounted on the expansion buss of the computer.

A BASIC computer program handles almost all aspects of experimental control and data acquisition. The susceptometer can be programmed to automatically perform measurements either at constant temperature with varying magnetic field or at constant field with varying temperature. For each data point, the sample is moved up and down through the sensing coils twice in each direction at about 0.25 mm/sec. The SQUID output is recorded once a second for a total of about 200 values. A typical profile for a measurement at one temperature and field is shown in Figure II-3. The profile is analyzed by the computer to determine the four peak-to-peak values. These four values are then averaged and stored on floppy disk with information about the temperature and the magnetic field. A graphical display of the data (*e.g.*, susceptibility *vs.* temperature or magnetic moment *vs.* field) can be displayed at any time during an experiment.

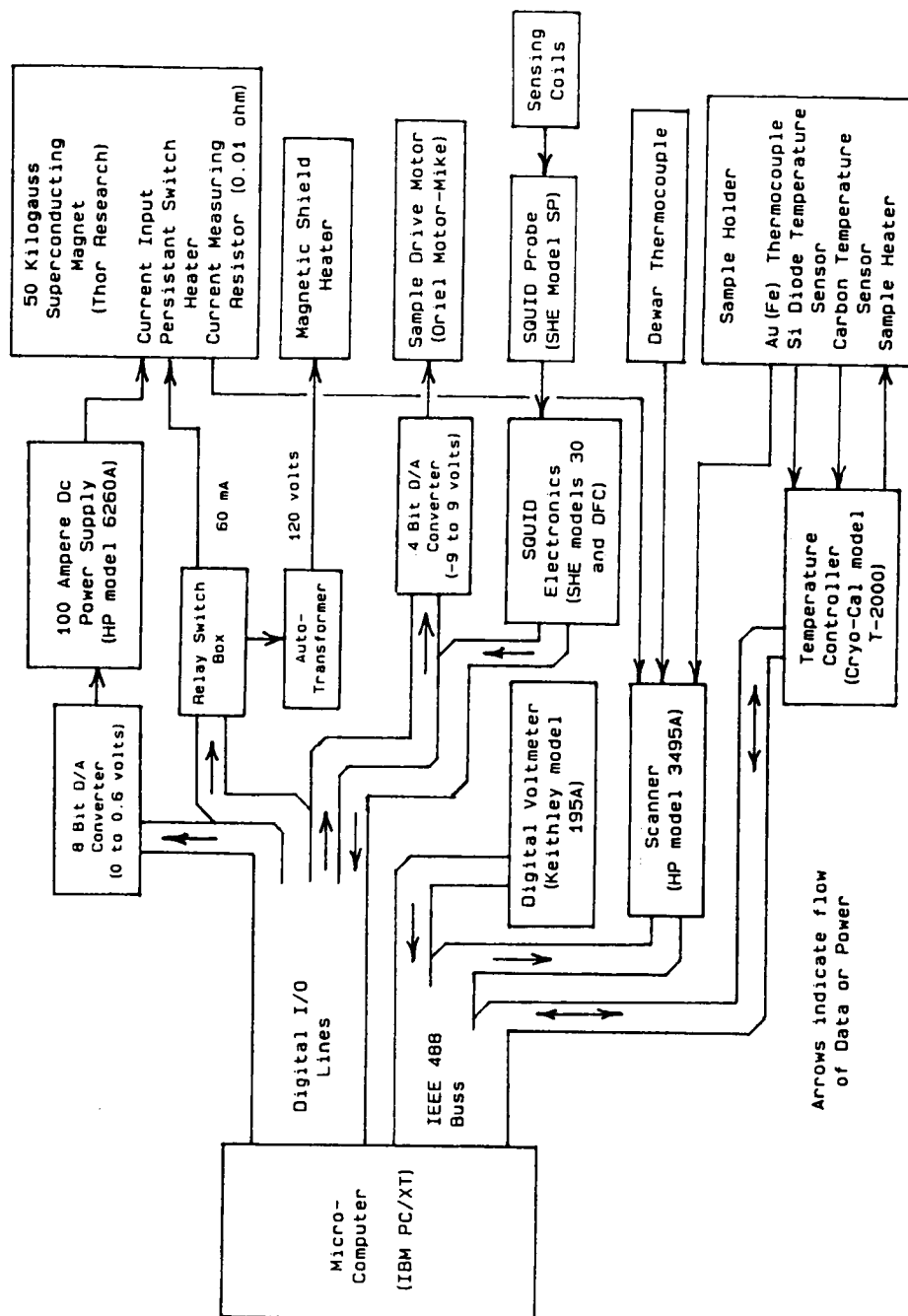


Figure II-2. Block diagram of the susceptometer data acquisition and control system.

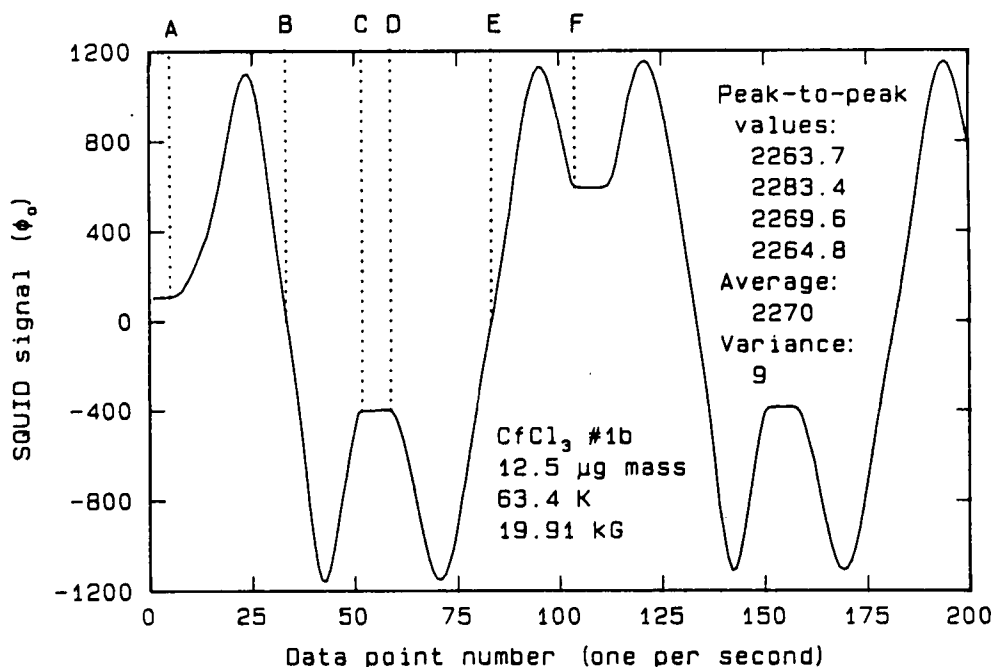


Figure II-3. Raw data for a typical susceptometer measurement at one magnetic field and temperature.

For data points 1 to 110:

- A - Sample begins motion down through the first coil (wound clockwise).
- B - Sample reaches midpoint between the coils.
- C - Sample finishes motion through the second coil (wound counter-clockwise).
- D - Sample begins reverse motion back up through the second coil.
- E - Sample reaches midpoint between the coils.
- F - Sample finishes motion through the first coil.

For data points 111 to 200:

Sequence A to F is repeated.

System Details

Flux Sensing System

The flux sensing circuit of the susceptometer consists of two oppositely wound coils that form part of a superconducting loop that is connected to a SQUID probe. Since the magnetic flux through the superconducting loop must remain constant, current is induced in the loop as a magnetic sample passes through either coil. The double coil arrangement makes the system insensitive to changes in uniform ambient magnetic fields. The SQUID measures the current in the loop and gives as an output the number of flux quanta ($\phi_0 = 2.07 \times 10^{-7}$ gauss cm²) coupled to the SQUID. This output is not the same as the flux change in the sensing loop caused by the sample, but is proportional to it. Therefore, all raw data are recorded in terms of the flux quanta output of the SQUID and then are converted to actual magnetic moments using an experimentally determined calibration constant for the device. The SQUID probe in the susceptometer has a sensitivity of 1.12×10^{-7} amperes per ϕ_0 . Typical measured peak-to-peak flux counts for samples studied in this work range between 10 and 200,000 flux quanta at magnetic fields of several kilogauss and above.

The physical arrangement of the sensing coils is shown in Figure II-4. Each coil consists of 15 turns in a single layer with an inner diameter of 4.09 mm. The center-to-center spacing of the coils is 5 mm. The self-inductance of the sensing coil pair is $2.1 \mu\text{H}$, which when combined with the $2 \mu\text{H}$ inductance of the SQUID input maximizes the coupling of the sample flux to the SQUID. All leads are carefully twisted to minimize stray inductances. The wire of the superconducting loop is 0.102 mm in diameter

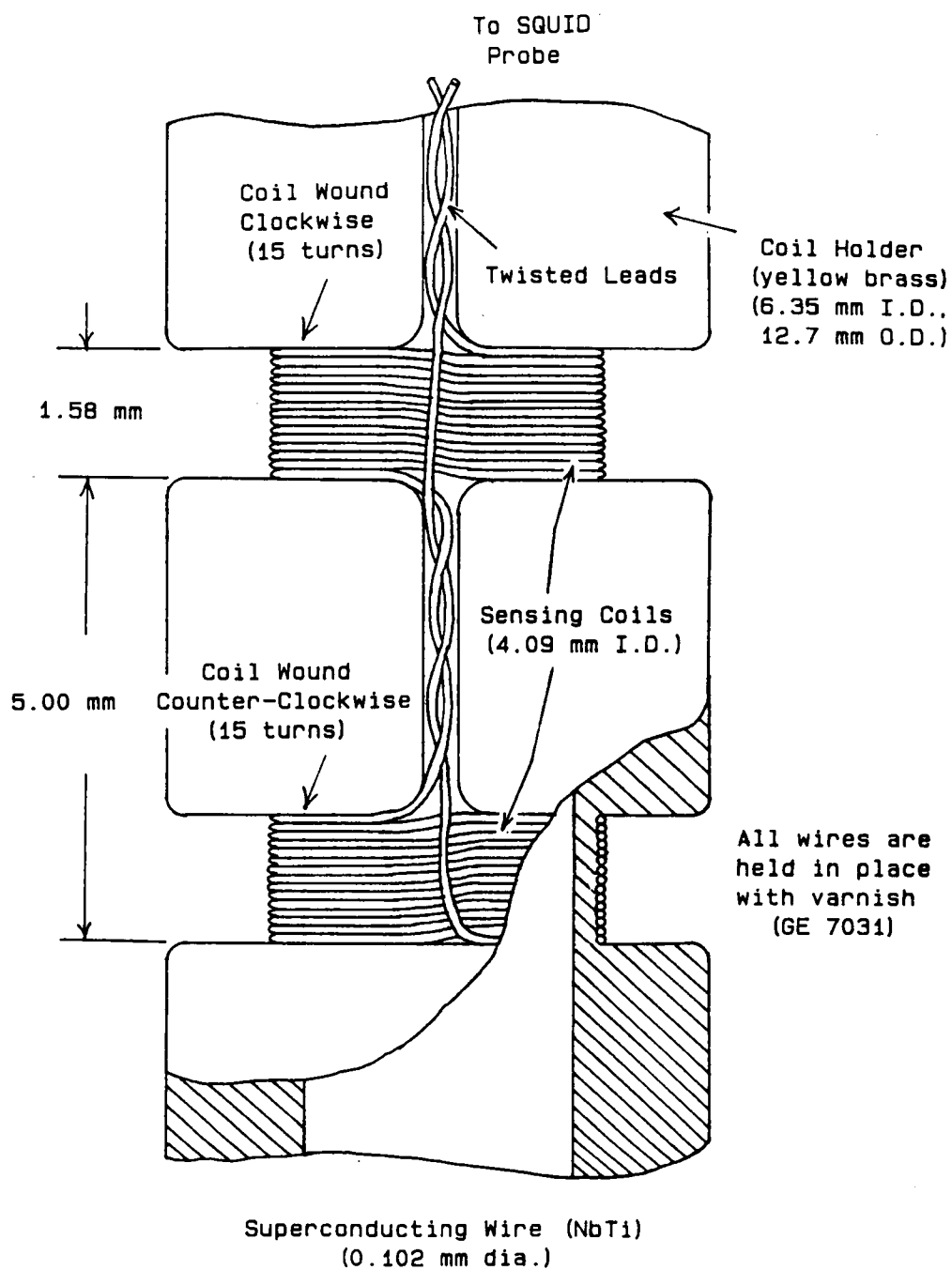


Figure II-4. Details of the susceptometer sensing coils.

with a core of niobium-titanium and an outer sheath of copper. The coils are wound in slots machined in a yellow brass tube and held in place with varnish. The twisted wires leading to the SQUID probe are fed through a niobium capillary tube that provides shielding from both AC and DC magnetic fields. Vacuum grease inside the capillary tube helps prevent noise due to motion of the leads. The SQUID probe, which is also shielded by a niobium tube, is located outside the high field region of the superconducting magnet in an area where the magnetic field is less than 900 gauss (the critical field of Nb at 4.2 K).

The response of the sensing system depends upon sample geometry. The sample is constrained by the sample holder to remain close to the axis of the coil system so that off-axis effects are minimized. The theoretical SQUID signals for samples with the same total moment but different lengths (assumed to be infinitely thin and on-axis) are shown in Figure II-5. Most samples that are measured are less than one-half millimeter in any dimension and can be considered as point sources.

Superconducting Magnet

The magnetic field that is applied to the sample is generated by a superconducting magnet with a 25.4 mm clear bore. It can provide fields of up to 50 kilogauss (with 92.2 amperes of current). The magnet has a field uniformity of better than one percent over a cylindrical volume 100 mm long and 10 mm in diameter (see Figure II-6).

A 100 ampere DC power supply drives the magnet. The power supply is usually computer-controlled through an 8-bit D/A converter, which allows control in steps of about 200 gauss. When lower fields and finer control are

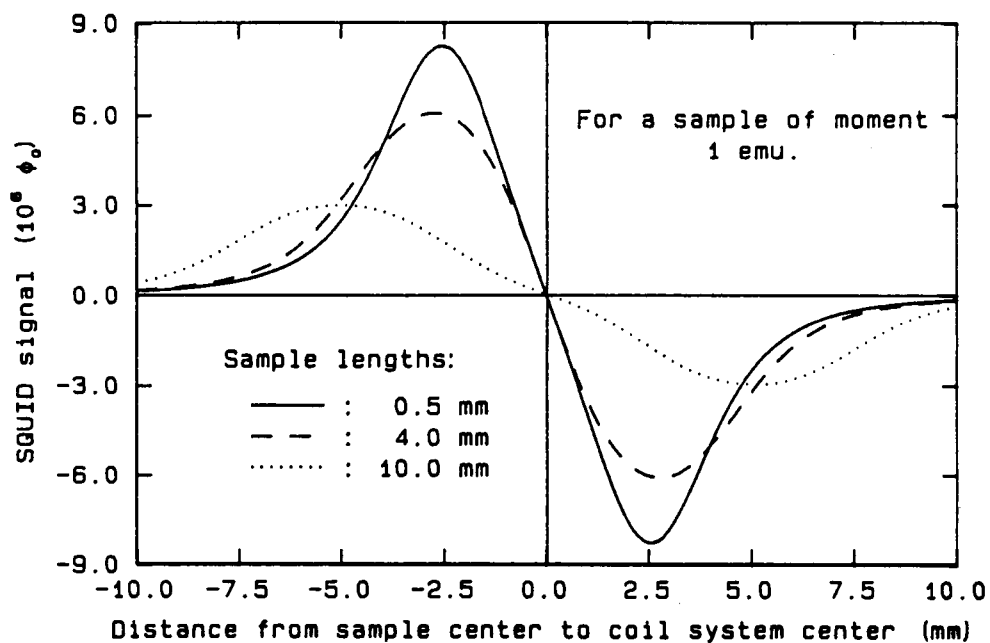


Figure II-5. Theoretical SQUID signal as a sample passes through the sensing coils on-axis.

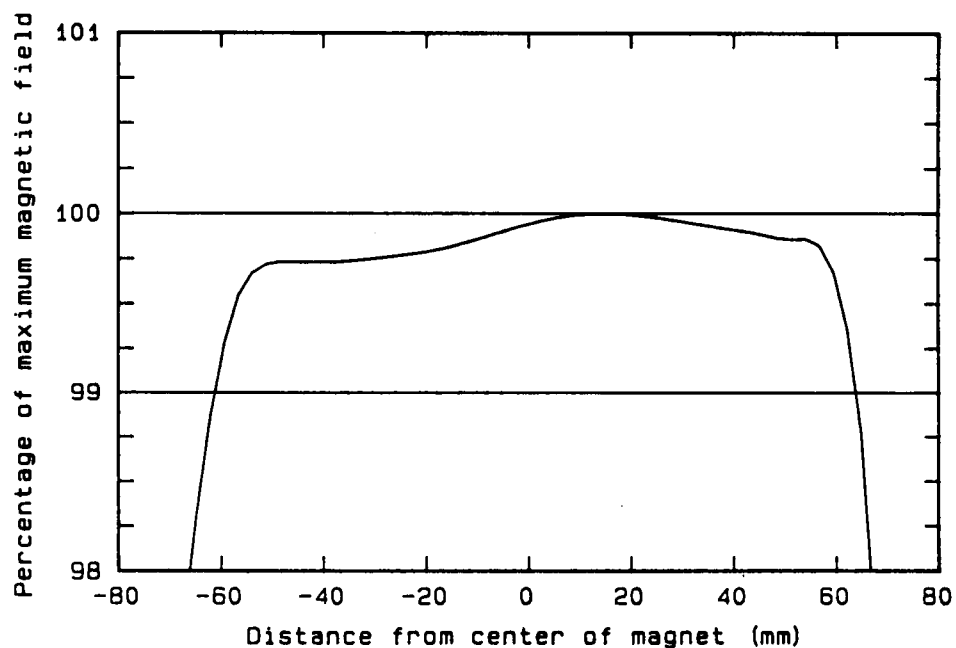


Figure II-6. Magnetic field uniformity of the superconducting magnet (on-axis).

required, the power supply is operated manually. The voltage drop in a 0.01 ohm resistor in series with the magnet is monitored for determining the applied field. A crow-bar circuit cuts off the power supply if a voltage greater than 0.5 volts is sensed across the magnet leads at the top of the cryostat. Two 100 ampere reverse-biased diodes connected across the leads at the top of the cryostat provide protection for the magnet when the energy in the magnet must be dissipated and the power supply has shut down.

Current to the magnet enters the dewar through leads that are internally cooled by He boil-off gas and can operate continuously at 100 amperes. The magnet is usually operated in a persistent current mode. The heater that controls the persistent switch can be operated either manually or by the computer. In most cases, the computer is used to control and monitor the power supply and persistent switch in the sequence of operations required for changing the current in the magnet.

Magnetic Shielding

A cylindrical tube of NbTi (45% Nb, 55% Ti) superconductor provides magnetic shielding for the sensing coils and sample. The shield is 100 mm long, and has a 12.7 mm diameter and 0.5 mm wall thickness. It is located in the volume of the superconducting magnet that is already uniform to one percent and enhances that uniformity to a greater degree while it also provides shielding from time-varying magnetic fields. A 750-ohm bifilar nichrome heater is wrapped on the outside of the shield and is used to heat the shield above its critical temperature whenever the applied magnetic field is changed and must be allowed to penetrate into the sample space. The heater is powered from an auto-transformer which is operated either manually or by relays

through the computer. The arrangement of the superconducting magnet, shield and sensing coils is shown in Figure II-7.

Temperature Control and Measurement

Figure II-8 gives a detailed view of the sample package that is suspended in the cryostat. The upper part of the package is a piece of machined brass to which a Si diode sensor, carbon sensor and electrical heater are thermally anchored. This part of the package always remains well outside of the superconducting shield. The lower part of the package consists of a copper tube that thermally connects the upper part with the sample holder. A tantalum tube is usually slipped over both the sample holder and the copper tube to provide mechanical protection for the sample.

A microprocessor-based temperature controller is used to regulate the sample temperature. The sample package is suspended in a vacuum and the only two sources of cooling for the sample are radiative cooling to the nearby walls which are at liquid helium temperature and cooling by the admission of small amounts of He gas into the vacuum space. Radiative cooling is sufficient to allow temperature control down to about 50 K, but exchange gas must be used to cool to lower temperatures. The signal from the Si diode sensor is used by the temperature controller at temperatures above about 35 K. At lower temperatures, the diode is affected by magnetic fields and the carbon sensor (which is not a very sensitive thermometer above 100 K) is used.

Since the sample is located approximately 60 mm from the diode and carbon sensors, a differential thermocouple arrangement is used to measure the difference in temperature between the sensors and the sample holder. Gold-iron *vs.* chromel junctions are used since they are quite sensitive at low

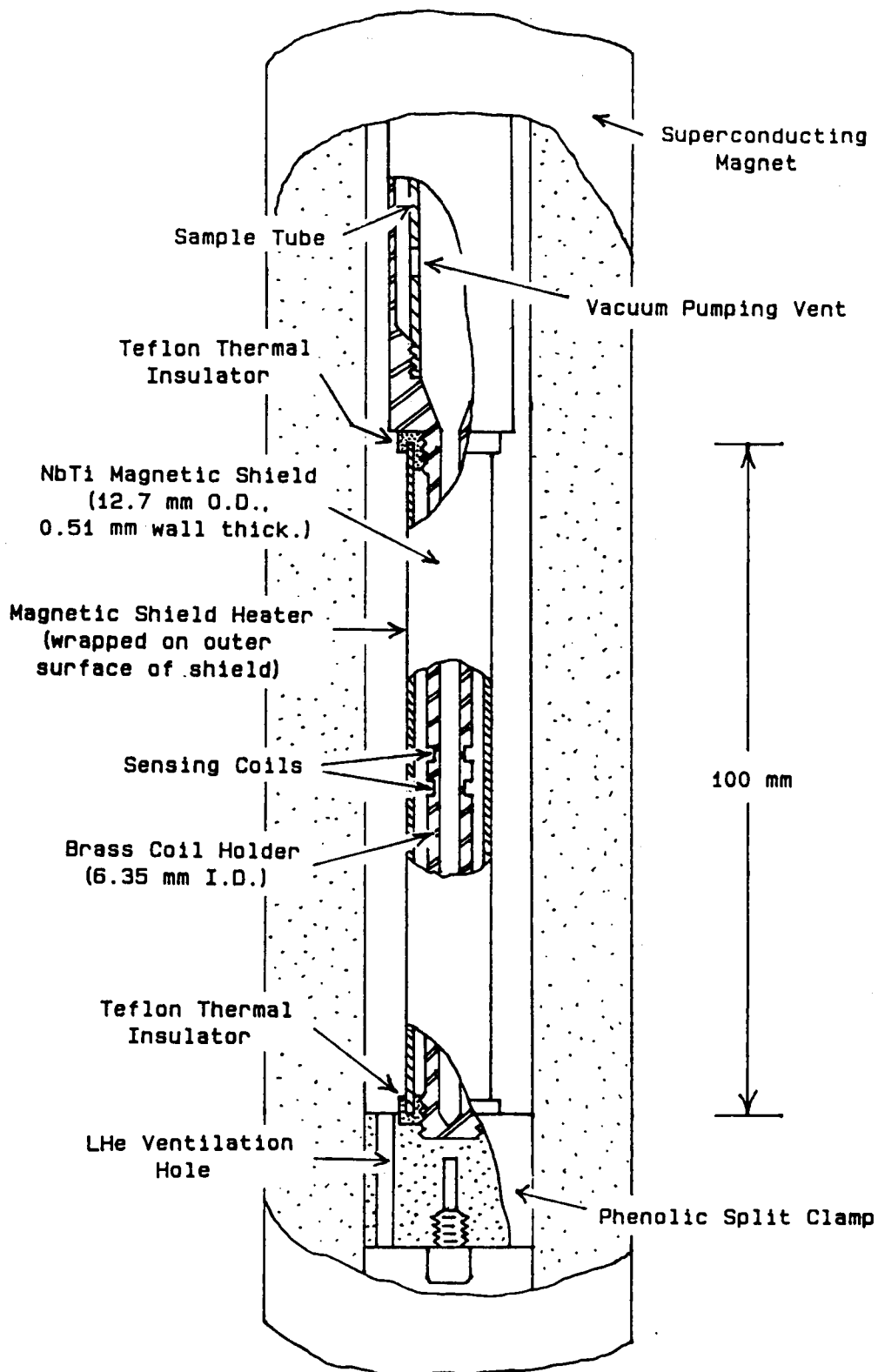


Figure II-7. Details of the susceptometer sample region.

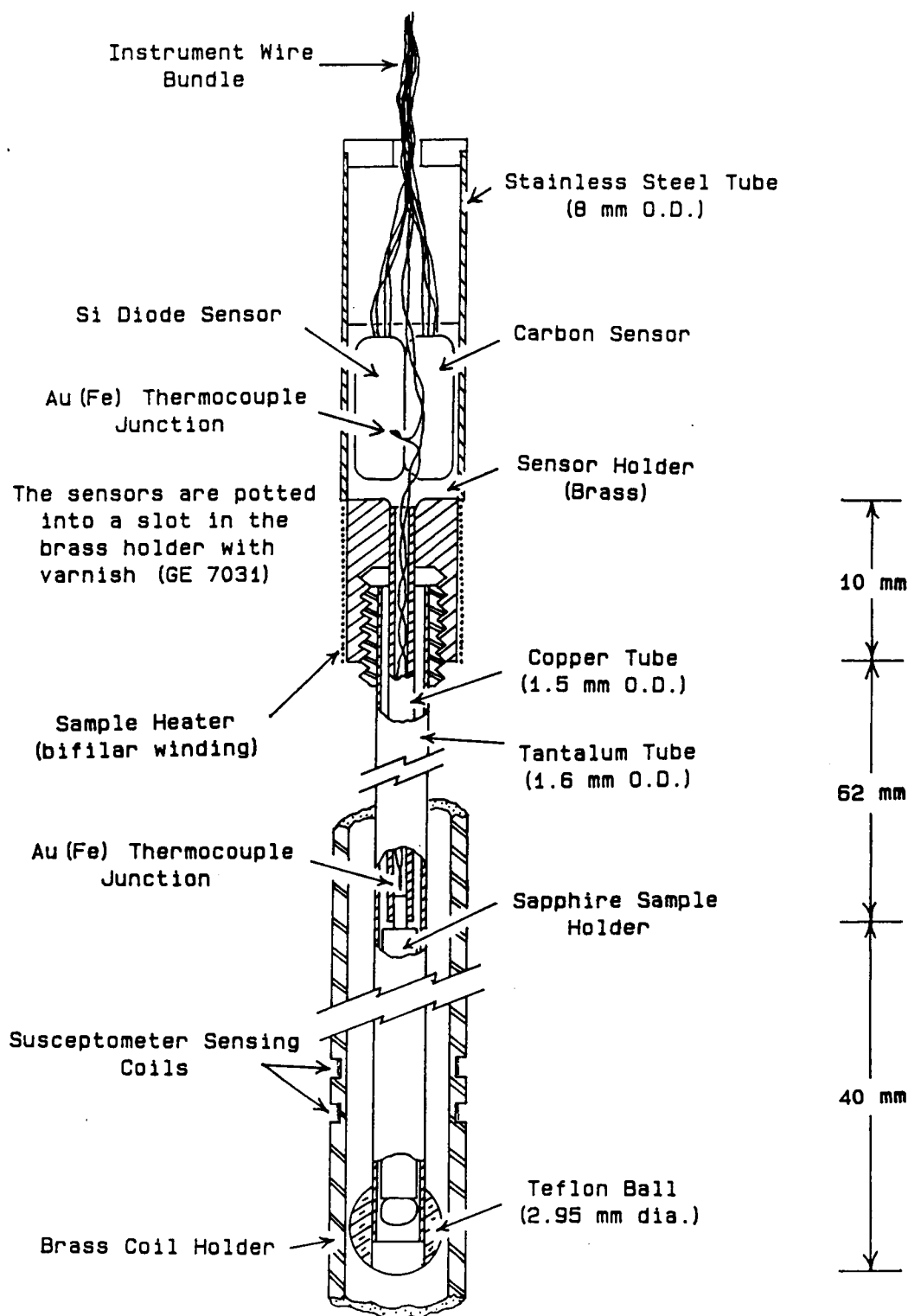


Figure II-8. Details of the temperature sensors and sample heater.

temperatures (about 14 microvolts per degree K). At the highest sample temperatures (about 340 K) the temperature difference between the controlling sensors and the sample holder is typically 5 K or less. The difference is smaller at lower temperatures and is usually less than 1 K at 200 K. At temperatures below 20 K, when the He pressure of the sample space must be increased to provide cooling, gradients of several degrees can be generated and must be corrected for.

Sample Holder

Since the samples that are studied in the susceptometer are relatively small, it is important that sample holder effects be minimized. This essentially means avoiding any physical features in the sample holder that would generate a magnetic signal while the sample is passing through the sensing coils. One way that this has been accomplished is shown in Figure II-9.

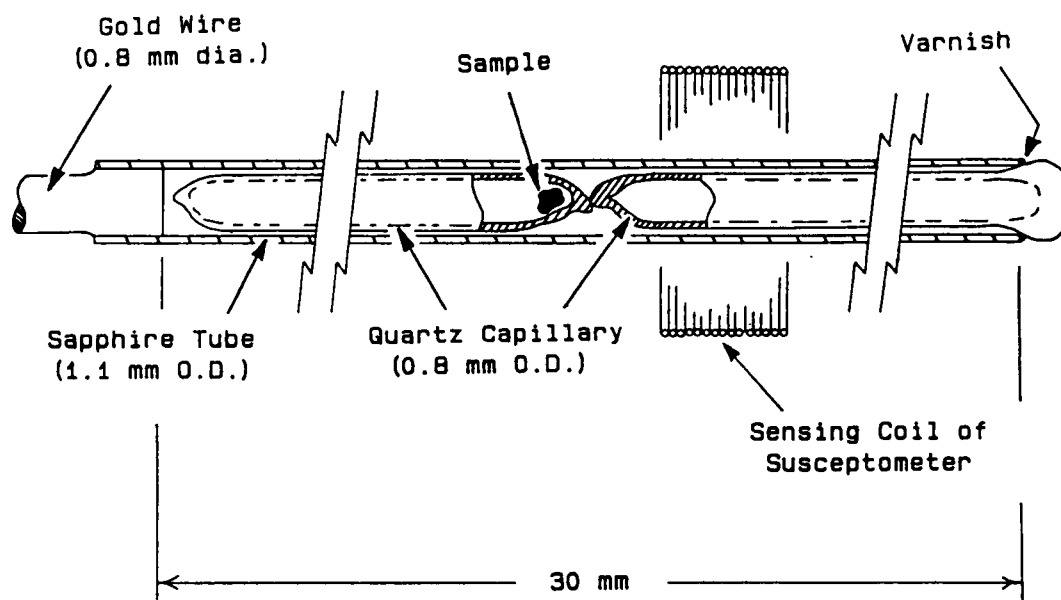


Figure II-9. Sapphire sample holder.

Most of the samples studied were prepared and/or characterized by X-ray diffraction in a small (about 0.8 mm diameter) quartz (fused silica) capillary. If the capillary is inserted into another larger tube with another similar piece of quartz, the sample appears, in terms of its magnetic signal, to be fixed at the center of a single long piece of quartz. If the ends of the quartz and outer tube are at least 15 mm from the sample and are not heavily contaminated with magnetic material, they do not significantly interfere with the sample measurement.

The outer tube is connected to the copper tube that holds the Au(Fe) thermocouple (see Figure II-8) by a gold wire to minimize thermal gradients between the thermocouple and the sample holder. It is important that the sample holder tube have a reasonably high thermal conductivity so that thermal gradients within the sample holder are not large. A high electrical conductivity must be avoided, however, since it can result in the generation of Johnson noise (electrical noise due to thermally induced electrical currents). For most measurements, sample holder tubes of single-crystal sapphire have been used since sapphire has a relatively high thermal conductivity and is a good electrical insulator. Sapphire sample holders generate noticeably less Johnson noise than do sample holders made from gold, copper or aluminum.

Sample Drive System

The linear motion of the sample through the sensing coils is provided by a motorized micrometer. The motion is transmitted from the micrometer to the sample through a water-filled hydraulic system that dampens vibrations generated by the motor and allows remote mounting of the micrometer for vibration isolation. The direction and speed of the micrometer can be

controlled either manually with switches or by the computer through a 4-bit D/A (digital-to-analog) converter (providing 3 speeds in either direction). The maximum and normal operating speed for taking data is about 15 mm per minute.

The points at which the direction of motion of the sample is reversed are usually updated continually by the computer as data is taken. This allows for compensation for variations in backlash in the hydraulic system, for thermal expansion and contraction of the sample support wires, and for variations in sample speed due to friction of the drive rod running through its vacuum feed-through. When the data profile is noisy or irregular and turning points cannot be reliably determined from the data by the computer, then fixed turning points are used, which must be occasionally adjusted manually to keep the sample centered between the sensing coils.

System Calibration

The susceptometer has been calibrated using three different methods. The first calibration method uses a small six-turn coil of 0.10 mm diameter copper wire wound onto a 0.76 mm diameter tungsten wire. A current of 10 to 20 milliamperes is passed through the coil and the susceptometer signal is measured as the coil is moved through the sensing coils. The calculated theoretical moment for the test coil is 3.51×10^{-6} emu per milliampere and the measured peak-to-peak flux change is $58.4 \phi_0$ per milliampere. This results in a calibration constant for the system of $16.6 \times 10^6 \phi_0$ per emu unit of magnetic moment. This method of calibration is independent of the magnetic field in the system but requires an accurate knowledge of the physical dimensions of the test and sensing coils.

The second calibration method is performed by measuring the effective paramagnetic moment of a paramagnetic sample ($429 \mu\text{g}$ of Gd_2O_3). Data taken for three different measurements of the sample in different sample holders is shown in Figure II-10. A linear least-squares fit to the plot of (field/flux) *vs.* temperature when compared with literature values for the effective paramagnetic moment of the sample² ($7.90 \mu_B$) results in a calibration constant of $16.7 \times 10^6 \phi_0$ per emu. The uncertainty in this value is slightly larger than the uncertainty in the constant calculated in the first method and is due primarily to the uncertainties in the sample mass and in the literature value for the effective paramagnetic moment.

The final method is to measure the magnetization of a small ($184 \mu\text{g}$) sphere of superconducting lead. Figure II-11 is a plot of flux *vs.* field for the sphere at a temperature of 4.4 K. For a perfect superconducting sphere, one would expect a linear rise in flux up to a field that is $2/3$ the critical field (since the demagnetizing field for a sphere is $3/2$ times the applied field) and a linear fall to zero at the critical field.³ Figure II-11 approximates this behavior, but non-linearity in the measurements, due perhaps to impurities in the lead, allows fitting a straight line to the data only over fields of 120 gauss and less. This fit results in a calibration constant for the device of $16.3 \times 10^6 \phi_0$ per emu. The sphere was formed by melting lead on a graphite surface and allowing it to form into a sphere by surface tension effects. Measurements of the diameter of the sphere indicate deviations from a perfect sphere of less than one part in 75. Since the demagnetization factor for an ellipsoid that is

²G. Foex, C.-J. Gorter, and L.-J. Smits, *Tables de Constantes et Données Numérique 7, Constantes Sélectionnées, Diamagnétisme et Paramagnétisme* (Masson, Paris, 1957), p. 254.

³M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), p. 97.

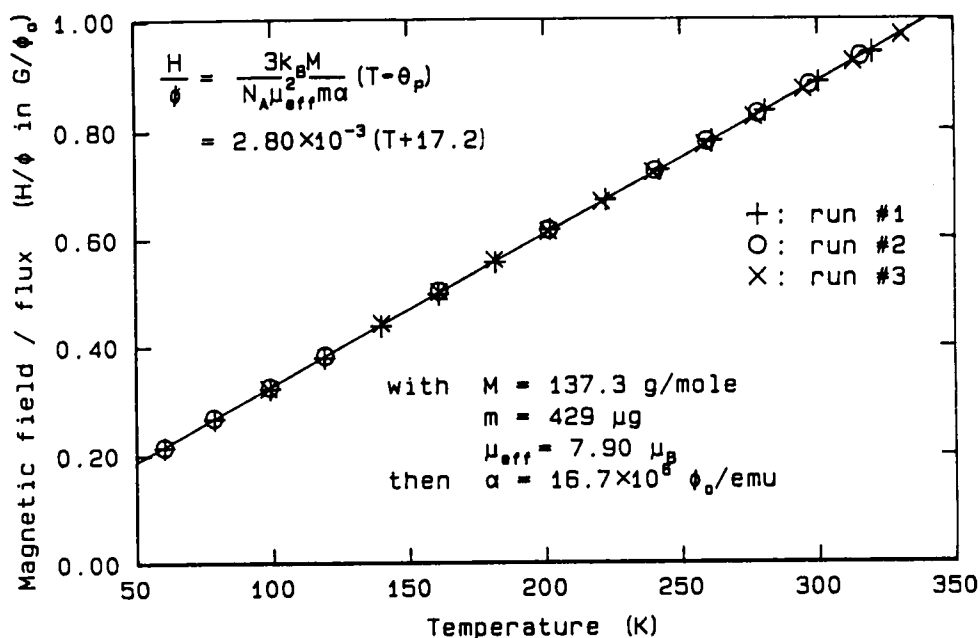


Figure II-10. Calibration of the susceptometer with Gd_2O_3 .

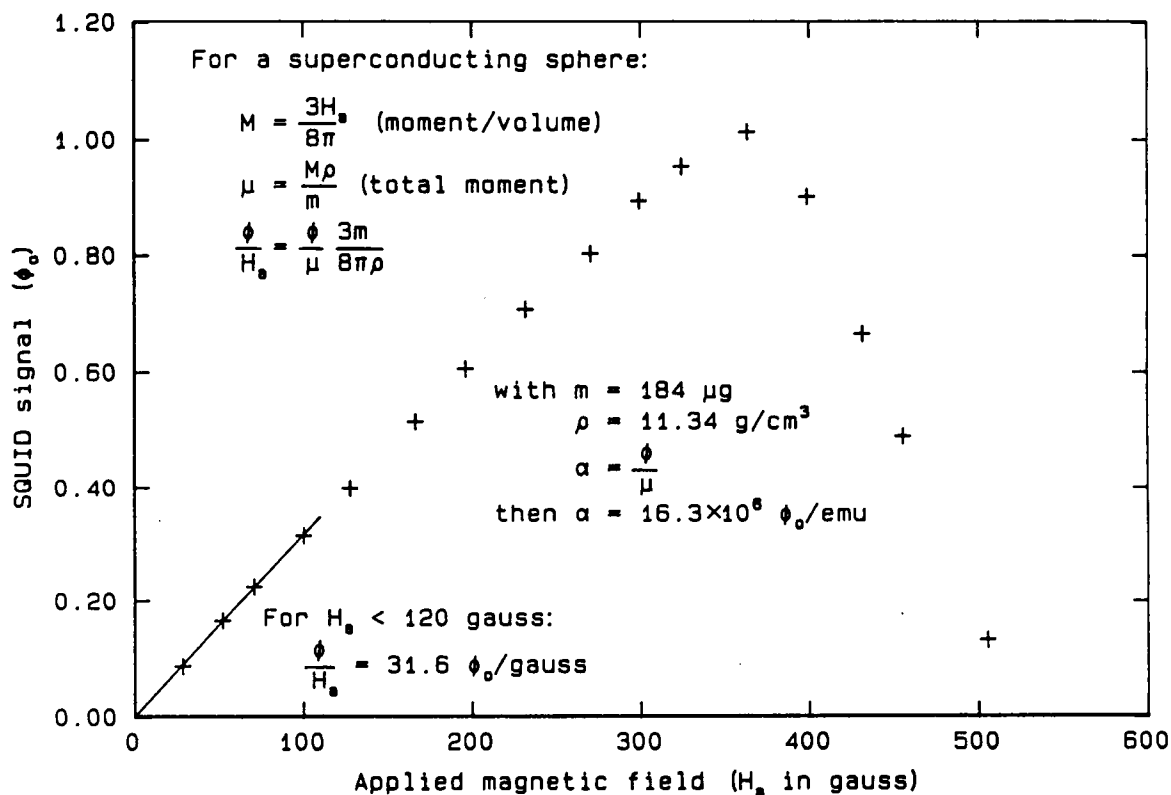


Figure II-11. Calibration of the susceptometer with a lead sphere.

nearly spherical is proportional to the eccentricity of the ellipsoid,⁴ the uncertainty in sphericalness results in an uncertainty of about $0.22 \times 10^6 \phi_0$ per emu in the calibration factor.

Considering all three of these calibrations, a value of $(16.6 \pm 0.15) \times 10^6 \phi_0$ per emu has been used for all magnetic moment determinations for the experiments described in this work. Figure II-12 shows how the peak-to-peak SQUID signal should vary with sample length using the above calibration constant for a point sample.

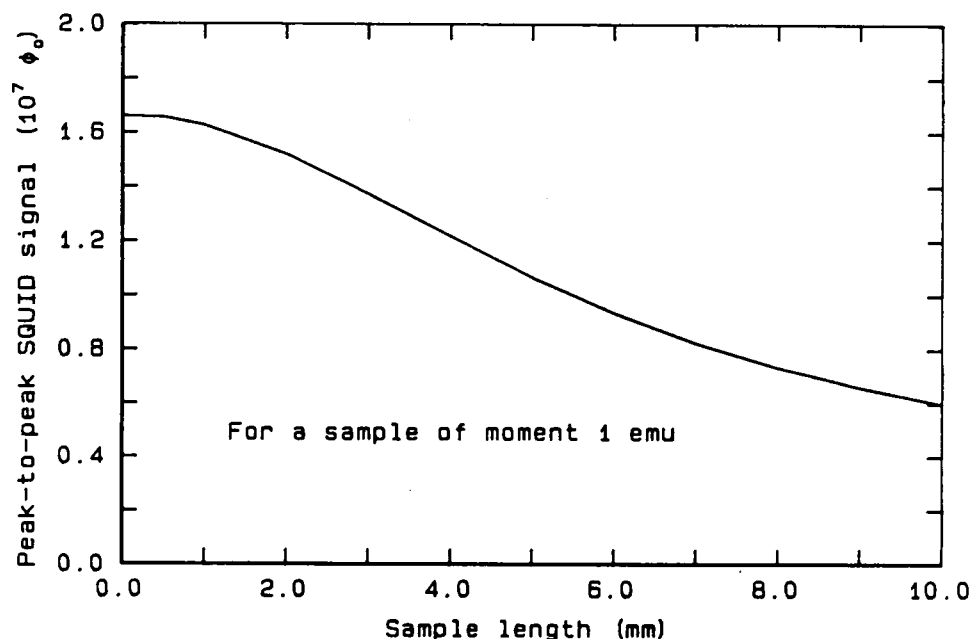


Figure II-12. Theoretical dependence of the susceptometer peak-to-peak SQUID signal on sample length. A calibration constant of $1.66 \times 10^6 \phi_0$ per emu is assumed for a point sample.

⁴A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965), p. 10.

Noise and Sensitivity

There are two major sources of noise that influence the sensitivity of the susceptometer. The first is fluctuations in the SQUID output that are present when the sample is stationary. These fluctuations are due principally to vibrational motion of various parts of the susceptometer relative to the sensing coils. This causes rapid changes in the superconducting loop current and in the SQUID output that are approximately proportional in magnitude to the applied magnetic field. In terms of the flux quanta at the output of the SQUID, they produce peak-to-peak noise of about $0.1 \phi_0$ per kilogauss of field. This source of noise limits the differential sensitivity of the device to about $\pm 6 \times 10^{-12}$ emu per gauss of applied field.

A second, sometimes more troublesome, source of noise is that generated as the sample moves. This noise is due principally to the rubbing of the sample assembly against the walls of the sample space. Under most conditions, this source of noise is not a problem and does not limit the sensitivity. If rubbing occurs because of misalignment of the sample holder, however, the SQUID electronics will usually only be able to stay locked on the noise below a certain magnetic field.

Another limit to the sensitivity is a tendency of the SQUID signal to drift at magnetic fields of about 20 kilogauss and above. The actual mismatch in the two coils of the sensing circuit is not known, but a one-hundredth-turn mismatch can cause a one ϕ_0 change in the SQUID output for a 70×10^{-6} gauss change in the ambient field. Consequently, any small changes in field will cause a background drift. Background drifts of tens of ϕ_0 per minute at 30 kilogauss are not uncommon. For large sample signals of several thousand

ϕ_0 (typical for tens of micrograms of californium) this is not a problem since the effects of a slight linear background drift are self-compensating. However, for small samples of weakly magnetic materials, the drift can place a practical limit on the maximum applied magnetic field.

CHAPTER III

ELECTRONIC STRUCTURE

Since the magnetic behavior of an atom is a manifestation of its electronic structure, the general features of the electronic energy levels of californium must be understood before its magnetic behavior can be interpreted. A partial knowledge of the energy levels allows interpretations of the magnetic data that can in turn give more detailed information about the electronic structure.

The ground state of neutral californium has the $5f^{10}6d^07s^2$ electronic configuration (showing only the electrons beyond the closed radon core). Californium exists in solids with charge states of +4, +3 and +2 which have the $5f^8$, $5f^9$ and $5f^{10}$ configurations, respectively. In divalent californium, the levels of the $5f^{10}$ configuration span about $110,000\text{ cm}^{-1}$ and are overlapped by levels of the $5f^97s^1$ configuration which start about $20,000\text{ cm}^{-1}$ above the ground state.^{1,2} In the tri- and tetravalent ions, the $5f^{n-1}6d^1$ configuration contributes levels that are closest to the $5f$ ground state, but those levels are more than $50,000\text{ cm}^{-1}$ from the ground state. The general pattern of the lowest energy levels of all three ions can be explained without having to consider any interactions between the different configurations. But to get reasonable agreement between energy level calculations and the results of optical absorption and fluorescence measurements, configuration interactions must to some extent be taken into account.

As noted in Chapter I, the energy levels and wavefunctions of the

¹ $1\text{ cm}^{-1} \leftrightarrow 0.124\text{ meV} \leftrightarrow 1.44\text{ Kelvin}$.

²J. R. Peterson *et al.*, Radiochem. Radioanal. Lett. **31**, 277 (1977).

californium ion in the solid are essentially the same as those of the free ion, because of the limited radial extension of the $5f$ wavefunctions. The effects of the crystalline electric field, applied magnetic fields and magnetic ordering can, therefore, be considered as perturbations to the free ion system. Consequently, the free ion energy levels and wavefunctions must be considered in some detail.

Free Ion Energy Levels

The two interactions that most influence the energy levels of the free ion are the electrostatic interaction between electrons and the magnetic interaction between the spin and angular momenta of the individual electrons (the spin-orbit interaction). If the spin-orbit contribution were small (the Russell-Saunders limit), each energy level could be described in terms of a pure LS state with degenerate J levels that would be split by the spin-orbit interaction. The spin-orbit interaction is, however, a relativistic effect and is consequently large and important for heavy elements. If the spin-orbit interaction were to dominate the electrostatic term, then jj coupled states would be a convenient set of basis states to use. For californium and other actinides, the electron-electron electrostatic and spin-orbit interaction energies are of roughly equal magnitude and must be treated equally. The resulting wavefunctions can be described by linear combinations of either LS states or jj states with the same J value, and are intermediate coupling states. The calculation of the intermediate coupling energy levels and wavefunctions is simply the diagonalization of the energy matrix that includes both the spin-orbit and the electrostatic interaction.

For all the calculations in this work, wavefunctions are described in terms of LS coupled states. Each LS term is designated $|\alpha LS\rangle$, where α is an

additional quantum number that is required because the L and S quantum numbers do not always uniquely specify a term in the f^n configurations. Table III-1 lists all possible LS terms that can be constructed for the f^8 , f^9 and f^{10} configurations. The terms are grouped to show which have common J values.

Electrostatic Interaction

The electrostatic matrix elements are usually formulated as

$$\begin{aligned} \langle \alpha LS | \mathcal{H}_{es} | \alpha' LS \rangle &= \langle \alpha LS | \sum_{i,j} \frac{e^2}{r_{ij}} | \alpha' LS \rangle \\ &= \sum_{\substack{k=2 \\ \text{even}}}^6 f_k F^k. \end{aligned} \quad (\text{III-1})$$

The F^k are direct Slater integrals and involve integrals over the radial dependence of the wavefunctions and are treated as parameters that are derived from experimental optical spectra. The f_k are angular integrations that can be evaluated exactly. No exchange integrals are present since only equivalent electrons are involved. The sum can be terminated at 6 since for terms from f -electron configurations all higher order integrals vanish. The $k=0$ term is an additive constant that can be ignored.

In order to simplify hand calculations involving configurations of f electrons, Racah³ defined the following linear combinations of the Slater integrals:

$$\begin{aligned} E^1 &= \frac{14}{405} F^2 + \frac{7}{297} F^4 + \frac{350}{11583} F^6, \\ E^2 &= \frac{1}{2025} F^2 - \frac{1}{3276} F^4 + \frac{175}{1656369} F^6, \end{aligned}$$

³G. Racah, Phys. Rev. **76**, 1361 (1949).

Table III-1. LS terms of the f^8 , f^9 and f^{10} configurations, grouped by possible J values.

<u>f^8 configuration</u>					
J	Singlets	Triplets	Quintets	Septets	Number of terms
0	$S(4)^a$	$P(6)$	$D(3)$	$F(1)$	14
1	$P(1)$	$P(6), D(5)$	$P(1), D(3), F(2)$	$F(1)$	19
2	$D(6)$	$P(6), D(5), F(9)$	$S(1), P(1), D(3), F(2), G(3)$	$F(1)$	37
3	$F(4)$	$D(5), F(9), G(7)$	$P(1), D(3), F(2), G(3), H(2)$	$F(1)$	37
4	$G(8)$	$F(9), G(7), H(9)$	$D(3), F(2), G(3), H(2), I(2)$	$F(1)$	46
5	$H(4)$	$G(7), H(9), I(6)$	$F(2), G(3), H(2), I(2), K(1)$	$F(1)$	37
6	$I(7)$	$H(9), I(6), K(6)$	$G(3), H(2), I(2), K(1), L(1)$	$F(1)^b$	38
7	$K(3)$	$I(6), K(6), L(3)$	$H(2), I(2), K(1), L(1)$		24
8	$L(4)$	$K(6), L(3), M(3)$	$I(2), K(1), L(1)$		20
9	$M(2)$	$L(3), M(3), N(1)$	$K(1), L(1)$		12
10	$N(2)$	$M(3), N(1), O(1)$	$L(1)$		8
11	$Q(1)$	$N(1), O(1)$			3
12		$O(1)$	Total of 119 terms.		1

<u>f^9 configuration</u>				
J	Doublets	Quartets	Sextets	Number of terms
1/2	$P(4)$	$P(2), D(3)$	$F(1)$	10
3/2	$P(4), D(5)$	$S(1), P(2), D(3), F(4)$	$P(1), F(1)$	21
5/2	$D(5), F(7)$	$P(2), D(3), F(4), G(4)$	$P(1), F(1), H(1)$	28
7/2	$F(7), G(6)$	$D(3), F(4), G(4), H(3)$	$P(1), F(1), H(1)$	30
9/2	$G(6), H(7)$	$F(4), G(4), H(3), I(3)$	$F(1), H(1)$	29
11/2	$H(7), I(5)$	$G(4), H(3), I(3), K(2)$	$F(1), H(1)$	26
13/2	$I(5), K(5)$	$H(3), I(3), K(2), L(1)$	$H(1)$	20
15/2	$K(5), L(3)$	$I(3), K(2), L(1), M(1)$	$H(1)^b$	16
17/2	$L(3), M(2)$	$K(2), L(1), M(1)$		9
19/2	$M(2), N(1)$	$L(1), M(1)$		5
21/2	$N(1), O(1)$	$M(1)$		3
23/2	$O(1)$		Total of 73 terms.	1

Table III-1. (continued)

J	<u>f^{10} configuration</u>			Number of terms
	Singlets	Triplets	Quintets	
0	$S(2)$	$P(3)$	$D(1)$	6
1		$P(3), D(2)$	$D(1), F(1)$	7
2	$D(4)$	$P(3), D(2), F(4)$	$S(1), D(1), F(1), G(1)$	17
3	$F(1)$	$D(2), F(4), G(3)$	$D(1), F(1), G(1)$	13
4	$G(4)$	$F(4), G(3), H(4)$	$D(1), F(1), G(1), I(1)$	19
5	$H(2)$	$G(3), H(4), I(2)$	$F(1), G(1), I(1)$	14
6	$I(3)$	$H(4), I(2), K(2)$	$G(1), I(1)$	13
7	$K(1)$	$I(2), K(2), L(1)$	$I(1)$	7
8	$L(2)$	$I(2), L(1), M(1)$	$I(1)^b$	7
9		$L(1), M(1)$		2
10	$N(1)$	$M(1)$	Total of 47 terms.	2

^aThe number in parenthesis is the number of terms with the same L and S values.

^bHund's rule ground state.

$$E^3 = \frac{1}{135} F^2 + \frac{2}{1089} F^4 - \frac{175}{42471} F^6. \quad (\text{III-2})$$

Although the use of computers has eliminated the need for this set of parameters, they are still frequently used in describing f -electron systems and will be used in this work. In terms of these parameters and the corresponding angular parts,

$$\langle \alpha LS | \mathcal{H}_{es} | \alpha' LS \rangle = \sum_{k=0}^3 e_k E^k. \quad (\text{III-3})$$

Details of the calculation of the e_k are given in Appendix A. The e_k are diagonal in L , S and J but not in α . Carnall *et al.*⁴ have obtained sufficiently detailed and complete optical absorption spectra for CfCl_3 to determine the E^k values for Cf^{3+} . Carnall and Crosswhite⁵ have developed techniques for estimating the E^k parameters for the +2 and +4 species even though no complete optical spectra are available.

Spin-Orbit Interaction

The spin-orbit contribution to the atomic Hamiltonian can be written as

$$\mathcal{H}_{so} = \sum_{i=1}^N \xi(r_i) (\mathbf{s}_i \cdot \mathbf{l}_i), \quad (\text{III-4})$$

where N is the number of electrons and the $\xi(r_i)$ include all radial dependencies. Appendix A gives the details for calculating the matrix elements. The radial dependencies of the matrix elements are expressed in terms of a single parameter ζ , the spin-orbit parameter. The selection rules for the matrix elements are

⁴W. T. Carnall *et al.*, J. Chem. Phys. **58**, 1938 (1973).

⁵W. T. Carnall and H. M. Crosswhite, Argonne National Laboratory Report No. ANL-84-90, 1985 (unpublished), p. 72.

$$|S - S'| \leq 1$$

and $|L - L'| \leq 1$.

Other Interactions

If only the parameters E^k and ζ are used to fit the optical spectra of lanthanides and actinides, the energy levels usually cannot be reproduced to better than several hundred cm^{-1} . Numerous other parameters are typically employed that account for other magnetic interactions within the f^n configuration and interactions with other configurations. Three additional parameters that are frequently used are the α , β and γ two-body parameters. These parameters account for two-body configuration interactions of the forms $\alpha L(L+1)$, $\beta G(G_2)$ and $\gamma G(R_7)$. $G(G_2)$ and $G(R_7)$ are eigenvalues of Casimir operators of the groups G_2 and R_7 ⁶ and have been tabulated by Wybourne.⁷

It should be noted that although the various parameters that are used in the fitting of the optical spectra are assumed to represent a particular interaction, all interactions with that same functional form will determine the final value of that parameter. Many configuration interactions are accounted for by the Slater integrals,⁸ and these fitted parameters may not correspond well with values calculated using Hartree- or Dirac-Fock techniques.

Intermediate Coupling Results

Since all of the contributions to the Hamiltonian for the intermediate coupling calculation are diagonal in J , the matrix of the Hamiltonian can be

⁶B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw Hill, New York, 1963), p. 106.

⁷B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965), p. 73.

⁸K. Rajnak and B. G. Wybourne, *Phys. Rev.* **132**, 280 (1963).

diagonalized by diagonalizing the sub-matrices for each individual value of J separately. The last column of Table III-1 lists the dimensions of these matrices. The largest is 46 by 46. Tables III-2 to III-4 show the results of the intermediate coupling calculations. The energies for all J manifolds within 12,000 cm^{-1} of the ground state are listed along with the major LS components of the wavefunctions. The energy levels are shown schematically in Figure III-1. In Figure I-1, page 4, some of the higher calculated energy levels are compared with the optical absorption spectrum. The Hund's rule ground state term for Cf^{2+} makes up 77 percent of the intermediate coupling ground state wavefunction. The first excited J manifold lies about 8400 cm^{-1} above it. For both Cf^{3+} and Cf^{4+} , the ground state is 69 percent the Hund's rule term while the first excited manifolds are about 6400 and 4700 cm^{-1} , respectively, above the ground manifold.

For Cf^{2+} and Cf^{4+} , the original parametric fits of Carnall *et al.* to the optical spectra and extrapolations from the Cf^{3+} spectrum include additional parameters not included in the present calculations. Consequently, the energy levels calculated here differ slightly from those that are based on the larger set of parameters. The results are sufficiently good, however, to serve as a starting point for additional perturbation calculations.

Crystal Field Splitting

The largest perturbation to the energy levels of a californium ion in a solid is that due to the electric field generated by the other ions in the crystal. The electric field reflects the symmetry of the crystal and the contribution to

Table III-2. Intermediate coupling free ion wavefunctions of $\text{Cf}^{2+} (f^{10})$.

Parameters ^a (cm^{-1})	J	Energy (cm^{-1})		Major LS components
$E^1 = 3997$	8	0		77% 5I , 20% 3K , 1% 1L
$E^2 = 19.13$	5	8458 ^b	(8368) ^c	41% 3G , 34% 5F , 12% 3H , 4% 2H
$E^3 = 350.4$				89% 5I , 9% 3K 1% 3I
$\zeta = 3446$	7	9328	(9271)	
$\alpha = 30.0$	2	10286	(10284)	27% 3D , 25% 3P , 15% 1D , 15% 5S
$\beta = -800$				40% 5I , 33% 3H , 20% 5G , 4% 3I
$\gamma = 1200$	6	11275	(11183)	

^aW. T. Carnall and H. M. Crosswhite, Argonne National Laboratory Report No. ANL-84-90, 1985 (unpublished), p. 78.

^bCalculated using the limited set of parameters in the table.

^cEnergies based on the complete set of parameters of Carnall and Crosswhite, p. 80.

Table III-3. Intermediate coupling free ion wavefunctions of $\text{Cf}^{3+} (f^9)$.

Parameters ^a (cm^{-1})	J	Energy (cm^{-1})	Major LS components
$E^1 = 4173$	15/2	0	69% 6H , 24% 4I , 4% 2K , 1% 4K
$E^2 = 19.84$	11/2	6422	45% 6F , 30% 4G , 13% 6H , 6% 2H
$E^3 = 391.4$	9/2	6437	40% 4F , 30% 6F , 14% 4G , 9% 2G
$\zeta = 3602$	13/2	8063	83% 6H , 13% 4I , 3% 4H , 1% 4K
$\alpha = 35.37$	3/2	11445	32% 4D , 21% 6F , 19% 2P , 11% 2D
$\beta = -748.0$	11/2	11456	43% 6H , 33% 6F , 14% 4G , 5% 4H
$\gamma = 1200$			

^aW. T. Carnall *et al.*, J. Chem. Phys. **58**, 1938 (1973).

Table III-4. Intermediate coupling free ion wavefunctions of $\text{Cf}^{4+} (f^8)$.

Parameters ^a (cm^{-1})	J	Energy (cm^{-1})		Major LS components
$E^1 = 4327$	6	0		69% 7F , 24% 5G , 5% 3H , 1% 5H
$E^2 = 17.59$	4	4904 ^b	(4680) ^c	44% 7F , 27% 5D , 10% 5F , 9% 3F
$E^3 = 399.2$	5	6039	(6100)	79% 7F , 13% 5G , 5% 5F , 1% 3H
$\zeta = 3765$	2	8942	(8600)	52% 7F , 24% 5D , 10% 3P , 6% 5F
$\alpha = 30.12$	3	8982	(8920)	66% 7F , 19% 5D , 9% 5F , 3% 5G
$\beta = -660$	1	11248	(11040)	67% 7F , 25% 5D , 4% 3P , 3% 5F
$\gamma = 1200$	0	11427	(11170)	64% 7F , 26% 5D , 7% 3P , 2% 1S

^aW. T. Carnall and H. M. Crosswhite, Argonne National Laboratory Report No. ANL-84-90, 1985 (unpublished), p. 94.

^bCalculated using the limited set of parameters in the table.

^cEnergies based on the complete set of parameters of Carnall and Crosswhite, p. 95.

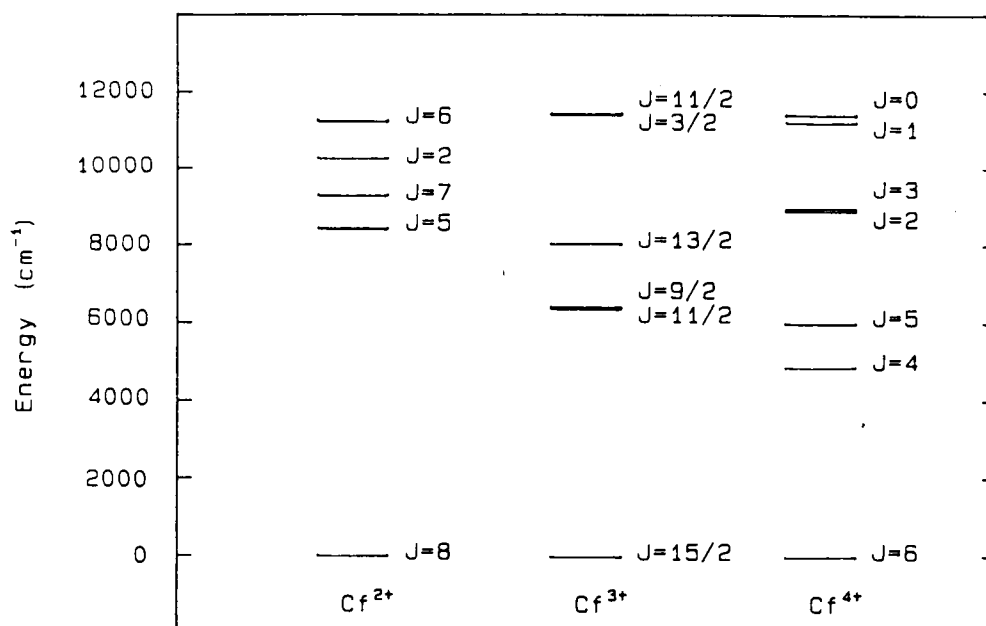


Figure III-1. Free ion energies of the J manifolds of californium below $12,000 \text{ cm}^{-1}$.

the Hamiltonian can be written as an expansion in spherical harmonics,⁹

$$\mathcal{H}_{\text{cf}} = \sum_{\substack{k=2 \\ \text{even}}}^6 \sum_{q=-k}^k (B_q^k)^* \left[\frac{4\pi}{2k+1} \right]^{\frac{1}{2}} Y_k^q(\theta, \phi). \quad (\text{III-5})$$

In this formulation, many-body effects are ignored and the individual f electrons are assumed to interact independently with the crystal field. The B_q^k encompass all radial dependencies and are treated as parameters. The B_q^k can be complex and have the property $(B_q^k)^* = (-1)^q B_{-q}^k$. The summation is limited to terms having non-vanishing matrix elements between LS states from the same f -electron configuration. Only even values of k less than or equal to six are needed. The strengths of the crystal field in substances having

⁹C. A. Morrison, Harry Diamond Laboratories Report No. HDL-SR-87-1, 1987 (unpublished), p. 81.

different crystal symmetries can be compared using Auzel's¹⁰ scalar crystal field parameter,

$$N_v = \left[\sum_{k,q} \frac{4\pi}{2k+1} |B_q^k|^2 \right]^{\frac{1}{2}}. \quad (\text{III-6})$$

In general, the crystal field parameters of order k , B_q^k , are proportional to $\langle r^k \rangle$, the average value of the k^{th} power of the radial extension of the f electrons. In Table III-5, the values of $\langle r^k \rangle$ for Cf^{3+} are compared with those of two trivalent lanthanide ions, praseodymium and dysprosium (californium's isoelectronic homologue).

Table III-5. Expectation values of r^k for the f electrons of Pr^{3+} , Dy^{3+} and Cf^{3+} .

	$\langle r^2 \rangle$ (in units of the Bohr radius)	$\langle r^4 \rangle$	$\langle r^6 \rangle$	Reference
Pr^{3+}	1.09	2.82	15.73	a
Dy^{3+}	0.73	1.32	5.10	a
Cf^{3+}	1.52	4.59	25.35	b

^aA. J. Freeman and R. E. Watson, *Phys. Rev.* **127**, 2058 (1962).

^bJ. P. Desclaux and A. J. Freeman, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1984), Vol. 1, p. 26.

The use of equation III-5 has proven very useful in the parameterization of crystal field measurements in the actinides and the lanthanides. The development of physical models that can be used to predict the crystal field

¹⁰F. Auzel and O. L. Malta, *J. Phys. (Paris)* **44**, 201 (1983).

parameters has, however, been somewhat less successful. The simplest model for the crystal field is the point charge model, in which the ions surrounding the ion of interest are considered as point charges. This model has been helpful in the interpretation of some lanthanide and actinide compounds, but in general is not useful in its simplest form. Other models that include higher-order electric multipoles of the ions and considerations of covalency have been more successful in providing an *ab initio* means of calculating crystal field parameters.^{11,12}

Appendix A gives details on evaluating the matrix elements of the crystal field interaction using tensor operator techniques. The selection rules for evaluating matrix elements of the form $\langle \alpha LS, JM | Y_q^k | \alpha' L' S', J' M' \rangle$ are

$$\begin{aligned} |S - S'| &= 0, \\ |L - L'| &\leq k, \\ |J - J'| &\leq k \\ \text{and } |M - M'| &= q. \end{aligned}$$

Unlike the other terms of the Hamiltonian that have been considered so far, the crystal field matrix elements are not diagonal in J and M . Therefore, when a crystal field is present, excited states with different J values may interact with the ground state and mix other J values into the ground state wavefunction. The importance of J mixing in californium will be discussed later in this chapter.

The number and degeneracies of the crystal field split levels for a particular J manifold in a crystal field with a particular symmetry are uniquely determined by group theoretical considerations. The number of possible levels

¹¹D. J. Newman, J. Phys. C 10, 4753 (1977).

¹²M. Faucher and D. Garcia, J. Less-Common Met. 111, 207 (1985).

into which the ground state manifolds of the three californium ions can be split are listed in Table III-6. Cf^{3+} has an odd number of electrons (half-integral J value) and is split no further than Kramer's doublets. The other two charge states have integral J values and can be split into singlets. The order of the levels and their spacing will depend upon the values of the B_q^k crystal field parameters. They are determined for a particular set of parameters by diagonalizing the matrix constructed from the matrix elements of the crystal field interaction within the set of intermediate coupling free ion states. If the set of states is truncated to include only those of the ground state manifold, a first order perturbation calculation results and no J mixing occurs.

Table III-6. Crystal field splitting of the ground state of californium ions.

	Crystal field symmetry				
	Cubic	Hexagonal	Tetragonal	Lower symmetry	
Cf^{2+} ($J=8$)	1 ^a 2 4	5 6	9 4	17	singlets ^b doublets ^c triplets
Cf^{3+} ($J=15/2$)	2 3	8	8	8	doublets quartets
Cf^{4+} ($J=6$)	2 1 3	5 4	7 3	13	singlets ^b doublets ^c triplets

^aNumber of levels.

^bNon-magnetic levels.

^cNon-magnetic in a cubic crystal field.

If the magnitude of the crystal field interaction is large enough so that a first order calculation is unsatisfactory, then more J manifolds must be included in the calculation. In practice, the set of states must still be truncated to keep matrix sizes manageable. If all J manifolds are included in the matrix, for the f^2 configuration the matrix is a manageable 92 by 92, but for f^9 it is 2002 by 2002.

Cubic and Hexagonal Symmetries

The simplest symmetry that can occur is cubic symmetry. Of the californium compounds measured in this work, CfO_2 , BaCfO_3 and the californium pnictides all have cubic crystal structures and have cubic symmetry at the californium sites. The non-zero crystal field parameters for cubic symmetry are B_0^4 , B_4^4 , B_0^6 , and B_4^6 . But since the following relations hold,

$$\begin{aligned} B_4^4 &= \left[\frac{5}{14} \right]^{\frac{1}{2}} B_0^6 \\ \text{and } B_4^6 &= -\left[\frac{7}{2} \right]^{\frac{1}{2}} B_0^6, \end{aligned} \quad (\text{III-7})$$

there are only two independent parameters required to specify any crystal field with cubic symmetry. Lea *et al.*¹³ have summarized the information on the splitting of energy levels in f -electron systems by a cubic field (without J mixing) in a very useful tabular and graphical form.

Table III-7 lists the wavefunctions of the crystal field split ground states of californium if J mixing is neglected. Each level is labeled by its group representation using Bethe's Γ notation.¹⁴ The wavefunctions with non-constant coefficients vary with the ratio of B_0^6 to B_4^4 . The others are

¹³Lea *et al.*, J. Phys. Chem. Solids **23**, 1381 (1962).

¹⁴H. A. Bethe, Ann. Phys. **3**, 133 (1929).

Table III-7. Splitting of the ground state manifold of Cf^{2+} , Cf^{3+} and Cf^{4+} in a cubic crystal field with no J mixing.^a

Representation ^b		Wavefunctions
Cf^{2+} ($J=8$)	Γ_1	$.411 8\rangle + .270 4\rangle + .718 0\rangle + .270 -4\rangle + .411 -8\rangle$
	$\Gamma_3(2)^c$	$a_1 8\rangle + a_2 4\rangle + a_3 0\rangle + a_2 -4\rangle + a_1 -8\rangle$ $b_1 6\rangle + b_2 2\rangle + b_2 -2\rangle + b_1 -6\rangle$
	$\Gamma_4(2)$	$a_1 \pm 7\rangle + a_2 \pm 3\rangle + a_3 \mp 1\rangle + a_4 \mp 5\rangle$ $b_1 8\rangle + b_2 4\rangle + b_3 0\rangle - b_2 -4\rangle - b_1 -8\rangle$
	$\Gamma_5(2)$	$a_1 \pm 7\rangle + a_2 \pm 3\rangle + a_3 \mp 1\rangle + a_4 \mp 5\rangle$ $b_1 6\rangle + b_2 2\rangle - b_2 -2\rangle - b_1 -6\rangle$
Cf^{3+} ($J=15/2$)	Γ_6	$.582 \pm 15/2\rangle + .331 \pm 7/2\rangle + .718 \mp 1/2\rangle + .191 \mp 9/2\rangle$
	Γ_7	$.633 \pm 13/2\rangle + .582 \pm 5/2\rangle - .451 \mp 3/2\rangle - .239 \mp 11/2\rangle$
	$\Gamma_8(3)$	$a_1 \pm 15/2\rangle + a_2 \pm 7/2\rangle + a_3 \mp 1/2\rangle + a_4 \mp 9/2\rangle$ $b_1 \pm 13/2\rangle + b_2 \pm 5/2\rangle + b_3 \mp 3/2\rangle + b_4 \mp 11/2\rangle$
Cf^{4+} ($J=6$)	Γ_1	$-.661 4\rangle + .354 0\rangle - .661 -4\rangle$
	Γ_2	$-.395 6\rangle + .586 2\rangle + .586 -2\rangle - .395 -6\rangle$
	Γ_3	$.586 6\rangle + .395 2\rangle + .395 -2\rangle + .586 -6\rangle$ $.250 4\rangle + .935 0\rangle + .250 -4\rangle$
	Γ_4	$.685 \pm 3\rangle - .433 \mp 1\rangle + .586 \mp 5\rangle$ $-.707 4\rangle + .000 0\rangle + .707 -4\rangle$
	$\Gamma_5(2)$	$a_1 \pm 3\rangle + a_2 \mp 1\rangle + a_3 \mp 5\rangle$ $b_1 6\rangle + b_2 2\rangle - b_2 -2\rangle - b_1 -6\rangle$

^aLea *et al.*, J. Phys. Chem. Solids **23**, 1381 (1962).

^bBethe's notation.

^cThe number in parenthesis is the number of times the representation is present in the manifold.

independent of that ratio. If J mixing is included, the resulting wavefunctions will be mixtures of wavefunctions with the same symmetries (having the same Γ designations) from the mixing manifolds.

Several of the californium materials studied in this work have hexagonal symmetry at some or all of the californium sites (the dhcp metal, bcc Cf_2O_3 , and hexagonal CfCl_3). Four independent crystal field parameters are required for the most symmetric hexagonal crystal fields: B_0^2 , B_0^4 , B_0^6 and B_6^6 . The wavefunctions of the ground state manifold of Cf^{3+} when split by this type of hexagonal crystal field are listed in Table III-8. Less symmetric hexagonal symmetries also occur that require the parameters above plus B_4^3 and B_6^3 .

Table III-8. Splitting of the ground state manifold of Cf^{3+} ($J = 15/2$) in an hexagonal crystal field with no J mixing.

Representation ^a	Wavefunctions (Kramer's doublets)	Number of times present in manifold
Γ_7	$a_1 \pm 13/2\rangle + a_2 \pm 1/2\rangle + a_3 \mp 11/2\rangle$	3
Γ_8	$b_1 \pm 7/2\rangle + b_2 \mp 5/2\rangle$	2
Γ_9	$c_1 \pm 15/2\rangle + c_2 \pm 3/2\rangle + c_3 \mp 9/2\rangle$	3

^aBethe's notation.

Importance of J Mixing

Lam and Chan¹⁵ have demonstrated the importance of including J mixing for crystal field calculations involving the f -electron configurations up to f^6 ,

¹⁵S.-K. Chan and D. J. Lam, in *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic Press, New York, 1974), Vol. I, p. 22.

and have suggested using all J manifolds within $12,000 \text{ cm}^{-1}$ (1.5 eV) of the ground state. The results of crystal field calculations for the $2+$, $3+$ and $4+$ charge states of californium indicate that $12,000 \text{ cm}^{-1}$ is also an appropriate truncation point for the $5f^8$, $5f^9$ and $5f^{10}$ configurations. Figures III-2 to III-4 show how the splitting of the ground state in a cubic field for the three configurations depends upon the ratio of B_6^0 to B_4^0 and the magnitude of B_4^0 . The curves show the splitting with J mixing of manifolds up to $12,000 \text{ cm}^{-1}$ included. Without J mixing, the level splitting increases linearly with the strength of B_4^0 for a fixed B_6^0 to B_4^0 ratio. The linear extrapolation of the curves without J mixing are marked and labeled at the edges of each graph. As would be expected, Cf^{2+} is least affected by J mixing since its first excited manifold is higher than that for Cf^{3+} or Cf^{4+} . In all cases, the effect of J mixing is smallest when the ratio of B_6^0 to B_4^0 is small or when the magnitude of the crystal field is small. Of significant importance is the fact that the inclusion of J mixing in the perturbation calculation can lead to the prediction of a different order of energy levels and sometimes a different ground state than that predicted without J mixing.

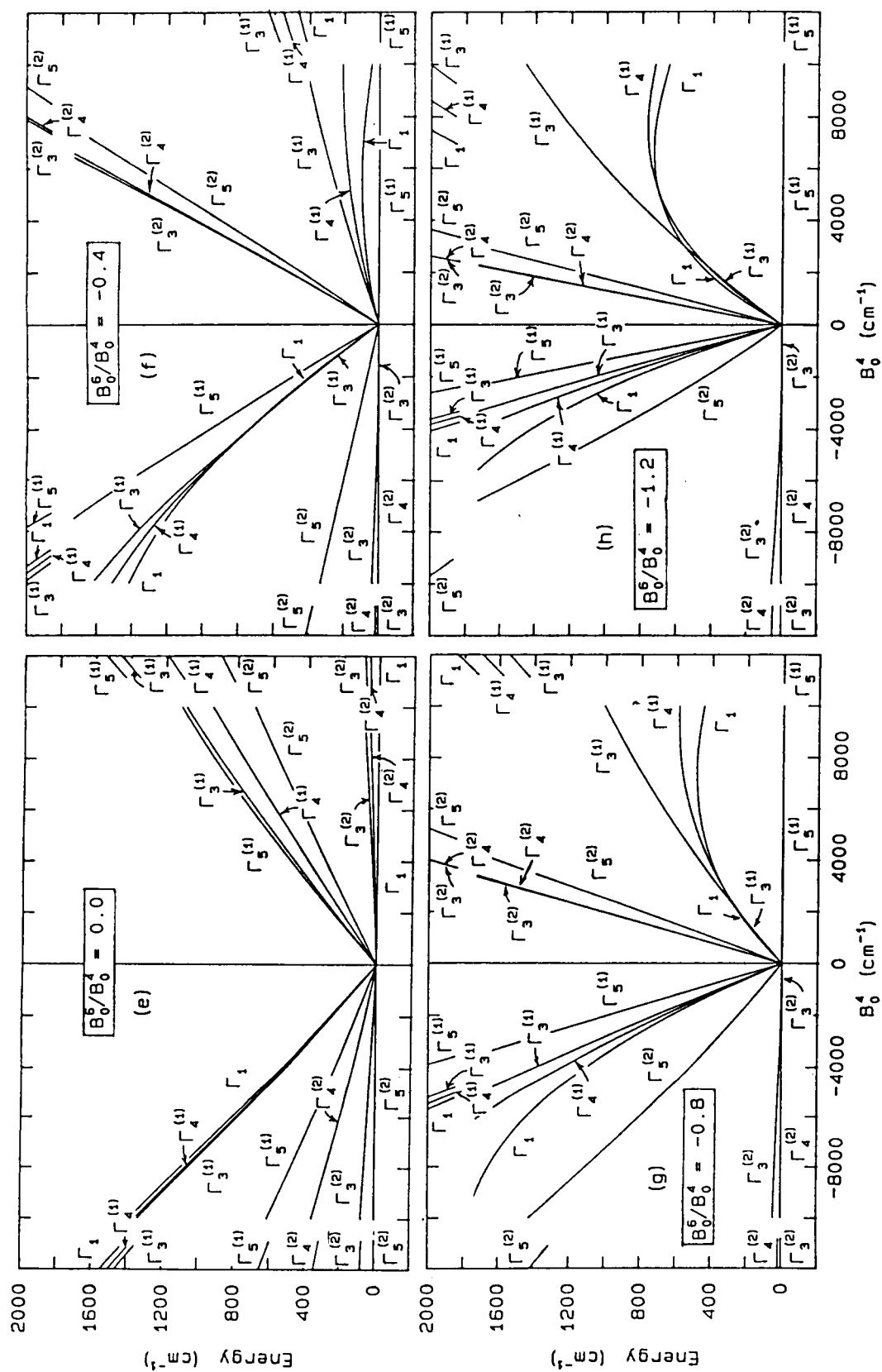


Figure III-2. (continued)

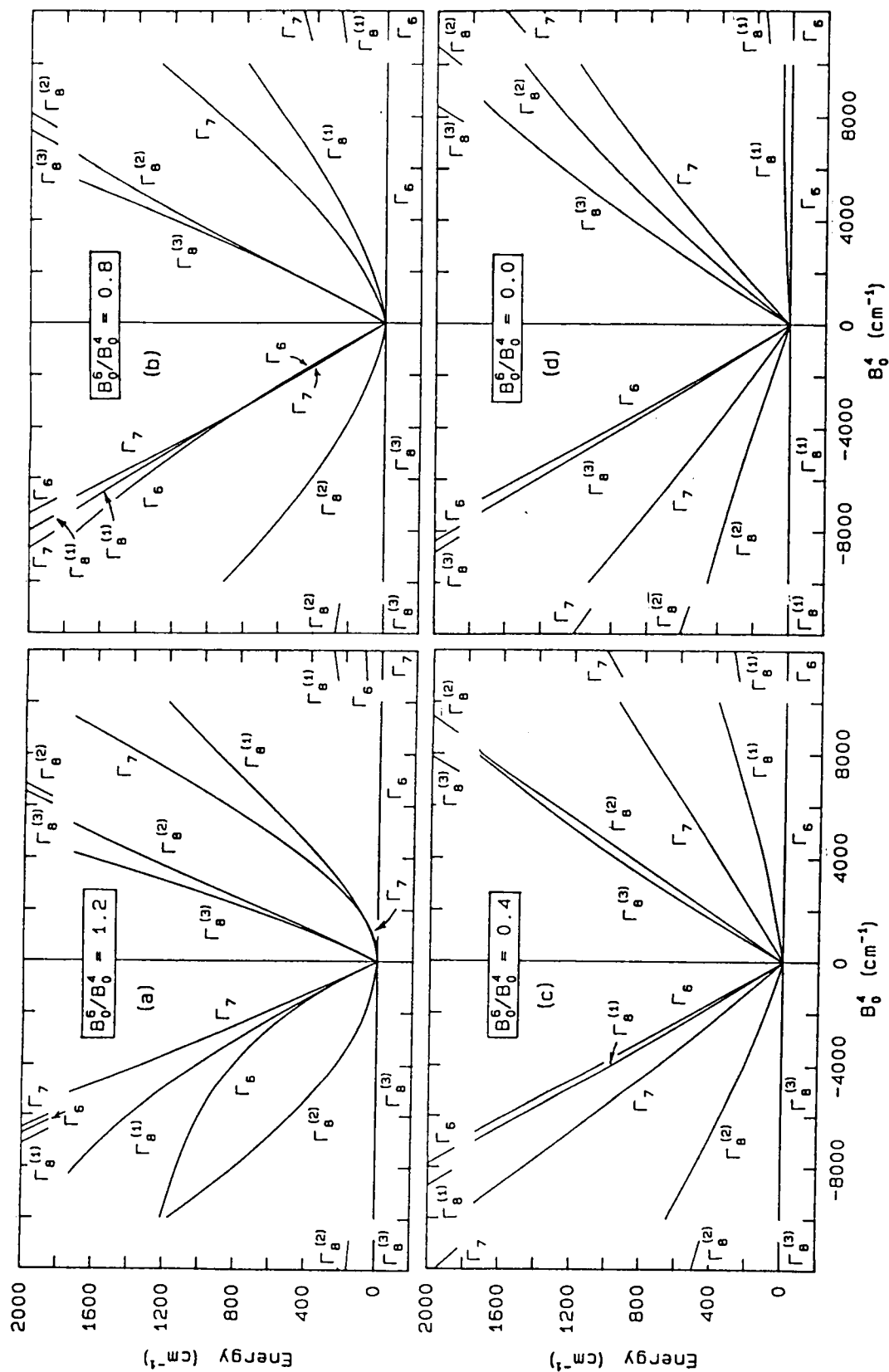


Figure III-3. Splitting of the ground state manifold of Cf^{3+} in a cubic crystal field.

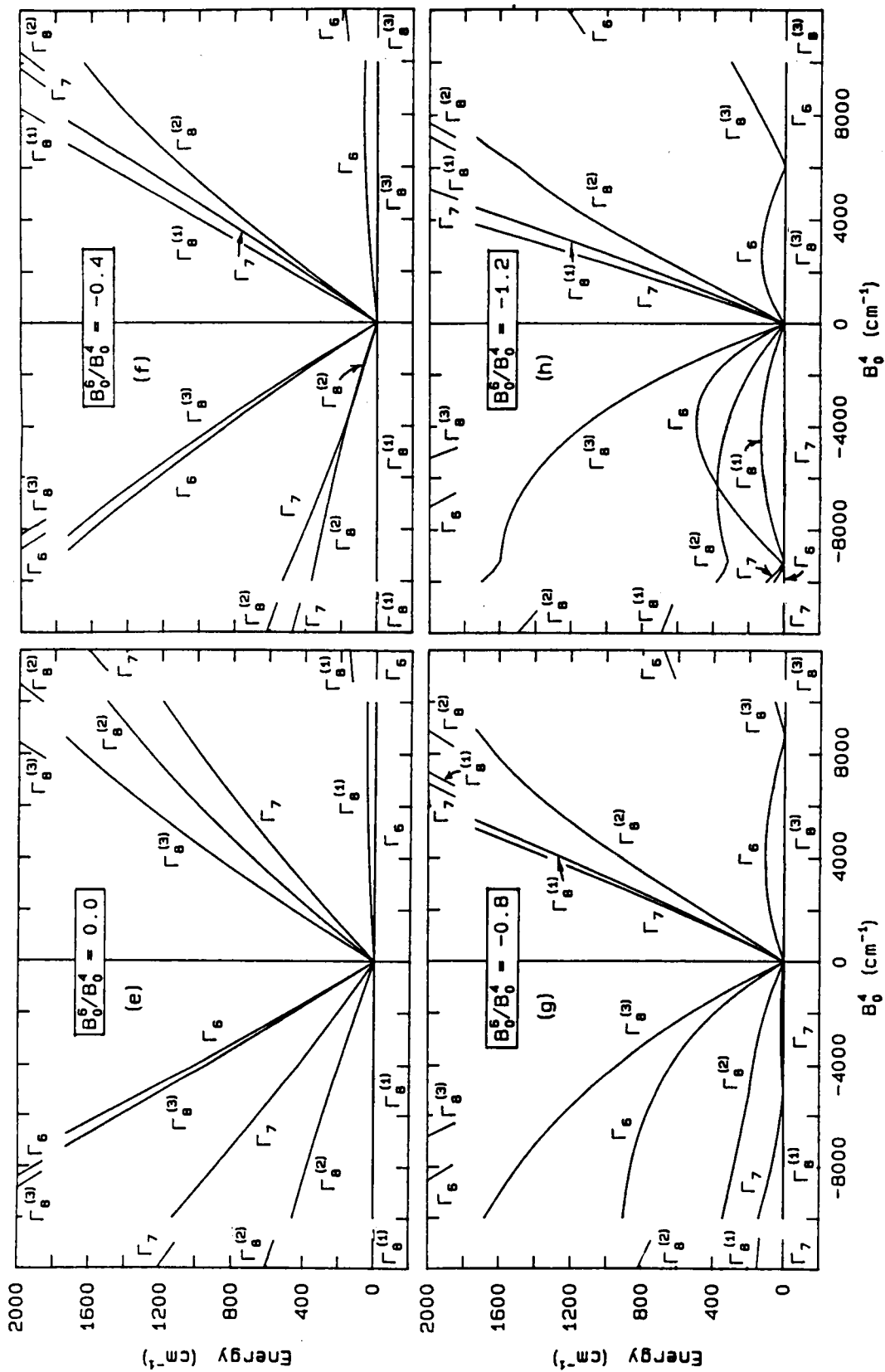


Figure III-3. (continued)

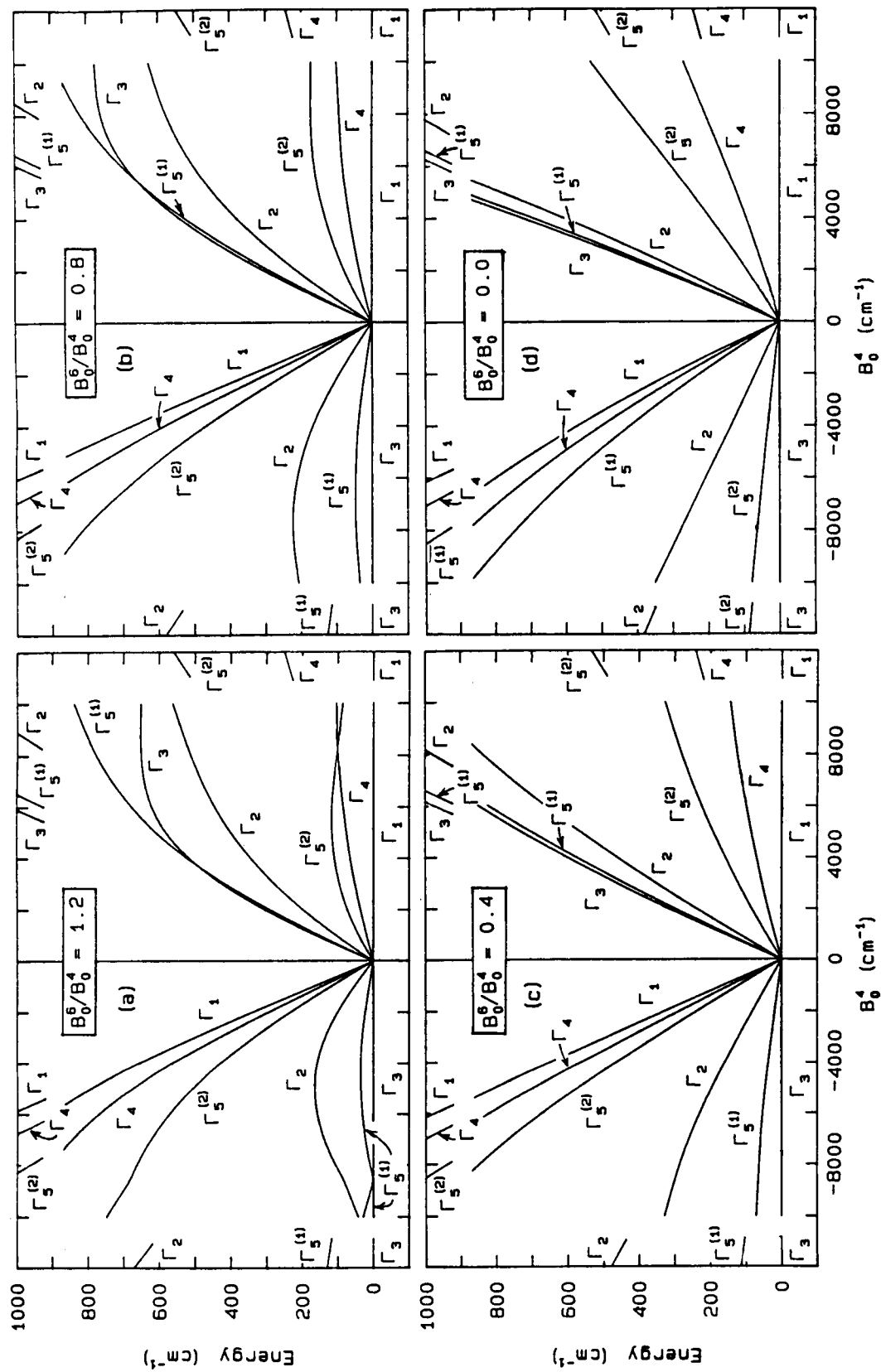


Figure III-4. Splitting of the ground state manifold of Cf^{4+} in a cubic crystal field.

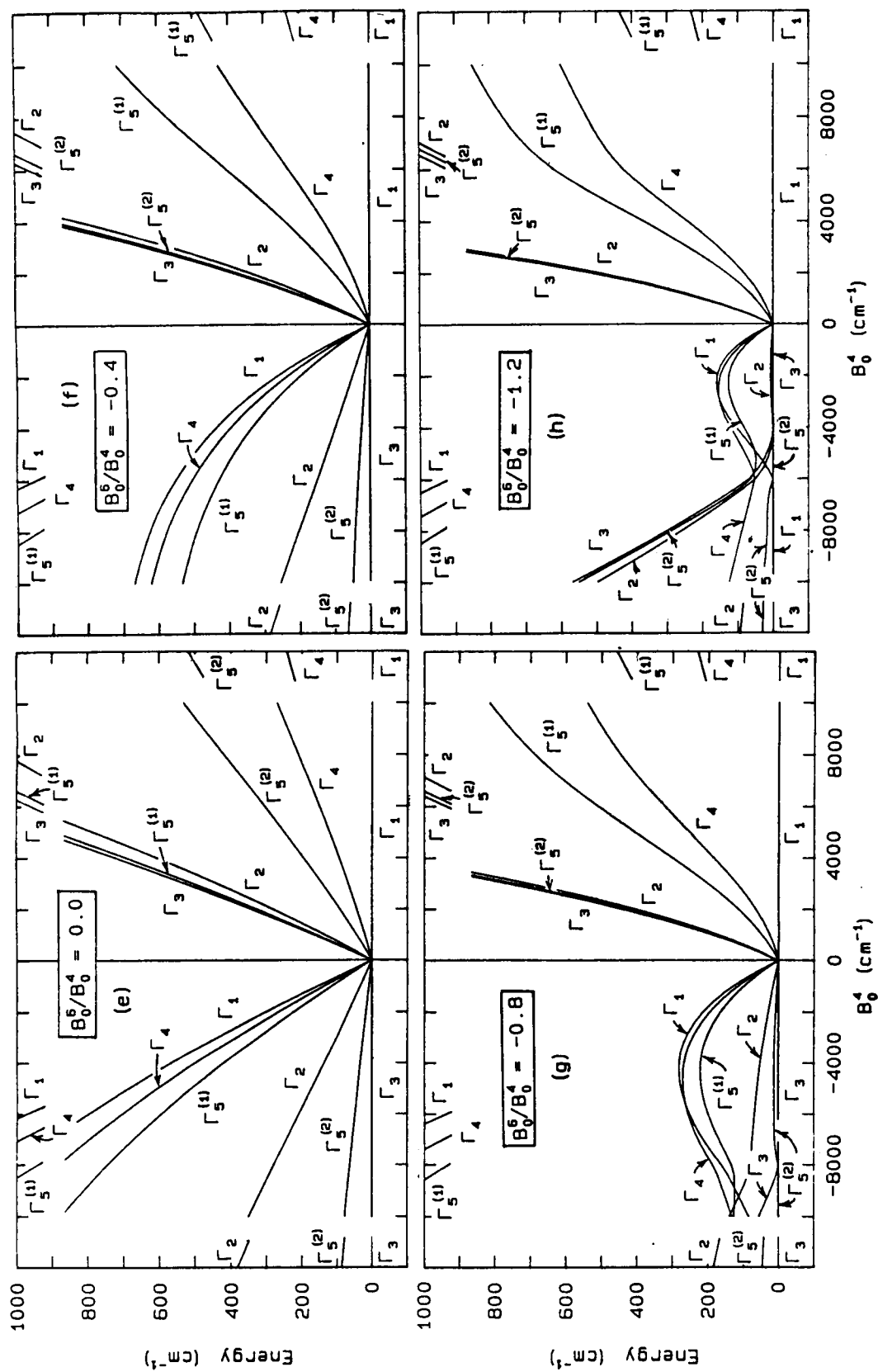


Figure III-4. (continued)

Magnetic Susceptibility

The final step in making the connection between electronic structure and magnetic properties is the calculation of the magnetic susceptibility from the electron energy levels. This is done using the Van Vleck equation,¹⁶

$$\chi_M(T) = \frac{N_A \mu_B^2}{Z} \left\{ \sum_{\Gamma} e^{-E/k_B T} \left[\frac{1}{k_B T} \sum_{\Gamma'}' |\langle \Gamma | \mu | \Gamma' \rangle|^2 - 2 \sum_{\Gamma''}'' \left| \frac{\langle \Gamma | \mu | \Gamma'' \rangle \langle \Gamma'' | \mu | \Gamma' \rangle}{E - E''} \right|^2 \right] \right\}, \quad (\text{III-8})$$

where χ_M is the molar susceptibility, E and E' are the energies of the states Γ and Γ' and Z is the partition function ($\sum_{\Gamma} e^{-E/k_B T}$). The primed sum is over states that are the same or degenerate with Γ and the double-primed sum is over all other states. For californium, all levels except those of the crystal field split ground state can be ignored at the temperatures considered in this work (below $350 \text{ K} \approx 250 \text{ cm}^{-1} \approx 0.03 \text{ eV}$). The $\langle \Gamma | \mu | \Gamma' \rangle$ are matrix elements of μ_x , μ_y or μ_z , and details of their calculation are given in Appendix A.

In a crystal with cubic symmetry, the susceptibility is isotropic and $\chi(T)$ is calculated from the matrix elements of either μ_x or μ_z . In a crystal with axial symmetry (such as hexagonal or tetragonal), the susceptibility when the magnetic field is parallel to the symmetry axis, $\chi_{\parallel}$, is calculated from the matrix elements of μ_z . The perpendicular susceptibility, $\chi_{\perp}$, is calculated from the matrix elements of μ_x . For a polycrystalline sample with axial symmetry and a uniform distribution of all crystal orientations, the average susceptibility

¹⁶Chan and Lam, p. 29.

is

$$\chi_P = \frac{1}{3} \chi_{||} + \frac{2}{3} \chi_{\perp}. \quad (\text{III-9})$$

For a single-crystal sample with axial symmetry and with the magnetic field applied at an angle θ from the crystal symmetry axis, the susceptibility is

$$\chi_{\theta} = \cos^2 \theta \chi_{||} + \sin^2 \theta \chi_{\perp}. \quad (\text{III-10})$$

Effective Paramagnetic Moment: Full Manifold

If only the ground state manifold of a free ion is populated, then the Van Vleck equation simplifies to a form that directly shows the Curie behavior,

$$\begin{aligned} \chi_M(T) &= \frac{N_A \mu_{\text{eff}}^2}{3k_B T}, \\ \text{with } \mu_{\text{eff}} &= [J(J+1)]^{\frac{1}{2}} g_J \mu_B \\ \text{and } g_J^2 &= \sum_{L,S} \left[1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right]^2 A_{LS}. \end{aligned} \quad (\text{III-11})$$

μ_{eff} is the effective paramagnetic moment and g_J is the intermediate coupling averaged Landé g -factor. The A_{LS} 's are the coefficients of the various LS terms in the intermediate coupling wavefunctions. If the effects of crystal field splitting and/or magnetic interactions are included, then the susceptibility of many substances can frequently be described in terms of the Curie-Weiss law,

$$\chi_M(T) = \frac{N_A \mu_{\text{eff}}^2}{3k_B (T - \theta_P)}. \quad (\text{III-12})$$

The Curie-Weiss behavior is parameterized by the effective paramagnetic moment and the Weiss constant, θ_P .

The effective paramagnetic moment is easily determined experimentally from the susceptibility of a material having Curie-Weiss behavior over some

temperature range. The effective paramagnetic moments of the three californium ionic species calculated using both the Russell-Saunders and intermediate coupling models are listed in Table III-9. The effective paramagnetic moments of some other actinides are displayed in Figure III-5.

Effective Paramagnetic Moment: Crystal Field Split States

If only the lowest level of a crystal field split manifold is populated then the value of the effective moment at that temperature will depend only on the symmetry of that level. In a cubic crystal field:

- Singlets and doublets from configurations with integral J are non-magnetic. The susceptibility is temperature-independent at low temperatures.

- Kramer's doublets from configurations with half-integral J values and with components $|+\rangle$ and $|-\rangle$ have an effective moment

$$\mu_{\text{eff}} = \sqrt{3} g_J \mu_B |\langle + | J_z | + \rangle|. \quad (\text{III-13})$$

- Triplets with components $|+\rangle$, $|-\rangle$ and $|0\rangle$ have an effective moment

$$\mu_{\text{eff}} = \sqrt{2} g_J \mu_B |\langle + | J_z | + \rangle|. \quad (\text{III-14})$$

- Quartets with components $|\pm r\rangle$ and $|\pm s\rangle$ have an effective moment

$$\mu_{\text{eff}} = \sqrt{2/3} g_J \mu_B \left\{ |\langle +r | J_z | +r \rangle|^2 + |\langle +s | J_z | +s \rangle|^2 \right\}^{\frac{1}{2}}. \quad (\text{III-15})$$

Magnetic Ordering Effects

The influence of exchange on paramagnetic behavior above magnetic ordering temperatures can be developed using the mean field approximation.¹⁷ If the magnetization of the material, M , is assumed to generate an additional

¹⁷B. Bleaney, Proc. Roy. Soc. (London) **A276**, 19 (1963).

Table III-9. Effective paramagnetic moments of californium ions.

	Russell-Saunders coupling	(μ_B)	Intermediate coupling ^a
Cf ²⁺	10.61		10.34
Cf ³⁺	10.65		10.25
Cf ⁴⁺	9.72		9.30

^aBased on the wavefunctions listed in Tables III-2 to III-4 (pages 37 and 38).

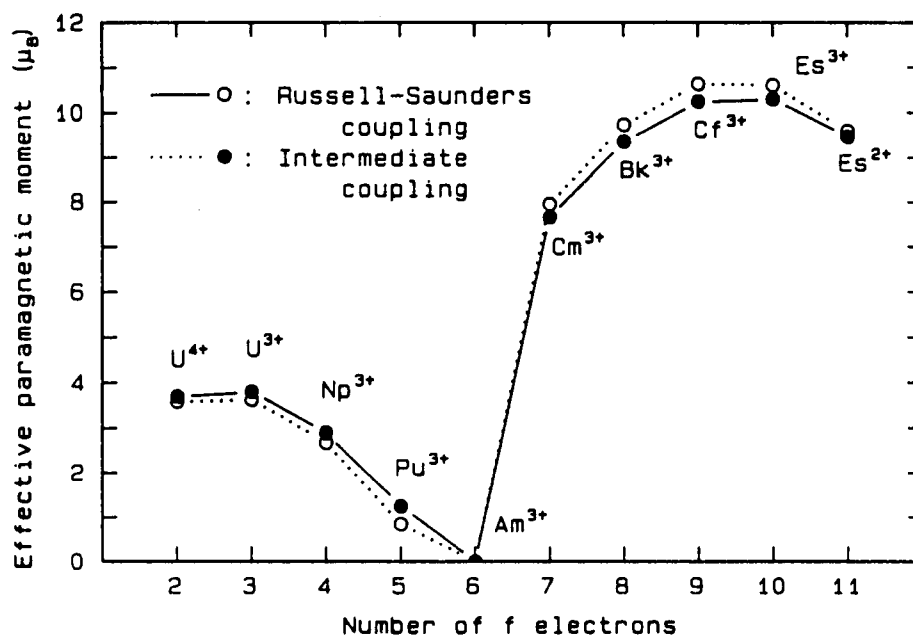


Figure III-5. Effective paramagnetic moments of some actinide ions.

internal magnetic field λM , then the effective field in the material is $H_a + \lambda M$, where H_a is the applied field. If χ_{VV} is the susceptibility determined from equation III-8, and χ_{obs} is the observed susceptibility, then

$$\frac{1}{\chi_{obs}} = \frac{1}{\chi_{VV}} - \lambda \quad (\text{III-16})$$

and the effect of the exchange is to shift the inverse susceptibility curve by an amount λ . If χ_{VV} is of the form C/T , then

$$\chi_{obs} = \frac{C}{T - \lambda C}, \quad (\text{III-17})$$

which is the Curie-Weiss relationship. All of the substances studied in this work exhibit Curie-Weiss behavior over some temperature range, with the value of θ_p depending upon both the crystal field splitting and exchange.

Diamagnetic Susceptibility

The diamagnetic susceptibility is calculated from

$$\chi_D = -\frac{Ze^2 N_A}{6mc^2} \langle r^2 \rangle, \quad (\text{III-18})$$

where Z is the atomic number and $\langle r^2 \rangle$ is the average of r^2 for all electrons. If relativistic Dirac-Fock wavefunctions of neutral californium¹⁸ are used, then $Z\langle r^2 \rangle = 52(a_0)^2$, where a_0 is the Bohr radius, and $\chi_D = 35 \times 10^{-6}$ emu/mol. This is an upper limit on the estimate since the Cf^{3+} wavefunctions have somewhat smaller $\langle r^2 \rangle$ values than the neutral Cf wavefunctions. The smallest susceptibility measured for any of the californium materials studied in this work is about 0.02 emu/mol, so that the diamagnetic contribution to the susceptibility is at most about 0.2 percent. That percentage is less than one-third of the uncertainty in the calibration of the susceptometer and the

¹⁸J. P. Desclaux, Atomic Data and Nucl. Tables 12, 350 (1973).

diamagnetic contribution to the susceptibility has therefore been ignored for all measurements in this work.

CHAPTER IV

CALIFORNIUM METAL

The magnetic properties of the metals of the rare earths have been studied in great detail, and a variety of types of collective magnetic behavior has been observed: ferromagnetism, antiferromagnetism and ordering with helical and other complicated structures. The actinide metals might be expected to exhibit similar behavior, but none of the actinide metals lighter than curium has been observed to order magnetically. This behavior in the actinides through plutonium has been explained by assuming an itinerant nature for the $5f$ electrons.¹ Americium, the next actinide after plutonium, has a $J=0$ ground state that would not be expected to have a local moment. Curium and berkelium, however, do order magnetically, supporting the assumption that the transplutonium actinides have relatively localized f electrons, and that the metals will behave magnetically in a manner similar to the lanthanides. Consequently, californium metal would be expected to exhibit cooperative magnetic behavior, and the magnetic measurements show this to be the case.

Crystallography of the Metal

Californium metal has been determined to crystallize in a number of different crystal structures² (see Appendix B, Table B-1, page 146). The room temperature, normal pressure form has the double hexagonal close-

¹J.-M. Fournier and L. Manes, in *Actinides - Chemistry and Physical Properties*, edited by L. Manes (Springer-Verlag, Berlin, 1985), p. 24.

²R. G. Haire and L. B. Asprey, *Inorg. Nucl. Chem. Lett.* **12**, 73 (1976).

packed structure in which the californium is assumed to be in the trivalent state, *i.e.*, giving up three electrons to the conduction band. Its lattice parameters and atomic volume continue the trend established by the trivalent dhcp Am, Cm and Bk metals. Under pressure, the dhcp californium metal can be converted to a face-centered cubic structure with approximately the same Cf-Cf spacing.³ Theoretical considerations indicate that californium is close to the boundary of a trivalent-divalent transition in the actinide metals and should therefore show some tendencies toward divalency.⁴ The lattice parameters of the divalent metal would be larger than those of the trivalent metal. Dhcp and fcc forms of californium metal have been prepared that have lattice parameters that are about 15 percent larger than the lattice parameters of the trivalent forms. These expanded forms have been interpreted as the divalent metal. All of the californium metal samples that were studied in this work have the dhcp structure and are presumed to be trivalent.

Experimental Details

The californium metal measurements were the first actinide measurements performed in the susceptometer, and a number of refinements to the device that are described in Chapter II had not yet been incorporated. Most of the temperature measurements were made using only the silicon diode temperature sensor. Since silicon diode sensors are extremely sensitive to strong magnetic fields at temperatures below about 30 K, there is considerable uncertainty in the temperature measurements in that range. Those

³R. G. Haire *et al.*, *Physica* **144B**, 19 (1986).

⁴B. Johansson *et al.*, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 248.

temperatures are well below the magnetic ordering temperature of the metal, however, and the uncertainties in temperature do not significantly affect any of the results. The initial measurements also did not account for temperature gradients between the sample and the temperature sensors. Subsequent to the initial measurements, a copper-constantan thermocouple was installed at the top of the sample holder. This arrangement remedied the temperature gradient problems, but the low sensitivity of the thermocouple at temperatures below 10 K (about 2 microvolts per degree Kelvin) limited the accuracy of the temperature measurements in that range.

Another difference in the operation of the susceptometer for these measurements is the manner in which the sample holders were supported. Instead of hanging by the instrument wires, the sample holders were rigidly attached to a 6 mm O.D. stainless steel tube that extended all the way from the upper vacuum feedthrough down to the sample region. The rigid tube arrangement was quite susceptible to the generation of noise by the rubbing of the sample against the walls of the sample region. The signals generated by the metal samples were, fortunately, sufficiently large to dominate effects due to noise.

The metal samples were measured in a holder that was similar to that shown in Figure II-9, page 21, except that the outer tube was made of gold instead of sapphire. Gold provides an excellent thermal connection between the sample and the temperature sensors, but it generates more Johnson noise than does sapphire. The large signals of the californium metal samples also minimized the Johnson noise problem.

The masses of the californium metal samples and of all the other samples studied in this work were determined using a γ -ray counting method. Californium-249 has a readily identifiable γ -ray peak at 388 keV that is emitted in

about 80 percent of all ^{249}Cf decays. The sample masses were determined by comparing the 388 keV γ -ray count rate of the samples with the count rate of a thin weighed piece of californium metal. The γ -counting was done after the samples had been sealed in their quartz capillaries. Comparisons of the unknown samples with weighed samples of both smaller and larger masses indicate that self-absorption is not significant for samples smaller than 100 micrograms. For samples that were solid chunks and well-localized in their capillaries (the metal, mononictides and CfCl_3), masses determined in this manner had an uncertainty of about 2 percent. In cases where the samples were very powdery and were spread over the capillary walls (some of the oxides), the uncertainty was larger.

Results of the Magnetic Measurements

The samples of the metal that were studied are described in Table IV-1. A brief description of the preparation method is given in Appendix C. During its preparation, the metal is formed as a thin sheet, which is cut up into smaller pieces. Sample C had a thin flat half-disc shape. Sample 16 was a

Table IV-1. Summary of the californium metal samples.

Sample designation	Mass (μg)	μ_{eff} (μB) ($150 < T < 340 \text{ K}$)	θ_{p} (K)	T_{C} (Curie temp.) (K)
C	73.0	9.6	41	52 ± 2
16	98.0	9.7	38	a
5	5.38	9.6	37	a

^aNot determined.

one mm long needle-shaped piece, and sample 5 consisted of just one small disc-shaped piece. All three of the samples were slightly contaminated with a magnetic impurity that contributed a magnetic signal that saturated at magnetic fields of about 5 kilogauss. The saturable signal is most likely due to small quantities of ferromagnetic iron that were introduced into the sample or its quartz capillary during preparation. All of the californium samples studied in this work showed this type of magnetic contamination to some degree. For the metal samples, the effects of the magnetic impurities were negligible at magnetic fields above 30 kilogauss at all temperatures and at fields above 5 kilogauss at temperatures below 200 K. Magnetization as a function of magnetic field for samples C and 16 is shown in Figure IV-1. There is a small positive offset in the curves, when they are extrapolated to zero field, that is

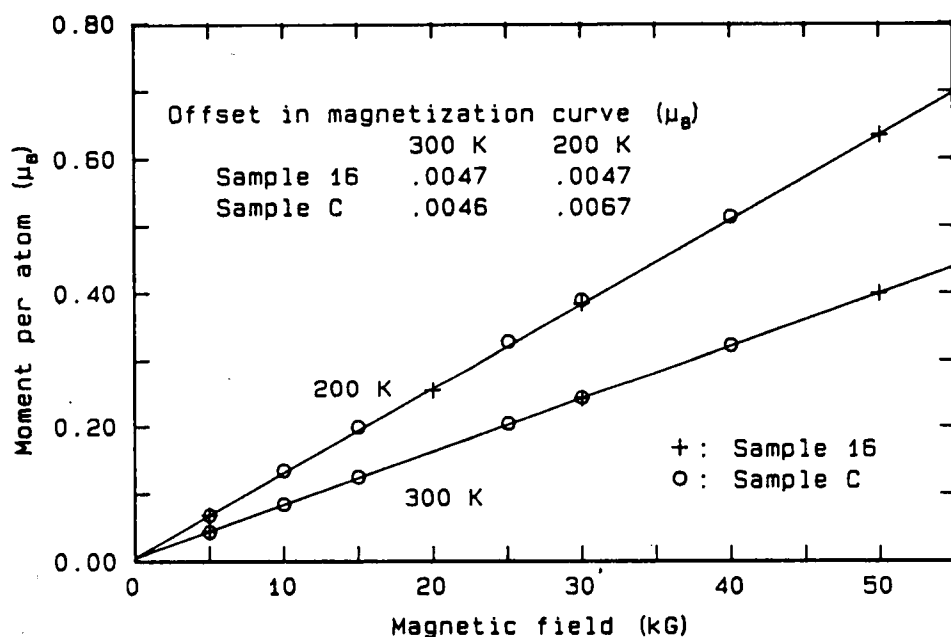


Figure IV-1. Magnetization of californium metal samples C and 16 as a function of magnetic field at 200 and 300 K. The offset in the curves at zero field indicates the presence of a saturable magnetic impurity.

due to the above mentioned magnetic impurities. The offset is relatively temperature independent at temperatures above 200 K.

The Curie-Weiss behavior of californium metal at temperatures above 100 K is clearly seen in the inverse magnetic susceptibility curves shown in Figures IV-2 and IV-3. The magnetic impurities cause an upward shift in the curves with increasing magnetic field. Linear fits to the inverse susceptibility data in the temperature range of 150 to 340 K give the effective paramagnetic moments, μ_{eff} , and the Weiss constants, θ_p , shown in the figures. The relatively large and positive value of θ_p is an indication of ferromagnetic ordering.

While samples 5 and 16 were measured mainly at temperatures above 100 K, sample C was measured at magnetic fields between 5 and 50 kilogauss and at temperatures between 5 and 340 K to study the cooperative magnetic behavior in detail. The moment per californium atom *vs.* temperature for sample C is plotted in Figure IV-4. The curves show that with decreasing temperature, the saturation moment per atom reaches a maximum of about $6 \mu_B$ at about 16 K, and then decreases somewhat at lower temperatures.

The large magnetization in the sample suggests the need to account for demagnetizing effects. The demagnetization factor D is defined by

$$H_i = H_a - 4\pi D M_v, \quad (\text{IV-1})$$

where H_a is the applied field, H_i is the field inside the sample and M_v is the sample magnetization per unit volume. Since sample C had a thin, flat shape and the magnetic field was directed in the plane of the sample, the demagnetization factor would not be expected to be very large. As limiting cases, it will be assumed that D falls somewhere between 0 (D for a needle-shaped sample that is parallel to the field) and $1/3$ (D for a sphere), although it

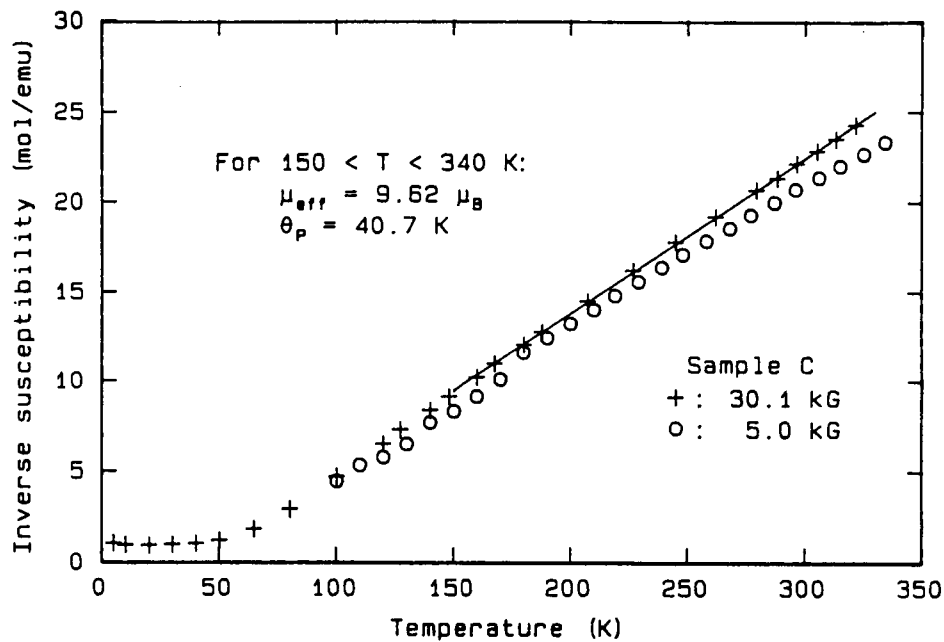


Figure IV-2. Inverse magnetic susceptibility of californium metal (sample C).

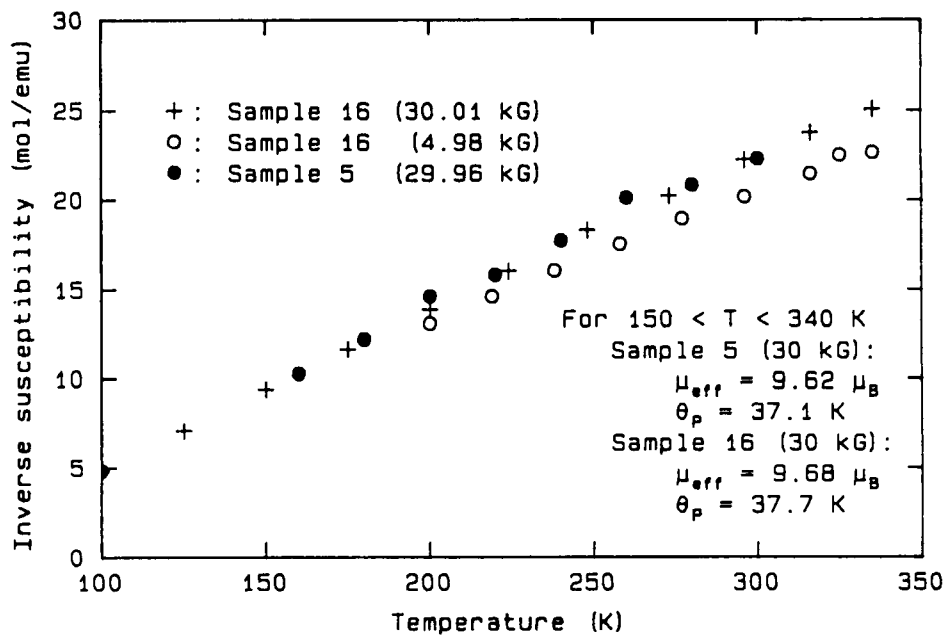


Figure IV-3. Inverse magnetic susceptibility of californium metal above 100 K (samples 5 and 16).

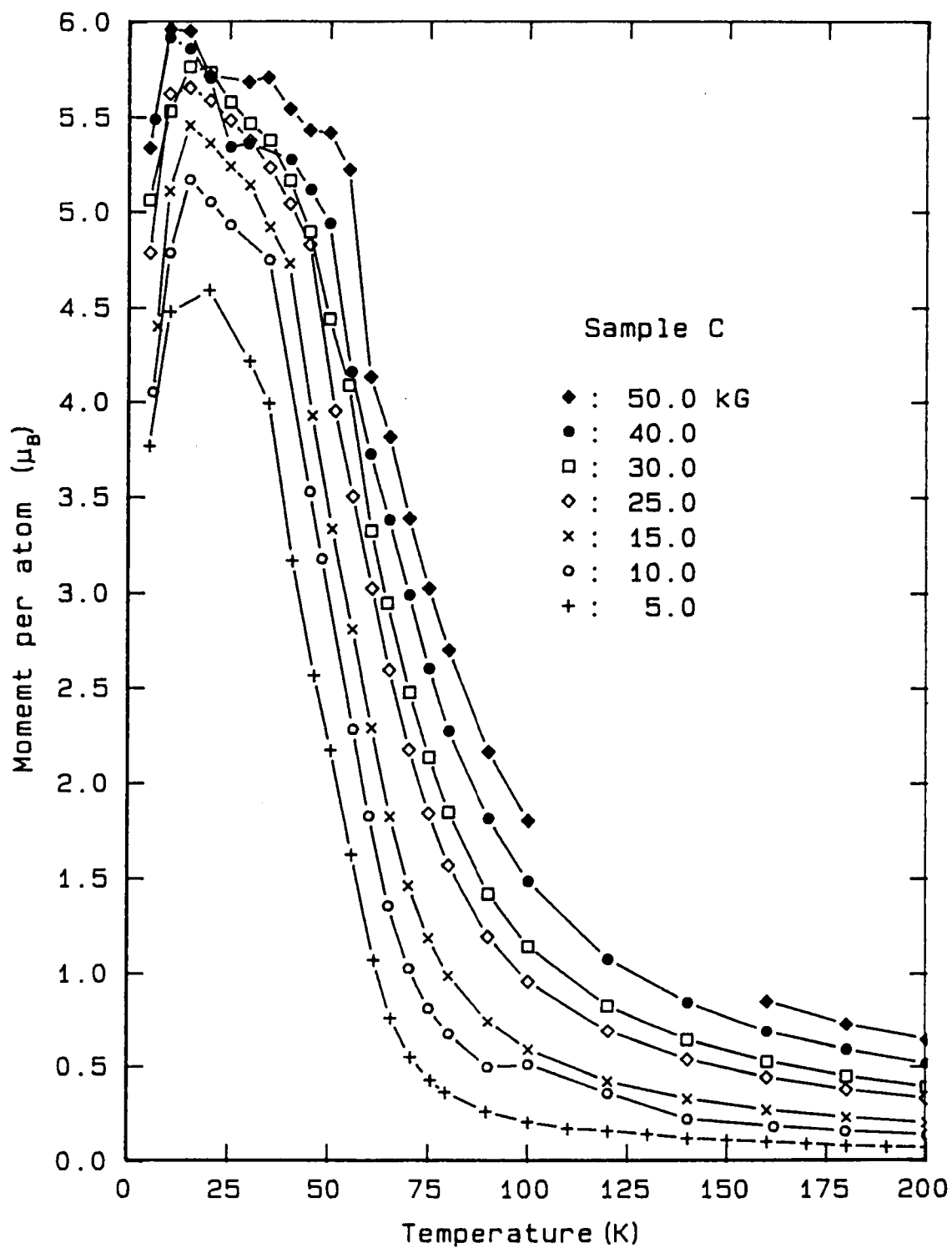


Figure IV-4. Moment per atom as a function of temperature for californium metal below 200 K.

would be expected to be closer to 0 than to 1/3.

The behavior of the sample in the ordered state can be clearly seen from plots of magnetic field *vs.* temperature at constant magnetization. These curves intersect the temperature axis at the temperature which has the corresponding spontaneous magnetization. The curves for small values of the moment are shown in Figure IV-5 and intersect at the ordering temperature, 52 ± 2 K. The curves for larger moments give the temperature dependence of the spontaneous magnetization below the ordering temperature. The experimental spontaneous magnetization curve, as developed from the isomagnetization plots, is shown in Figure IV-6.

A simple theoretical model of the spontaneous magnetization behavior can be derived from the mean field approximation.⁵ A ground state consisting of $2J + 1$ levels will have a magnetization

$$\begin{aligned} M(T) &= M(0) B_J(x), \\ \text{with } x &= \frac{Jg_J\mu_B}{k_B T} (H_a + \lambda M) \\ \text{and } M(0) &= N_A Jg_J\mu_B, \end{aligned} \tag{IV-2}$$

where $B_J(x)$ is a Brillouin function. If H_a is set to 0, the spontaneous magnetization curve is determined from equations IV-2 by numerically solving for the self-consistent values of $M(T)/M(0)$ as a function of temperature. The theoretical curves for $J = 15/2$ and $J = 1/2$, scaled to fit the $D = 0$ experimental data, are shown in Figure IV-6. The $J = 15/2$ curve would apply if the ground state were not significantly split by the crystal field. The $J = 1/2$ curve would apply if the ground state were an isolated Kramer's doublet. The scatter in the experimental data is too large to determine for certain which J

⁵A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965), p. 262.

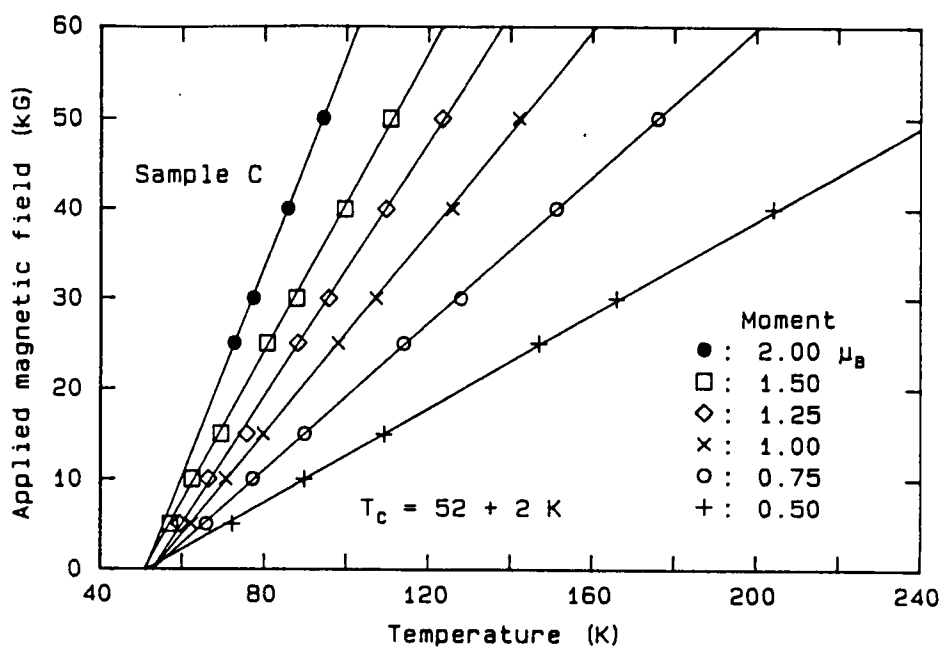


Figure IV-5. Determination of T_C for californium metal from iso-magnetization curves.

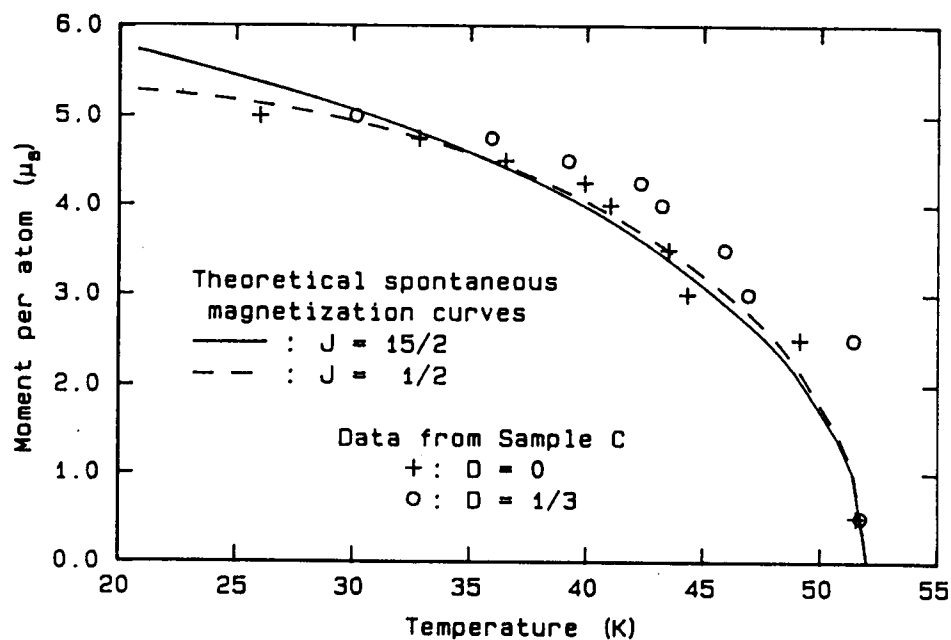


Figure IV-6. Spontaneous magnetization curve for californium metal. The experimental data is shown for two assumptions for the demagnetization factor, D . The theoretical curves are constrained to fit $T_C = 52$ K and to provide the best fit to the $D = 0$ data.

value fits the data better, but the $J=1/2$ curve has a smaller least-squares error. The curves for both values of J can be scaled to fit the $D=0$ data much better than the $D=1/3$ data.

The magnetization as a function of applied magnetic field for sample C at 16 K is shown in Figure IV-7. At an applied magnetic field of 50 kilogauss, the magnetization is still increasing slightly and has a magnitude of about $6 \mu_B$ per atom. A best-fit Brillouin function with $J=15/2$ is also shown in the figure for comparison.

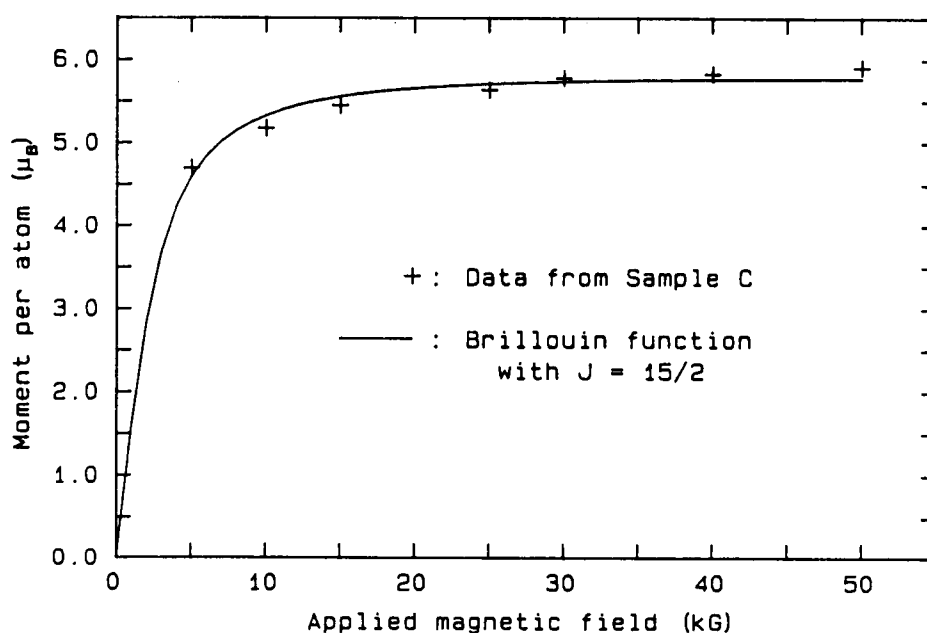


Figure IV-7. Magnetization of californium metal as a function of applied magnetic field at 16 K. The theoretical Brillouin function shown is that which best fits the data with $J=15/2$.

Interpretation of the Magnetic Measurements

Paramagnetic Behavior

The measured value of the effective paramagnetic moment, $9.7 \pm 0.2 \mu_B$, is consistent with, but slightly lower than, the calculated intermediate coupling value of $10.2 \mu_B$ (see Table III-9, page 56) for trivalent californium. Since the divalent value ($10.3 \mu_B$) is so close to the trivalent value, the magnetic measurement does not provide a way to distinguish the two, and other evidence, such as atomic volumes, must be relied upon.

Bulk magnetization measurements give the combined moment of the metal ions and the conduction electrons. In light actinide intermetallic compounds, spin polarization of the conduction electrons frequently results in the reduction of the measured ordered and paramagnetic moments.⁶ Conduction electron polarization may therefore account for the lowering of the effective paramagnetic moment in californium metal. In the heavy rare earth metals, however, experimental effective moments are in general slightly larger than the theoretical values,⁷ indicating that conduction electron polarization might be expected to enhance, rather than reduce, the moments of the heavy actinide metals.

Crystal Fields

The double hexagonal close-packed structure has two non-equivalent metal sites in its A-B-A-C layered structure. The ions in the B and C layers have a nearest-neighbor environment like that in the hexagonal close-packed

⁶P. Jena *et al.*, Phys. Rev. B 18, 3562 (1978).

⁷J. J. Rhyne, in *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliott (Plenum, London, 1972), p. 131.

(hcp) structure and have an overall site symmetry of D_{3h} . The ions in the A layers have a nearest neighbor environment like that in the cubic close-packed (fcc) structure and have an overall site symmetry of D_{3d} . To describe the crystal field at the D_{3h} site requires the crystal field parameters B_0^2 , B_0^4 , B_0^6 and B_6^6 , while those four parameters plus B_3^4 and B_3^6 are required for the D_{3d} site.

Several of the light lanthanide metals crystallize in the dhcp structure: lanthanum, praseodymium, neodymium and promethium. The results of magnetic susceptibility and neutron diffraction measurements on praseodymium and neodymium^{8,9} indicate that a point charge model provides a reasonably good account of the signs and relative magnitudes of the crystal field parameters.¹⁰ The nonuniform charge density of the conduction electrons is apparently of less importance. The parameters that have been determined for praseodymium are listed in Table IV-2 and can serve as a basis for estimating the parameters that might apply to californium. From Table III-5, page 40, it can be seen that the $\langle r^k \rangle$ values for the 5f electrons of Cf are roughly twice the magnitude of the $\langle r^k \rangle$ values for the 4f electrons of Pr. Crystal field parameters that are twice those of Pr metal might therefore serve as a rough estimate of the crystal field parameters of Cf metal.

If exchange is neglected and the bulk polycrystalline susceptibility is calculated from these crystal field parameters (assuming an equal contribution to the susceptibility from each site), a small θ_P of about -2 K is determined. The contribution to the θ_P of the experimental data due to exchange is

⁸J. G. Houmann *et al.*, Phys. Rev. B **20**, 1105 (1979).

⁹P. Touborg *et al.*, Phys. Rev. B **17**, 4454 (1978).

¹⁰T. Murao and L. Couture, J. Phys. Soc. Japan **52**, 4048 (1983).

Table IV-2. Crystal field parameters of dhcp
praseodymium metal.^a

	B_0^2	B_0^4	B_2^4	B_0^6 (cm^{-1})	B_2^6	B_4^6	N_V^b
D_{3h} site	144	50	—	205	—	130 ^c	360
D_{3d} site	0	-250	299 ^c	166	100 ^c	105 ^c	640

^aJ. G. Houmann *et al.*, Phys. Rev. B **20**, 1105 (1979).

^bAuzel scalar crystal field parameter (see equation III-6).

^cBased on theoretical nearest-neighbor point charge model ratios [B. Bleaney, Proc. Roy. Soc. (London) **A276**, 39 (1963)]:

$$B_2^4/B_0^4 = -10/\sqrt{70},$$

$$B_2^6/B_0^6 = 35/(4\sqrt{210}),$$

$$B_4^6/B_0^6 = 77/(8\sqrt{230}).$$

therefore about 43 K. This is equivalent to a molecular field constant λ of about 3.5 mol/emu. The corresponding exchange field when the californium moment is $6 \mu_B$ (roughly the saturated moment at 16 K) is about 10^5 gauss.

The crystal field at both sites will split the $J=15/2$ ground manifold into eight Kramer's doublets (see Table III-6, page 42). At the hexagonal site in zero field (*i.e.*, with no exchange), the lowest crystal field level would be a Γ_9 , consisting almost entirely of the $J=\pm 15/2$ states. The next higher level, lying about 20 cm^{-1} above the ground level would be a Γ_7 consisting principally of the $J=\pm 13/2$ states. The exchange field will mix the crystal field states, and the crystal field and Zeeman interactions must be treated as simultaneous perturbations to the intermediate coupling free ion states. The moments of the various levels as a function of θ , the angle between the z -axis (axis of symmetry) and the magnetic field, are calculated from

$$\mu(\theta) = \langle \mu_z \rangle \cos \theta + \langle \mu_x \rangle \sin \theta. \quad (\text{IV-3})$$

The expectation values are calculated using equations A-10 and A-12. When averaged over all angles, as appropriate for polycrystalline samples, and when Boltzmann weighting factors are applied to account for thermal population of the levels, the hexagonal sites are calculated to have a moment of about $5.7 \mu_B$ in an exchange field of 10^5 gauss at a temperature of 16 K. A similar calculation applied to the cubic site predicts a splitting between the lowest two Kramer's doublets of about 10 cm^{-1} and a total splitting of the manifold of about 200 cm^{-1} . The moment of the cubic site at 16 K with a 10^5 gauss exchange field would be $7.9 \mu_B$. This relatively simple-minded model of the crystal field therefore predicts a reduction in the saturated moment of the metal at 16 K from the maximum theoretical value of $g_J J = 9.6 \mu_B$ down to about $6.8 \mu_B$. The calculation is only intended to show that crystal field splitting might account for the magnitude of the measured moment at 50 kilogauss and 16 K (see Figure IV-7). It cannot, however, account for the reduction in moment at lower temperatures, because the moment of the lowest level at both sites is greater than the moments of the nearby levels, and a decrease in temperature would increase the moment.

Magnetic Ordering

The cooperative magnetic behavior of californium metal can be compared with the behavior of the other known magnetic actinide metals (Cm and Bk) as well as with the behavior of the lanthanide metals. Some details of the ordered states of those metals are listed in Table IV-3.

In the lanthanide metals, the dominant magnetic interaction between the

Table IV-3. Magnetic ordering in the lanthanide metals and the heavy actinide metals.

	No. of <i>f</i> electrons	Crystal structure	T _N (K)	T _C (K)	Weiss const. ^a (K)
Lanthanides ^b					
Pr	2	dhcp	—	—	
Nd	3	dhcp	19	—	
Gd	7	hcp	—	293	317
Tb	8	hcp	229	221	217
Dy	9	hcp	179	85	145
Ho	10	hcp	132	20	81
Actinides					
Cm ^c	7	dhcp	64	—	180–259
Bk ^d	8	dhcp	34	—	84–208
Cf	9	dhcp	60 ^e	52	41

^aPolycrystalline average

^bJ. J. Rhyne, in *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliot (Plenum, London, 1972), p. 131.

^cS. E. Nave and P. G. Huray, unpublished data (1980).

^dS. E. Nave *et al.*, in *Crystalline Electric Field and Structural Effects in *f*-Electron Systems*, edited by J. Crow *et al.* (Plenum, New York, 1980), p. 269

^eP. G. Huray *et al.*, in *13ème Journées des Actinides*, 1983 (unpublished).

metal ions is the Ruderman-Kittel-Kasuya-Yosada (RKKY) interaction.¹¹ The RKKY interaction is a type of indirect exchange, in which the interaction between metal ions is mediated by the spin polarization of conduction electrons. An effective Hamiltonian for this interaction can be written as

$$\mathcal{H}_{\text{RKKY}} = - \sum_{i,j} \mathcal{J}(\mathbf{R}_{ij}) (g_J - 1)^2 \mathbf{J}_i \cdot \mathbf{J}_j,$$

¹¹S. H. Liu, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Geschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 310.

$$\text{with } \mathcal{J}(\mathbf{R}) \propto \frac{[2k_F R \cos(2k_F R) - \sin(2k_F R)]}{(2k_F R)^4}. \quad (\text{IV-4})$$

k_F is the Fermi wave number of the conduction electrons and will depend upon the density of conduction electrons.¹² $\mathcal{J}(\mathbf{R})$ has a long range oscillatory spatial dependence.

The contribution made by the RKKY interaction to the Weiss constant can be written, for constant $\mathcal{J}(\mathbf{R})$, as¹³

$$\theta_P \propto (g_J - 1)^2 J(J + 1). \quad (\text{IV-5})$$

The DeGennes factor, $(g_J - 1)$, projects the spin contribution out of the total angular momentum J . The heavy lanthanide metals are all trivalent and have the same crystal structure (hcp), and the θ_P values follow the DeGennes scaling very well, as shown in Figure IV-8. If the same scaling is applied to Cm, Bk and Cf, however, the fit to the experimental data is not nearly as good. The θ_P values decrease from Cm to Cf, but the rate of decrease is steeper than predicted by the DeGennes scaling. The uncertainties in the θ_P values, especially for Cm and Bk, are quite large, however, and the comparison is therefore very uncertain. Figure IV-8 and Table IV-3 also show that the θ_P values and ordering temperatures of the heavy actinides are lower than those of the heavy lanthanides. This indicates that the overall interaction strengths in the heavy actinides are smaller than those in the heavy lanthanides.

In the heavy lanthanide metals, the overall interaction strength is determined primarily by the strength of the indirect exchange, but the magnetic

¹²P. Erdős and J. M. Robinson, *The Physics of Actinide Compounds* (Plenum, New York, 1983), p. 125.

¹³Liu, p. 314.

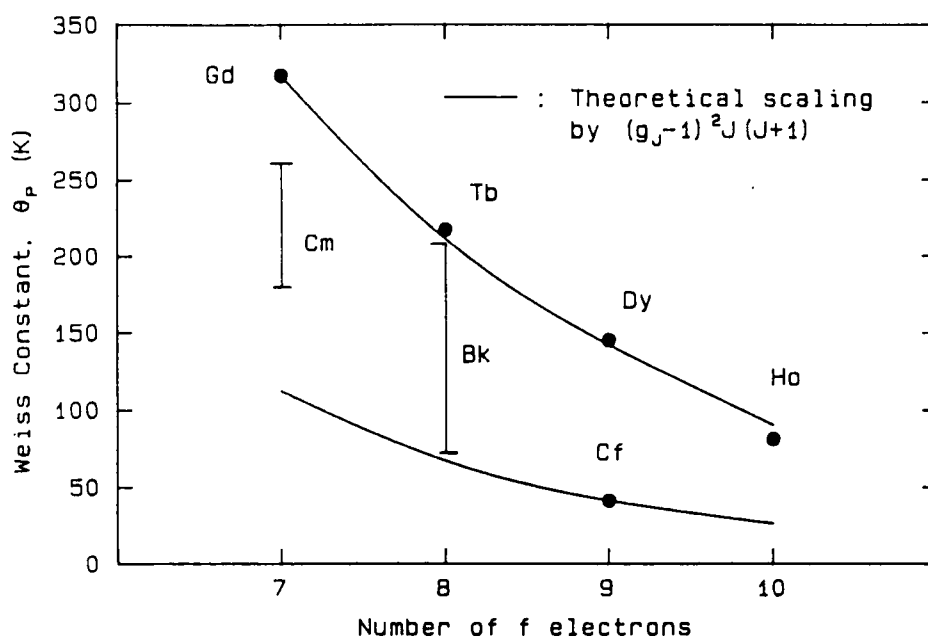


Figure IV-8. DeGennes scaling of the Weiss constants of the heavy lanthanide and actinide metals. The theoretical curve for the lanthanides is scaled from the Gd experimental data. The curve for the actinides is scaled from the Cf data. For references, see Table IV-3.

structure is influenced greatly by the crystal field anisotropy and magneto-elastic effects. In the light lanthanides, indirect exchange is smaller and closer in magnitude to the crystal field effects. The light lanthanide systems with the dhcp structure are further complicated by the existence of two non-equivalent metal sites. Neodymium has a very complicated field and temperature dependent behavior.¹⁴ The metal ions at the hexagonal and cubic sites order antiferromagnetically at different temperatures, 19 and 7.5 K, respectively. At lower temperatures, ferromagnetic ordering occurs, with different ordered moments at the two sites because of the different crystal fields at the two

¹⁴W. C. Koehler, in *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliott (Plenum, London, 1972), p. 117.

sites. Praseodymium has a singlet ground state and single-crystal samples in zero magnetic field do not order.¹⁵

The behavior of californium metal indicates the occurrence of ferromagnetic ordering at about 52 K in magnetic fields of 5 kG and greater. Huray *et al.*¹⁶ have reported observing antiferromagnetic ordering at about 60 K in fields below 200 gauss. The occurrence of antiferromagnetic ordering at low fields that changes to ferromagnetic ordering at higher magnetic fields and lower temperatures is similar to the behavior of dysprosium metal. As shown in the section on crystal fields, the reduction in the ordered moment from the theoretical maximum of $9.6 \mu_B$ to the measured value of about $6 \mu_B$ (at 50 kG and 16 K) can in part be explained by crystal field splitting. A complicated ordered structure could also contribute to the reduction in the measured moment. The decrease in the measured moment below 16 K may be an indication of a change in the ordered structure.

Comparison with the Results of Others

Other reports of magnetic measurements on californium metal samples have been made by Fujita *et al.*¹⁷ and Huray *et al.*¹⁶ The samples that Fujita *et al.* measured were apparently of the divalent fcc form. They had effective paramagnetic moments of 9.7 to $9.8 \mu_B$ and showed no magnetic ordering down to 22 K. The small measured values of the Weiss constant (-3 to 3 K) indicate that if any magnetic ordering occurs, it would probably occur at

¹⁵*Ibid.*, p. 119.

¹⁶P. G. Huray *et al.*, in *Proc. 13ème Journées des Actinides*, 1983 (unpublished).

¹⁷D. K. Fujita *et al.*, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 173.

temperatures well below 10 K. The measurements of Huray *et al.* were performed on metal samples that were prepared at the same time as the metal samples of this study. They were, however, studied only at fields of 1.6 kilogauss and less. Measurements in the paramagnetic region gave effective moments of about $10.8 \mu_B$, because the magnetic impurities were not saturated at the low fields. As previously mentioned, in magnetic fields below 200 gauss, an antiferromagnetic transition at a temperature about 10 K above the ferromagnetic transition was also observed. The present studies did not reexamine that behavior.

CHAPTER V

CALIFORNIUM OXIDES

The lanthanides and the heavy actinides form sesquioxides in which the metal ions are presumed to be in the trivalent state. Californium, like some other heavy actinides (Cm) and lanthanides (Pr and Tb) that can occur in the 4+ charge state, also forms the dioxide and other oxides with oxygen to metal ratios between 1.5 and 2.0.^{1,2} Magnetic measurements were performed on members of this oxide series (Cf_2O_3 , Cf_7O_{12} , and CfO_2) to provide information on the trends in paramagnetic behavior with changing charge state of the californium. The tetravalent state of a number of lanthanides and actinides has been shown to be exceptionally stable in the $\text{BaM}^{4+}\text{O}_3$ -type perovskite compounds.³ BaCfO_3 therefore serves as another example of californium in the 4+ charge state.

In order to examine crystal field effects in the oxides more closely, a sample of Y_2O_3 that was doped with californium was studied as well. The nonmagnetic Y_2O_3 provides nearly the same crystalline environment as occurs in the pure bcc Cf_2O_3 so that the crystal fields are nearly the same. The dilution of the californium by the yttrium was intended to eliminate californium-californium interactions, so that the effects of the crystal field on the magnetic susceptibility could be studied without interference from the effects of magnetic ordering.

¹R. D. Baybarz *et al.*, *J. Inorg. Nucl. Chem.* **34**, 557 (1972).

²J. B. MacChesney *et al.*, *J. Chem. Phys.* **44**, 596 (1966).

³R. G. Haire and J. Y. Bourges, in *Proc. 10ème Journée des Actinides*, edited by B. Johansson and A. Rosengren, 1980 (unpublished), p. 19.

Crystallography of the Oxides

The crystal structures of the pure oxides are closely related to one another. CfO_2 has the calcite fcc structure. Rhombohedral Cf_7O_{12} can be derived from CfO_2 by a rhombohedral distortion and removal of two oxygens for each set of 14 californium ions. Cf_7O_{12} has two non-equivalent californium sites. The removal of an appropriate one-fourth of the oxygens from the CfO_2 structure results in C-type bcc Cf_2O_3 , which also has two non-equivalent californium sites. B-type monoclinic Cf_2O_3 was also studied, and it has three non-equivalent Cf sites. BaCfO_3 has a perovskite structure that is very nearly cubic. See Appendix B, Tables B-2 to B-5 (pages 148 to 152), for additional details and references concerning the crystallography of the oxides.

Magnetic Measurements: Results and Interpretation

For all of the oxide measurements, sample temperatures were measured with the copper-constantan thermocouple arrangement described in Chapter IV. A few of the oxide measurements were performed using the rigid-rod sample holder, but most were done with the wire suspension system. Descriptions of all the oxide samples that were studied are given in Table V-1. The table also summarizes the results of the magnetic measurements that were performed on each sample.

Bcc Cf_2O_3

The body-centered cubic form of the sesquioxide was studied both as a pure substance and as a ten percent dilution in nonmagnetic Y_2O_3 ($\text{Y}_{1.8}\text{Cf}_{0.2}\text{O}_3$). The inverse susceptibility curves for the two cases are shown in Figure V-1. The effective paramagnetic moment of the pure form was

Table V-1. Summary of the californium oxide samples.

Sample designation	Crystal structure	Mass of Cf (μg)	μ_{eff}^a (μ_B)	θ_p^a (K)	T_N (K)
Cf_2O_3 #3	bcc	30.8	9.91	-120	22
Cf_2O_3 #1	monoclinic	10.6	10.1	-73	7
Cf_2O_3 #5	monoclinic	21.8	10.4	-92	7
$\text{Y}_{1.8}\text{Cf}_{0.2}\text{O}_3$	bcc	40.0	10.19	-41	2.5
Cf_7O_{12} #1	rhombohedral	100	9.45	-86	8
Cf_7O_{12} #1b	rhombohedral	41.9	9.22	-108	8
Cf_7O_{12} #2	rhombohedral	24.5	9.41	-93	7
CfO_2 #1	fcc	6.0	9.80	-63	7
$\text{Cf}(\text{Bk})\text{O}_2$	fcc	53.0	9.17	—	—
BaCfO_3	cubic perovskite	24.0	9.14	-180	7

^aThe applicable temperature ranges are shown on the inverse susceptibility plots for the individual compounds.

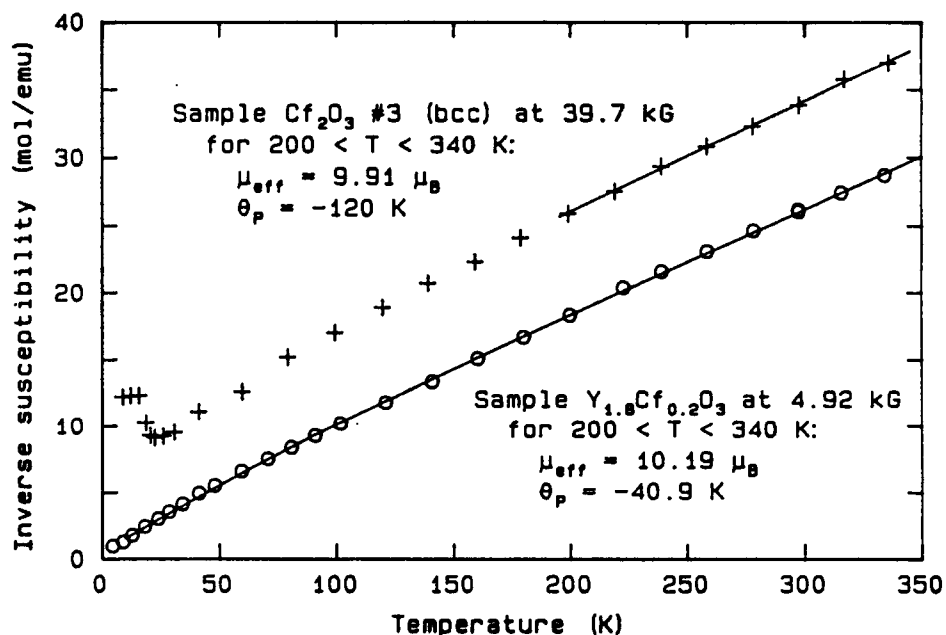


Figure V-1. Inverse magnetic susceptibility of body-centered cubic Cf_2O_3 and $\text{Y}_{1.8}\text{Cf}_{0.2}\text{O}_3$. The solid line through the $\text{Y}_{1.8}\text{Cf}_{0.2}\text{O}_3$ data corresponds to a crystal field model with parameters six times bigger than the Dy_2O_3 parameters (see Table V-2) and a molecular field constant of 0.5 mol/emu.

measured to be $9.9 \mu_B$ while the μ_{eff} of the dilute form was slightly higher at $10.2 \mu_B$. The pure material has a maximum in the susceptibility at about 22 K (see Figure V-2) that indicates the occurrence of antiferromagnetic ordering. Although the diluted sample was not expected to exhibit any magnetic ordering, a maximum in the susceptibility was observed at about 2.5 K. Therefore, the effects of exchange were not completely eliminated, but they were substantially reduced. The Weiss constant for the pure substance is significantly larger in magnitude than that for the dilution: -120 K vs. -40 K . The 80 K difference is presumably the result of magnetic interactions. In terms of a molecular field model (equation III-16), the shift in the inverse susceptibility curve of the pure Cf_2O_3 relative to the diluted sample can be described by a molecular field constant λ of about 8 mol/emu. The θ_P in the diluted sample can be attributed primarily to the effects of the crystal field, with perhaps

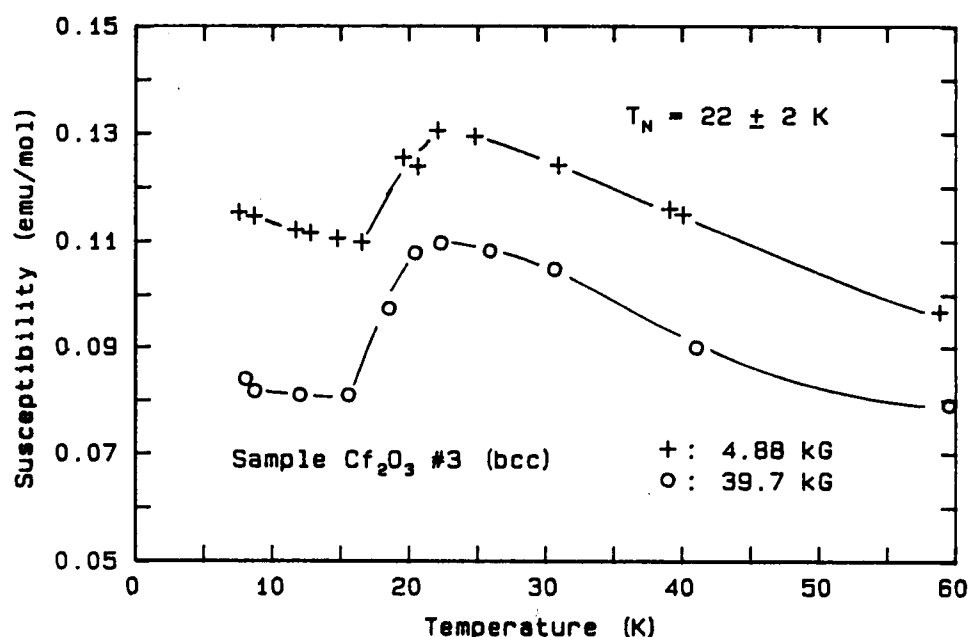


Figure V-2. Magnetic susceptibility of body-centered cubic Cf_2O_3 below 60 K.

some small influence of exchange still present.

Since the crystal symmetry is the same for both samples, and the crystal lattice parameters are not significantly different (10.83 Å for Cf_2O_3 vs. 10.60 Å for Y_2O_3), the crystal field effects in the diluted material should be close to those in the pure material. One of the two non-equivalent Cf sites in the bcc crystal structure has C_2 site symmetry and comprises three-fourths of the Cf sites. The other site has C_{3i} symmetry. To fully describe the effects of the crystal field at the C_2 sites using equation III-5 requires 9 different B_q^k , five of which are complex, resulting in 14 different parameters. At the C_{3i} sites, 8 parameters are required. The crystal field parameters for lanthanides doped into Y_2O_3 have been studied extensively using optical absorption measurements,^{4,5} and those results can be used as a basis for estimating the parameters that apply to bcc Cf_2O_3 .

The crystal field parameters that have been determined for bcc Dy_2O_3 are listed in Table V-2. The C_{3i} site has axial symmetry and therefore the contribution to the susceptibility from that site will have equal contributions from χ_x and χ_y (when the z-axis is the symmetry axis). For the C_2 site, χ_x and χ_y are not equal and must be calculated separately. χ_x is first calculated from the matrix elements of μ_x using equation A-12. The coordinate system in which the crystal field parameters are defined can then be rotated 90° about the z-axis so that the new x-axis becomes the original y-axis. The crystal field parameters in the new coordinate system are related to those in the old by a multiplicative factor of ± 1 or $\pm i$, depending upon k and q. A calculation of χ_x in the new system thus gives χ_y in the original coordinate

⁴N. C. Chang *et al.*, J. Chem. Phys. **76**, 3877 (1982).

⁵J. B. Gruber *et al.*, J. Chem. Phys. **82**, 5373 (1985).

Table V-2. Crystal field parameters of C-type Dy₂O₃.

Parameters	C ₂ site ^a		(cm ⁻¹)	C ₃ site ^b	
	Re	Im		Re	Im
B ₀ ²	-278	0		1425	0
B ₂ ²	-669	0		0	0
B ₄ ⁰	-1190	0		-629	0
B ₄ ²	-1409	-270		0	0
B ₄ ⁴	0	0		260	0
B ₄ ⁶	799	902		0	0
B ₆ ⁰	58	0		107	0
B ₆ ²	281	40		0	0
B ₆ ⁴	0	0		298	-479
B ₆ ⁶	385	319		0	0
B ₈ ⁰	-97	7		595	164
N _v ^c	3860			2690	

^aN. C. Chang *et al.*, J. Chem. Phys. **76**, 3877 (1982).

^bJ. B. Gruber *et al.*, J. Chem. Phys. **82**, 5373 (1985).

^cAuzel scalar crystal field parameter, see equation III-6.

system. The total susceptibility of the bcc sesquioxide is then determined by adding together the polycrystalline susceptibilities of the two sites, weighted by their relative occurrences in the structure.

In extrapolating from the Dy₂O₃ crystal field parameters to those that apply to Cf₂O₃, it is reasonable to assume that all parameters of the same order (having the same k) will maintain roughly the same relative magnitudes, so that only the relative magnitudes of the sets of parameters of order 2, 4 and 6 need be considered. In addition, the susceptibility is relatively

insensitive to variations as large as 50 percent in the relative magnitudes of the resulting three sets of parameters. It is therefore sufficient to scale all of the Dy_2O_3 parameters by the same factor to get a calculated susceptibility that fits the diluted Cf_2O_3 sample reasonably well. The theoretical inverse susceptibility curve in Figure V-1 is based on crystal field parameters that are six times larger than the Dy_2O_3 parameters, plus a small shift in the curve due to exchange, equivalent to a λ of 0.5 mol/emu. This λ corresponds to a contribution of about -5 K to the θ_p of -40 K of the diluted sample. The energy levels at both californium sites are split into eight Kramer's doublets. At the C_2 site, the splitting between the ground state doublet and first excited doublet, based on the crystal field model, is about 200 cm^{-1} and the total splitting of the manifold is about 2000 cm^{-1} . The corresponding energies for the C_{3i} site are 120 and 1200 cm^{-1} .

The magnetization of the diluted sample as a function of magnetic field is shown in Figure V-3. The experimental data are fit very well by a Brillouin function with $J=3$ that saturates at $3.0 \mu_B$. This is not consistent, however, with a ground state that is a well-isolated doublet, which should have a $J=1/2$ behavior for its saturation curve. Also shown in the figure is the magnetization curve calculated from the estimated crystal field parameters. The curve represents the Boltzmann averaged moment value of the two levels of the Zeeman split ground state for both sites. The moment at each site is calculated from

$$\frac{1}{3} (\langle \mu_x \rangle + \langle \mu_y \rangle + \langle \mu_z \rangle), \quad (\text{V-1})$$

where the expectation values are calculated for the appropriate level. The calculated curve rises much more rapidly (like a $J=1/2$ Brillouin function)

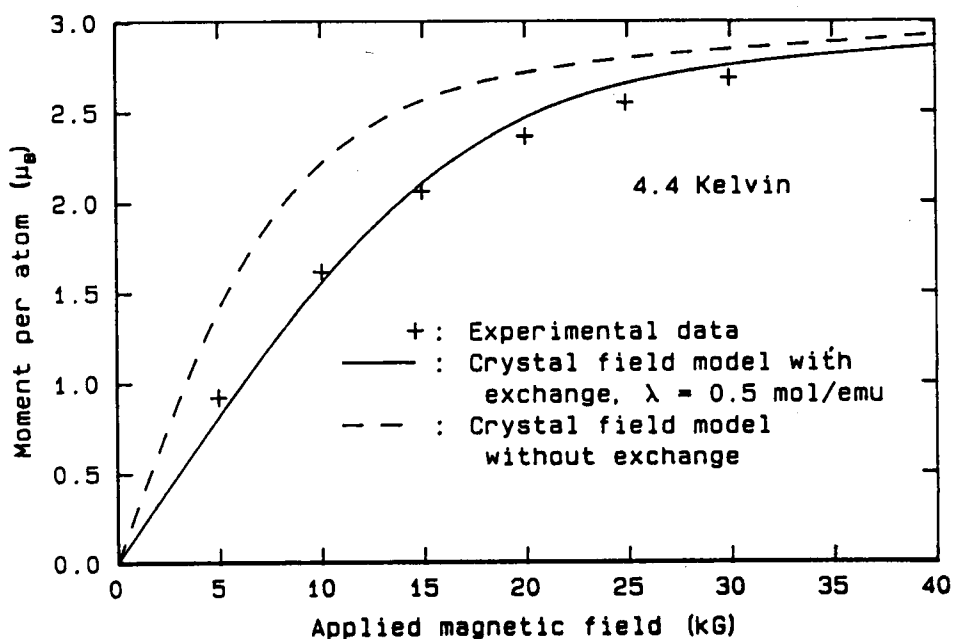


Figure V-3. Magnetization of $\text{Y}_{1.8}\text{Cf}_{0.2}\text{O}_3$ as a function of applied magnetic field at 4.4 K. The parameters of the crystal field model are those of Dy_2O_3 scaled up by a factor of six.

than the experimental curve and saturates at a slightly higher moment. Demagnetizing effects in the sample are small because of the dilution and cannot explain the discrepancy. If, however, an antiferromagnetic exchange field is assumed to be present that is consistent with the $\lambda = 0.5$ mol/emu that was estimated from the high temperature susceptibility, then there is reasonable agreement between the calculated magnetization and the experimental data obtained at 4.4 K.

Monoclinic Cf_2O_3

The magnetic susceptibility results for monoclinic Cf_2O_3 are shown in Figure V-4. The measured μ_{eff} is slightly higher than that in the bcc form ($10.2 \mu_B$ vs. $9.9 \mu_B$) and the Weiss constant is about -90 K. A maximum in the susceptibility indicates that antiferromagnetic ordering occurs at about

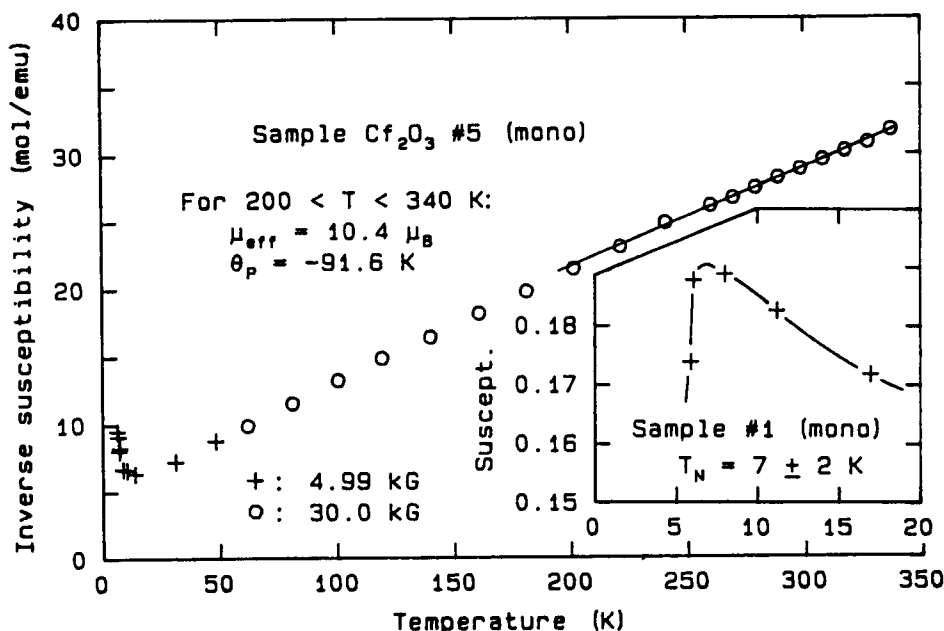


Figure V-4. Inverse magnetic susceptibility of monoclinic Cf_2O_3 . The magnetic susceptibility below 20 K is shown in the inset plot.

7 K, which is somewhat lower than the ordering temperature observed in bcc Cf_2O_3 . These ordering temperatures can be compared with those observed in the lanthanide sesquioxides. Dysprosium, the isoelectronic homologue of californium, has a T_N of 1.2 K for its sesquioxide.⁶ Tb_2O_3 has ordering temperatures of 7 K and 2 K for the two crystal structures, with the monoclinic form ordering at the higher temperature.⁷

The existence of three non-equivalent, low symmetry Cf sites in the monoclinic structure precludes any detailed crystal field analysis. Curvature in the inverse susceptibility curve does indicate, however, that the crystal field splitting is large enough to affect the susceptibility at temperatures up to 150 K.

⁶H. Bonrath *et al.*, Phys. Kondens. Mater. 4, 382 (1966).

⁷MacChesney *et al.*

Cf₇O₁₂

The results of the magnetic susceptibility measurements on the Cf₇O₁₂ samples are shown in Figures V-5 and V-6. The measured effective moment and Weiss constant are $9.4 \mu_B$ and -90 K, respectively. Antiferromagnetic ordering was detected at about 8 K. This can be compared with Tb₇O₁₂ which exhibits metamagnetic behavior with a Néel temperature at low magnetic fields of about 7 K.⁸

The stoichiometry of Cf₇O₁₂ indicates that for each formula unit, there should be on average three Cf ions in the 4+ charge state and four ions in the 3+ state. Cf₇O₁₂ has two non-equivalent californium sites, one which occurs only once in each unit cell and has C_{3h} site symmetry and the other which occurs six times and has C₃ symmetry. X-ray absorption spectroscopy measurements on Pr₇O₁₂ and Tb₇O₁₂ indicate that the 3+ and 4+ ions are located at different sites.⁹ That is, any particular ion has either a 3+ charge or a 4+ charge and the valence does not fluctuate between the two charge states. If the same situation is true in Cf₇O₁₂, then one Cf³⁺ ion would be expected to be located at the C_{3h} site, and the other three Cf³⁺ and the three Cf⁴⁺ ions would be distributed among the six C₃ sites.

The effective paramagnetic moment that would be expected from this system can be calculated based on the assumption that the total susceptibility is the sum of the susceptibilities due to the 3+ and 4+ ions. The total effective moment can then be calculated from

$$\mu_{\text{eff}}^2(\text{total}) = \frac{4}{7} \mu_{\text{eff}}^2(\text{Cf}^{3+}) + \frac{3}{7} \mu_{\text{eff}}^2(\text{Cf}^{4+}). \quad (\text{V-2})$$

⁸MacChesney *et al.*

⁹M. Gasgnier *et al.*, J. Less-Common Met. 127, 367 (1987).

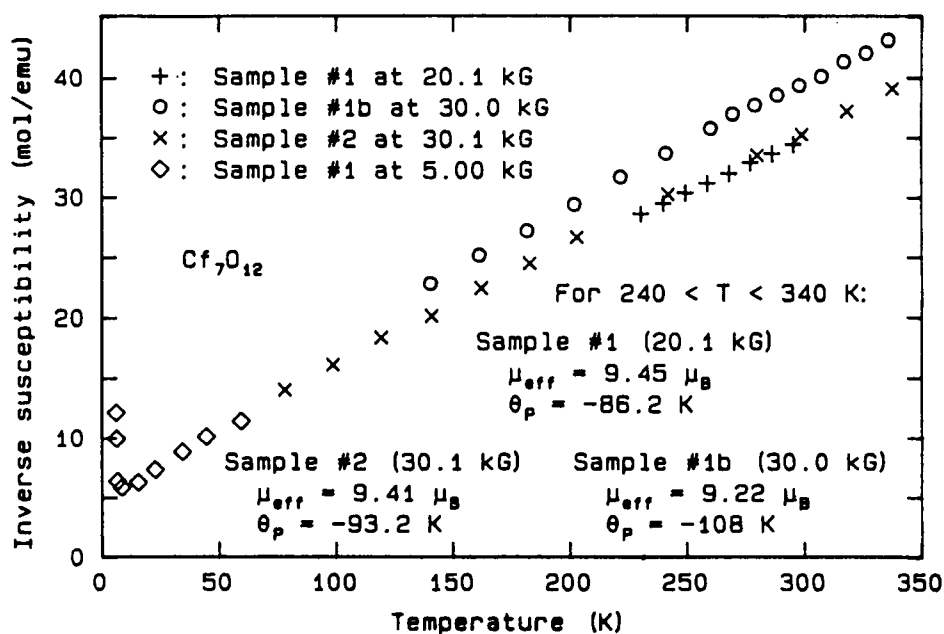


Figure V-5. Inverse magnetic susceptibility of Cf_7O_{12} .

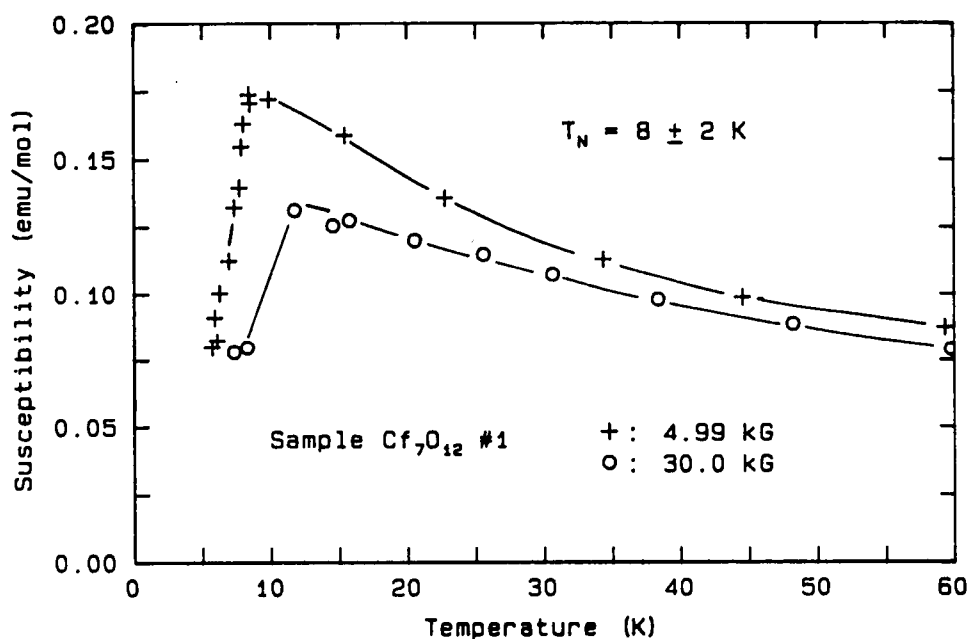


Figure V-6. Magnetic susceptibility of Cf_7O_{12} below 60 K.

Using the californium ion intermediate coupling effective moment values from Table III-9 (page 56), equation V-2 gives an expected $\mu_{\text{eff}}^2(\text{total})$ of $9.8 \mu_B$. This is slightly higher than the measured value.

CfO_2

The dioxide was studied as two samples that were originally BkO_2 and had radioactively decayed to CfO_2 . The half-life of ^{249}Bk is 320 days. Berkelium exhibits stronger tetravalent tendencies than does californium, and its dioxide is more easily prepared. The two samples were of different ages; one was about nine years old and contained less than one percent Bk, while the other contained about seven percent Bk. Powder X-ray analysis of the one-percent sample showed that the sample still had the fcc structure, and an analysis of the lattice parameter indicated an oxygen to Cf ratio of at least 1.95.¹⁰ The seven-percent sample was not analyzed in the same manner.

The measured effective paramagnetic moment of the seven-percent sample was $9.1 \mu_B$ (see Figure V-7). If an intermediate coupling value of $7.6 \mu_B$ is taken for Bk^{4+} (calculated in the same manner as the Cf values) and the contributions of the two ionic species to the total susceptibility are considered additive, then the effective moment due to the Cf^{4+} can be calculated from

$$\mu_{\text{eff}}^2(\text{total}) = 0.07 \mu_{\text{eff}}^2(\text{Bk}^{4+}) + 0.93 \mu_{\text{eff}}^2(\text{Cf}^{4+}). \quad (\text{V-3})$$

This gives an effective moment of $9.2 \mu_B$ based on the seven-percent sample. The effective moment measured for the one-percent sample was substantially higher, at $9.8 \mu_B$. The expected value of $9.3 \mu_B$ (see Table III-9, page 56) is

¹⁰R. G. Haire, private communication.

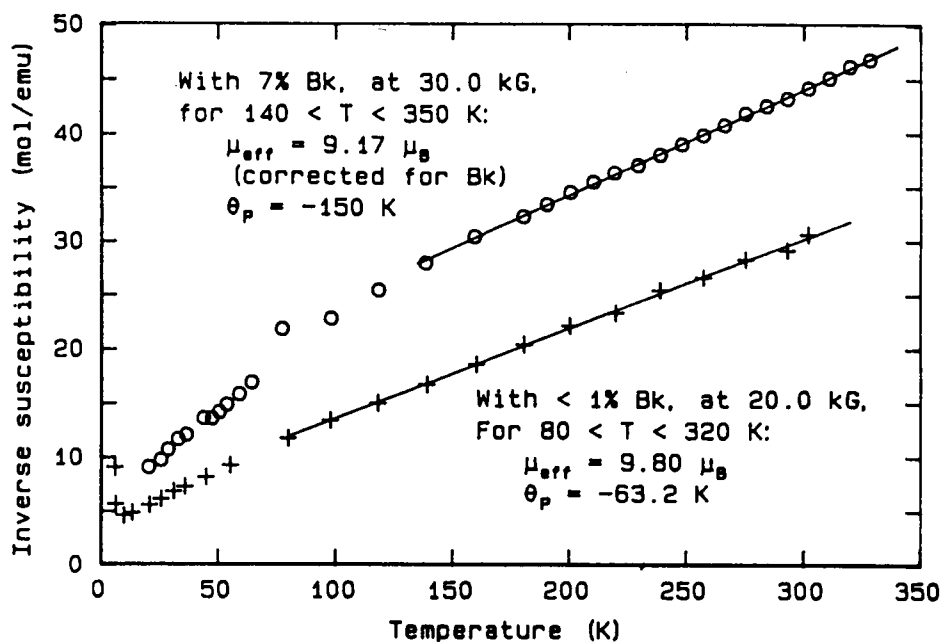


Figure V-7. Inverse magnetic susceptibility of CfO_2 .

more consistent with the results of the seven-percent sample. The one-percent sample was relatively small (about 6 micrograms) and the measurements for that sample were more susceptible to errors in mass determination and sample holder effects.

The seven-percent sample showed a great deal of structure in the susceptibility curve below 100 K, whereas, the one percent sample showed only an antiferromagnetic transition at about 7 K (see Figure V-8). The presence of Bk in the seven-percent sample apparently resulted in complex cooperative magnetic effects. For comparison, TbO_2 and PrO_2 order antiferromagnetically at about 3 K and 14 K, respectively.¹¹

Since the californium site in CfO_2 has cubic (O_h) symmetry, the crystal field can be parameterized in terms of just two parameters (see equation

¹¹MacChesney *et al.*

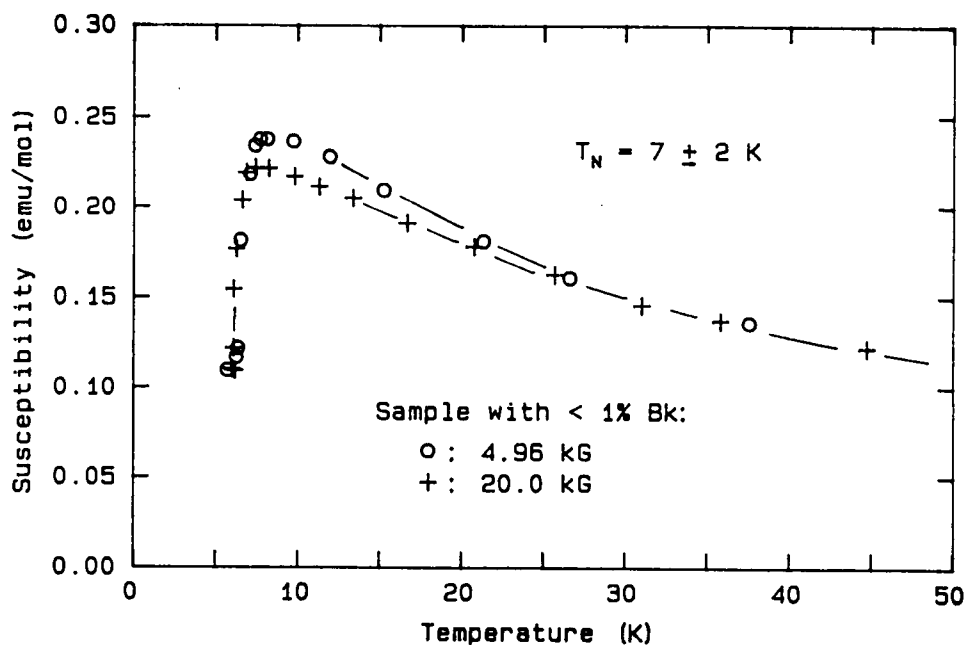


Figure V-8. Magnetic susceptibility of CfO_2 below 50 K.

III-7). The magnetic susceptibility data can therefore be fit to a model involving three parameters: B_0^4 , B_0^6 and the molecular field constant λ . EPR¹² and neutron diffraction measurements¹³ of the light actinides can provide guidance concerning the crystal field parameters that might be expected to apply to CfO_2 . In general, for the light actinides, B_0^4 is negative and of the order of 2000 to 5000 cm^{-1} , and the ratio B_0^6/B_0^4 is roughly -0.2 . These signs and relative magnitudes are more or less consistent with a point charge model. The parameters that result from a point charge calculation¹⁴ of CfO_2 , including contributions to the electric field from all ions in a cube consisting of 27 unit cells, are $B_0^4 = -3000 \text{ cm}^{-1}$ and $B_0^6 = 450 \text{ cm}^{-1}$. Figure III-4(e) (page 52) shows

¹²W. Kolbe *et al.*, J. Chem. Phys. **60**, 607 (1974).

¹³S. Kern *et al.*, Phys. Rev. B **32**, 3051 (1985).

¹⁴Using the computer program LEGO, developed and furnished by G. Amorette (University of Parma) and A. Blaise (C. E. N. Grenoble).

that the ground state for this crystal field is the non-magnetic doublet Γ_3 and that a Γ_5 triplet lies about 20 cm^{-1} above it. Mixing of the two levels by an exchange field would account for cooperative magnetic behavior. The susceptibility calculated from these parameters matches the measured susceptibility of the one-percent sample reasonably well, if the measured data is scaled to provide an effective paramagnetic moment of $9.3 \mu_B$ instead of the $9.8 \mu_B$ that was actually measured. A value for λ of 4.8 mol/emu is consistent with these crystal field parameters. The magnetic susceptibility is relatively insensitive to changes in the crystal field parameters, but the actual values cannot be significantly larger or smaller (perhaps within a factor of two) than the values suggested by the point charge model. Larger values split the Γ_5 level further from the ground state and the susceptibility becomes temperature independent at higher temperatures, and mixing with the ground level to allow magnetic behavior becomes less likely. Smaller values for the parameters result in too little curvature in the inverse susceptibility curve at temperatures below 100 K . Therefore, the parameters suggested by a point charge model seem to fit the data reasonably well, although this may be somewhat coincidental. The crystal field by itself, in this model, contributes about -10 K to the total θ_P of -65 K .

BaCfO₃

The results of the magnetic measurements on BaCfO_3 are shown in Figure V-9. At temperatures above 200 K , the effective paramagnetic moment is $9.1 \mu_B$ and the Weiss constant is -180 K . There is substantial deviation from Curie-Weiss behavior below 150 K , a possible indication of large crystal

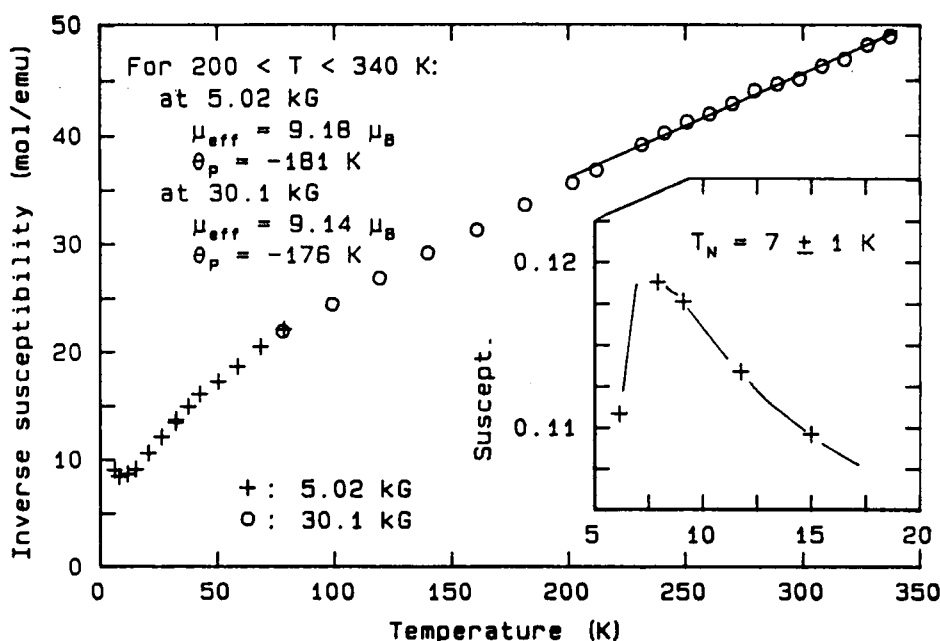


Figure V-9. Inverse magnetic susceptibility of BaCfO_3 . The magnetic susceptibility below 20 K is shown in the inset plot.

field effects. A maximum in the susceptibility at 7 K indicates the occurrence of antiferromagnetic ordering.

The symmetry of the californium site in BaCfO_3 , like that in CfO_2 , is cubic (O_h), but a crystal field model has not been determined that can satisfactorily explain the magnetic susceptibility. The significant departure from Curie-Weiss behavior up to temperatures above 200 K suggests that the splitting between the ground state and the first excited state is relatively large (perhaps at least several hundred cm^{-1}). Since only the Γ_5 levels are magnetic, the isolated ground state must be a Γ_5 . Figure III-4 (page 51) suggests that for $|B_8^6/B_8^4| < 1.2$, the ground state is never an isolated Γ_5 level. The tables and figures of Lea *et al.*¹⁵ show, however, that if $|B_8^6| \gg |B_8^4|$ then a Γ_5 level can be an isolated ground state. The slope of the inverse susceptibility curve

¹⁵K. R. Lea *et al.*, J. Phys. Chem. Solids **23**, 1400 (1962).

below 50 K is consistent with an isolated Γ_5 ground state when compared with the possible μ_{eff} values of the Γ_5 level, calculated using equation III-14. An extremely large value for B_6^0 (about 10^5 cm^{-1}) is required, however, to reproduce the measured susceptibility because the magnitude of the splitting of the crystal field levels is only very slightly dependent upon B_6^0 . The mixing of 5G terms with the 7F term in the intermediate coupling ground state results in a ten-fold decrease in the sensitivity to variations in B_6^0 as compared with the sensitivity of the pure 7F Russell-Saunders ground state. Therefore, there appears to be no set of credible crystal field parameters that can reproduce the measured susceptibility. This may indicate that there is a problem with the intermediate coupling model of the free ion wavefunctions that is used for Cf^{4+} . Alternatively, it may indicate that the curvature in the inverse susceptibility curve may be due not to crystal fields but to cooperative magnetic behavior at temperatures well above the observed antiferromagnetic transition at 7 K.

Indeed, relatively high magnetic ordering temperatures have been observed in some BaMO_3 compounds of the lanthanides and light actinides. BaTbO_3 has been studied by magnetic susceptibility and neutron diffraction measurements and orders antiferromagnetically at 37 K.¹⁶ The susceptibility curves for BaTbO_3 are not useful as an indicator of crystal field strength, however, since the ground state of Tb^{4+} consists primarily of the 8S term, which is virtually unsplit by crystal fields. BaNpO_3 has been studied magnetically and appears to order ferromagnetically at 31 K.¹⁷ The sudden increase in susceptibility in BaNpO_3 near its transition temperature is much sharper than

¹⁶B. C. Tofield *et al.*, J. Phys. C 5, 2887 (1972).

¹⁷B. Kanellakopulos *et al.*, Physica 102B, 221 (1980).

the increase observed in BaCfO₃. Further detailed study of the field and temperature dependences of the magnetization of BaCfO₃ at temperatures below 100 K might indicate whether cooperative magnetic behavior does occur in the neighborhood of 50 K.

Comparison with the Results of Others

Subsequent to the conclusion of the magnetic work on the californium oxides that is described in this chapter, Morss *et al.*¹⁸ reported the results of measurements of the magnetic susceptibility of bcc Cf₂O₃. They measured an effective paramagnetic moment of $9.7 \pm 0.2 \mu_B$ and a Weiss constant of -80 ± 10 K. The μ_{eff} is consistent with the results of the present work, but the θ_p is slightly smaller. Morss *et al.* did not detect any signs of antiferromagnetism at temperatures above 1.5 K. The samples they studied had masses of between one and three milligrams, which is considerably larger than the masses of the samples measured in this work. Radioactivity-induced self-heating may have biased the temperature measurements of the large samples and might account for the absence of the detection of antiferromagnetic ordering. An alternative explanation for the discrepancy is that the antiferromagnetic behavior is strongly influenced by the presence of magnetic impurities, such as other actinides. Sample purity and characterization problems have frequently led to discrepancies in the measurements of low temperature magnetic ordering behavior of lanthanide oxide materials.¹⁹

¹⁸L. R. Morss *et al.*, *J. Less-Common Met.* **127**, 251 (1987).

¹⁹L. Eyring, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 3, p. 391.

Summary of the Oxides

The numerical results of the susceptibility measurements on the californium oxides are included in the summary table in Chapter VIII. In general, the magnetic measurements indicate the following:

- The measured effective paramagnetic moments are reasonably consistent with the values predicted by the intermediate coupling calculations, when charge states are based on the stoichiometry.
- Crystal field splittings in the californium oxides are larger than the splittings in the lanthanide oxides. This would be expected from the greater radial extension of the $5f$ electrons compared to the $4f$ electrons.
- All of the californium oxide materials exhibited antiferromagnetic ordering at temperatures predominantly between 6 and 10 K (with bcc Cf_2O_3 ordering above 20 K). These temperatures are in general somewhat higher than the Néel temperatures that have been reported for the lanthanide oxides. It is expected that the greater radial extension of the $5f$ electrons could lead to larger exchange interactions and higher ordering temperatures in californium, compared to the lanthanides.
- The observed antiferromagnetic ordering in bcc Cf_2O_3 is in conflict with the results reported by others.

CHAPTER VI

CALIFORNIUM MONOPNICTIDES

The actinides and the lanthanides form binary compounds with the pnictogens (group VA elements) that have the NaCl-type fcc crystal structure (see Table B-6, page 153). The lanthanide and light actinide monopnictides are known to have partially filled conduction electron bands and display semi-metallic physical characteristics.^{1,2} The monopnictides of californium and the other heavy actinides are presumed to have similar characteristics. Since the presence of conduction electrons can have a significant effect on cooperative magnetic behavior, the magnetic properties of the monopnictides of the lanthanides and light actinides have been extensively studied. Magnetic measurements of the californium monopnictides indicate that their cooperative magnetic behavior is more similar to the behavior of the monopnictides of the lanthanides than to that of the light actinides.

Experimental Details

Magnetic measurements were performed on samples of CfN, CfAs and CfSb. The individual samples that were studied are described in Table VI-1. The monoarsenide and monoantimonide samples were prepared approximately six years prior to the taking of the magnetic data. X-ray analyses verified that the sample lattice parameters had not changed significantly since the

¹F. Hulliger, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 4, p. 162.

²J.-M. Fournier and R. Troc, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1985), Vol. 2, p. 84.

Table VI-1. Summary of the californium monopnictide samples.

Sample designation	Mass of Cf (μg)	μ_{eff} (μ_{B})	θ_{P} (K)	T_{N} (K)
CfN #3a	10.3	10.06 ^a	-44.1 ^a	25
CfAs #1	68.5	9.97 ^a	-19.8 ^a	17
CfAs #2	35.4	10.05 ^a	-24.2 ^a	17
CfSb #1	45.3	10.16 ^b	-14.0 ^b	20

^aFor the temperature range $80 < T < 340$ K.

^bFor the temperature range $120 < T < 340$ K.

preparation. The magnetic susceptibility of the antimonide sample was strongly field dependent at room temperature, indicating that the sample was much more heavily contaminated by a saturable magnetic material (probably iron) than were the other samples. The susceptibility data for that sample was taken at as high a magnetic field as possible (about 45 kilogauss). All of the other monopnictide samples contained about as much magnetic contamination as did the californium metal and oxide samples. The physical arrangement of the magnetic susceptometer was identical to the arrangement used for the californium oxide measurements.

Magnetic Measurements: Results and Interpretation

Paramagnetic Behavior

The results of the magnetic susceptibility measurements are shown in Figures VI-1 to VI-6 and are summarized in Table VI-1. All three of the monopnictides that were studied exhibit Curie-Weiss behavior at temperatures above about 100 K. The measured effective paramagnetic moments of the

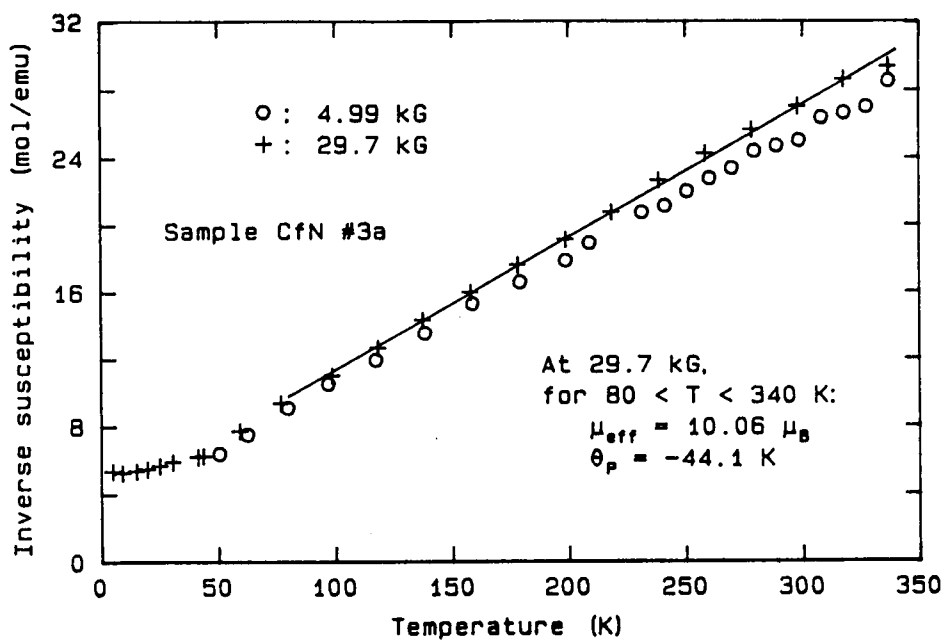


Figure VI-1. Inverse magnetic susceptibility of CfN.

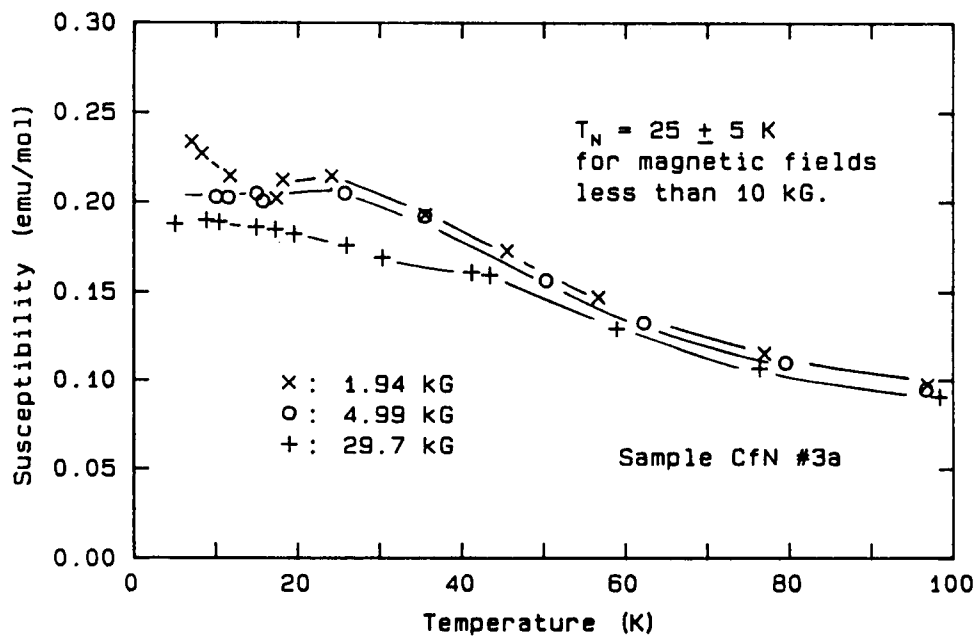


Figure VI-2. Magnetic susceptibility of CfN below 100 K.

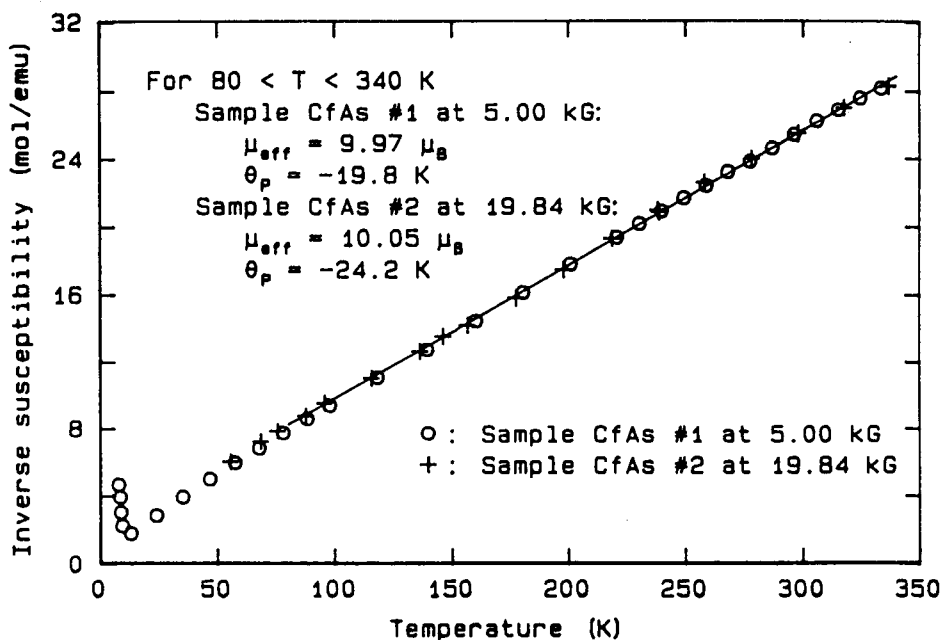


Figure VI-3. Inverse magnetic susceptibility of CfAs.

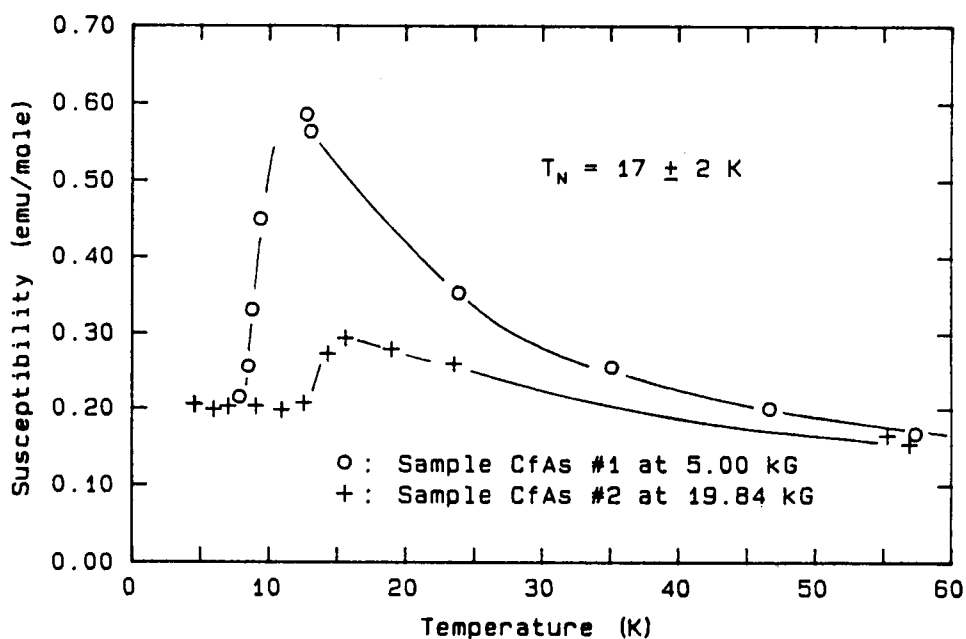


Figure VI-4. Magnetic susceptibility of CfAs below 60 K.

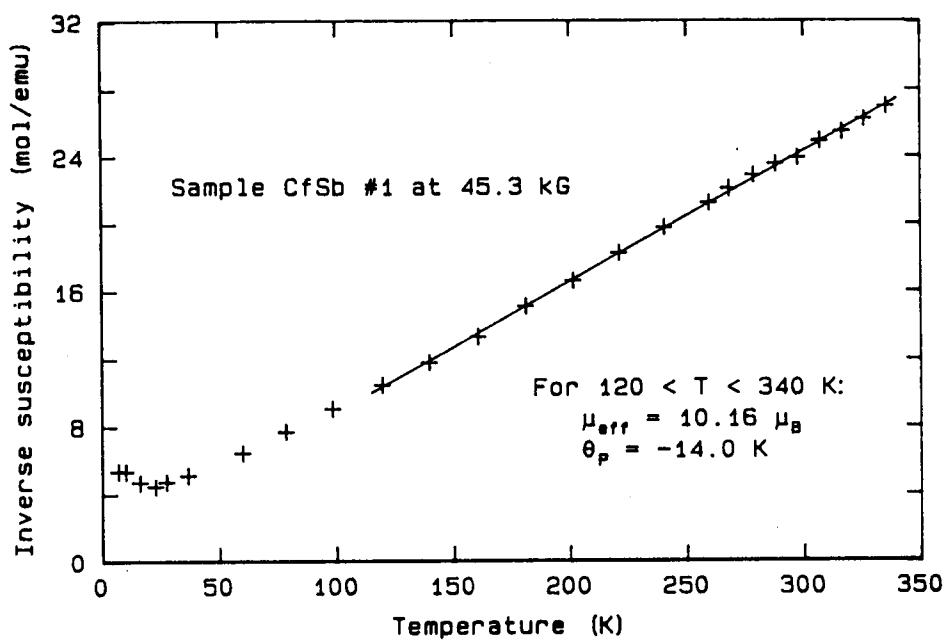


Figure VI-5. Inverse magnetic susceptibility of CfSb.

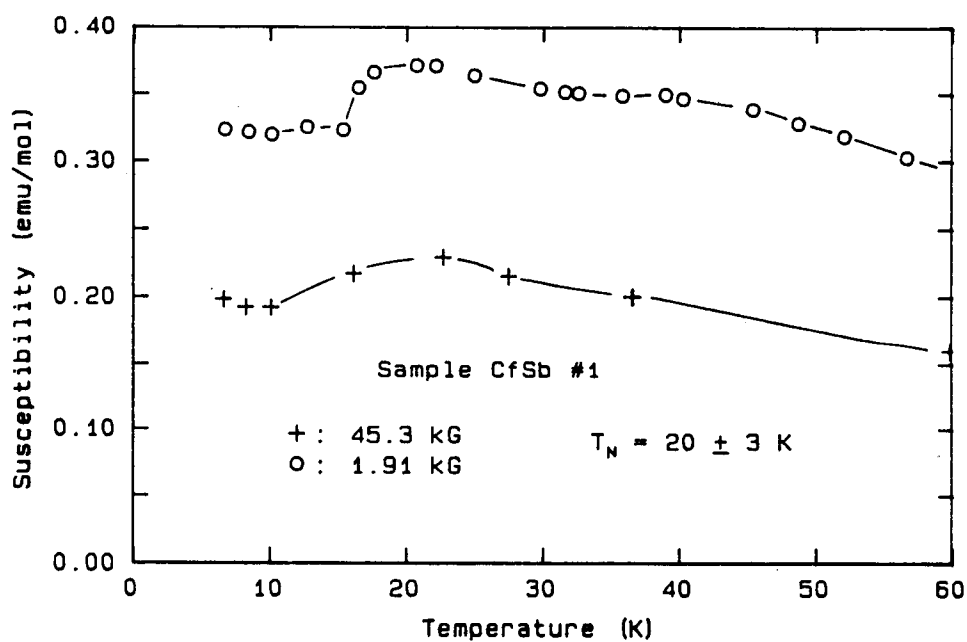


Figure VI-6. Magnetic susceptibility of CfSb below 60 K.

three compounds varied between $10.0 \mu_B$ and $10.2 \mu_B$, which is consistent with the assumption that the californium is in the 3+ charge state. Except for some cerium compounds, all lanthanide monopnictides are trivalent compounds.³ As noted previously, however, Cf^{2+} has approximately the same effective paramagnetic moment as Cf^{3+} and the effective paramagnetic moment does not conclusively indicate the charge state.

Polarization of conduction electrons by the 5f electrons has been observed in metallic light actinide compounds, including the monopnictides.⁴ A reduction in both the measured ordered moment and the effective paramagnetic moment can result from the polarization. The paramagnetic moments determined in these californium measurements are consistent with the expected intermediate coupling value, within the experimental uncertainty, and do not indicate a degree of polarization as great as may be present in californium metal. The Weiss constants that were measured in the mononitride, monoarsenide and monoantimonide are -45 ± 5 , -22 ± 5 and -15 ± 3 K, respectively.

Crystal Fields

Although the cubic (O_h) symmetry at the californium sites in the NaCl-type crystal structure of the monopnictides simplifies the consideration of crystal field effects, the magnetic susceptibility measurements are not suitable for detailed crystal field analysis. Since magnetic ordering occurs at relatively high temperatures, any effects the crystal field might have on the susceptibilities, other than a contribution to θ_P , are masked. The inverse susceptibility

³Hulliger.

⁴P. Jena *et al.*, Phys. Rev. B 18, 3562, 1978.

curves are reasonably linear, down to temperatures near the ordering temperatures and the ordering temperatures are not significantly different from the Weiss constants. Both of these factors indicate that the crystal field effects are smaller in the mononictides than in the oxides.

Crystal field parameters have been measured or estimated for most of the lanthanide mononictides.⁵ Inelastic neutron scattering has proven useful for measuring the splitting directly.⁶ In general, both B_2^0 and B_4^0 are positive and B_4^0 is about one-tenth as large as B_2^0 . For the lanthanide mononitrides, B_2^0 is roughly 1500 cm^{-1} , while for the monoarsenides and monoantimonides B_2^0 is typically about 500 cm^{-1} . In contrast to the lanthanides, no well-defined crystal field levels have been observed with neutron inelastic scattering in the light actinide NaCl-type compounds.⁷ This is apparently due to insufficient localization of the $5f$ electrons in comparison to the $4f$ electrons.

Assuming that the $5f$ electrons in the mononictides of californium are well-localized and that well-defined crystal field split levels exist, the magnitudes of the crystal field parameters can be estimated from the lanthanide values. A modified point charge model that ignores the conduction electrons has been shown to fit (although perhaps fortuitously) the lanthanide crystal field data reasonably well,⁸ and therefore an extrapolation to californium on the basis of $\langle r^k \rangle$ values may have merit. Based on the sizes of $\langle r^4 \rangle$ and $\langle r^6 \rangle$ for Cf^{3+} and Dy^{3+} (see Table III-5, page 40), a reasonable guess for the arsenide and antimonide crystal field parameters is $B_2^0 = 1500 \text{ cm}^{-1}$ and

⁵Hulliger, p. 172.

⁶R. J. Birgeneau *et al.*, Phys. Rev. B 8, 5345 (1973).

⁷M. B. Brodsky, Rep. Prog. Phys. 41, 1588 (1978).

⁸Birgeneau.

$B_8 = 150 \text{ cm}^{-1}$. Figures III-3(c) and 3(d) (page 49) indicate that for these parameters the ground state would be a Γ_6 doublet and that the first excited state, a Γ_8 quartet, would lie relatively close to the ground state. A detailed calculation using these parameters shows that the Γ_8 level would be about 25 cm^{-1} above the ground state Γ_6 and that the total splitting of the manifold would be about 350 cm^{-1} . The contribution to θ_p by this crystal field would be about -7 K . This analysis supports the indication that the crystal field splitting in the mononictides is significantly smaller than that in the oxides. The smaller lattice parameter of the mononitride results in larger crystal field splittings. In fact, the nitrogen ion is so small that the Cf-Cf distance in the nitride is not much greater than it is in the metal. If the parameters are a factor of about three larger for californium mononitride, as occurs in the lanthanides, then the total splitting of the manifold would be about 1000 cm^{-1} and the contribution to θ_p would be about -12 K .

Magnetic Ordering

All three of the mononictides that were studied exhibit cooperative magnetic behavior at temperatures below 50 K . The magnetic susceptibility of the mononitride shows a somewhat complex field-dependent behavior below about 30 K (see Figure VI-2). In applied magnetic fields of less than 10 kilogauss, antiferromagnetic ordering is indicated by a local maximum in the susceptibility at about 25 K . The maximum is very broad and shifts to lower temperatures in higher applied fields and may indicate a change in type of magnetic ordering, or metamagnetism.

The monoarsenide exhibits (see Figure VI-4) a very sharp maximum in the susceptibility at about 17 K that readily identifies antiferromagnetic

ordering. The monoantimonide susceptibility has structure that begins at about 50 K, with a relatively broad maximum occurring at about 20 K (Figure VI-6). If the crystal field parameters are roughly the magnitude estimated in the previous section, then the structure seen in the susceptibility measurements is primarily due to cooperative magnetic effects and not to crystal field effects.

The monpnictides of both the light actinides and the lanthanides exhibit a variety of cooperative magnetic behavior, and it is expected that the heavy actinides would behave in a related manner. In the light actinides, as the actinide-actinide distance increases with increasing pnictogen ion size (*i.e.*, from nitrogen to bismuth), ordering temperatures vary in a systematic manner, either monotonically increasing (U and Np) or increasing and then decreasing (Pu).⁹ The types of magnetic structures also vary systematically with actinide separation. Ordering temperatures are for the most part in the 100 to 300 K range. The increase in magnetic coupling with increasing actinide-actinide spacing is difficult to explain with direct exchange or superexchange, since both decrease in strength exponentially with increasing separation. Grunzweig-Genossar *et al.*¹⁰ have proposed an exchange mechanism that includes the RKKY-type interaction (see equation IV-4). The RKKY coupling has a very long range compared with direct and superexchange coupling. It also has a sinusoidal spatial behavior that can lead to the systematic variation in the magnetic ordering temperatures and structures that are seen in the light actinides as the distance between magnetic ions varies.¹¹

⁹D. J. Lam and A. T. Aldred, in *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974) Vol. I, p. 127.

¹⁰J. Grunzweig-Genossar *et al.*, *Phys. Rev* **173**, 562 (1968).

¹¹P. Erdös and J. M. Robinson, *The Physics of Actinide Compounds* (Plenum, New York,

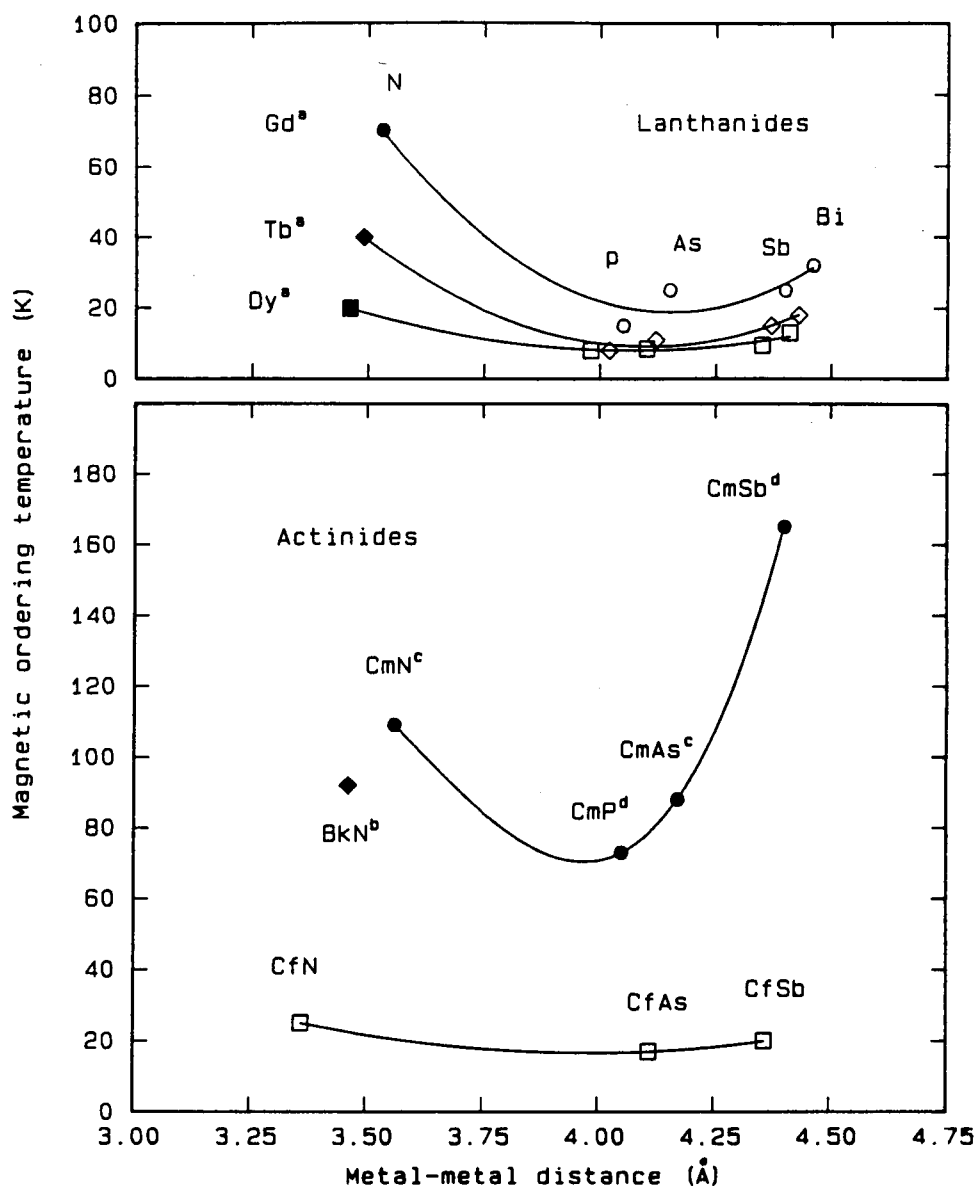
The lanthanide monopnictides order magnetically at temperatures that are generally well below 50 K and which are therefore much lower than the ordering temperatures of the light actinide monopnictides. Weaker exchange coupling is expected in the lanthanides due to the more limited radial extent of $4f$ wavefunctions compared to $5f$ wavefunctions. The RKKY coupling is also weaker in the lanthanides.¹² The dependence of ordering temperature on lanthanide-lanthanide distance is shown for several lanthanides in Figure VI-7(a). Most of the lanthanide mononitrides order ferromagnetically while the other monopnictides usually exhibit some form of antiferromagnetism or metamagnetism. The minimum ordering temperature usually occurs for the phosphide or arsenide. At the close lanthanide-lanthanide spacing of the nitrides, direct exchange apparently predominates over superexchange.¹³

The results of the californium monopnictide measurements and measurements on other heavy actinide monopnictides are shown in Figure VI-7(b). The behavior of the californium monopnictides is very similar to the behavior of the lanthanide monopnictides, indicating that the relative strengths of the various magnetic ordering mechanisms in californium may be similar to those in the heavy lanthanides. The curium monopnictides, in contrast, exhibit significantly higher transition temperatures than the californium monopnictides, and those temperatures vary substantially with actinide-actinide spacing. This behavior is more similar to the light actinide behavior. The limited data available for berkelium (only the mononitride has been studied) make it impossible to determine its behavior, but it is likely to fall between that of

1983) p. 125.

¹²Grunzweig-Genossar *et al.*

¹³Hulliger, p. 193.



^aF. Hulliger, in *Handbook of the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 4, p. 191.

^bS. E. Nave *et al.*, in Lawrence Berkeley Laboratory Report No. LBL-12441, 1981 (unpublished), p. 144.

^cB. Kanellakopoulos *et al.*, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 181.

^dS. E. Nave *et al.*, *Physica* 107B, 253 (1981).

Figure VI-7. Variation of the magnetic ordering temperatures of some heavy lanthanide and actinide monopnictides with the distance between the metal ions. The filled and open symbols indicate ferromagnetic and antiferromagnetic ordering, respectively.

Cm and Cf. The reduction in ordering temperatures for the californium monopnictides relative to the curium monopnictides is greater than the reduction predicted by DeGennes scaling (equation IV-5). This may indicate a smaller RKKY interaction for the californium monopnictides, due perhaps to a smaller conduction electron density. It may also indicate a smaller contribution of direct exchange and superexchange to the ordering behavior.

CHAPTER VII

CALIFORNIUM TRICHLORIDE

The two crystal structures of CfCl_3 are the UCl_3 -type hexagonal structure and the PuBr_3 -type orthorhombic structure. Details of the structures are given in Table B-7 (page 154) of Appendix B. Polycrystalline samples of both structures were studied as well as single-crystal samples of the hexagonal form.

A considerable amount of optical absorption work has been performed on the trichlorides of the lanthanides¹ and actinides² in the hexagonal UCl_3 -type crystal structure. In most of this work, the lanthanide or actinide was diluted in LaCl_3 , which provides the UCl_3 -type environment. Since californium trichloride crystallizes in the hexagonal structure, the studies on it have used the pure substance. Because of the relatively high site symmetry (C_{3h}) at the metal site in the UCl_3 -type structure, the splitting of the electronic levels due to the crystal field has been successfully parameterized. Data from the trichlorides has also been important in the development of *ab initio* methods for calculating the effects of the crystal field.³ The optical absorption spectrum of hexagonal CfCl_3 has been well characterized both at room temperature⁴ and at low temperatures and crystal field parameters have been

¹S. Hufner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic, New York, 1978), p. 56.

²W. T. Carnall and H. M. Crosswhite, Argonne National Laboratory Report No. ANL-84-90, 1985 (unpublished), p. 30.

³D. J. Newman and B. Ng, *J. Phys. C* **19**, 389 (1986).

⁴J. R. Peterson *et al.*, *Inorg. Chem.* **25**, 3779 (1986).

determined.⁵ The results from the optical studies can be compared with the present results from the magnetic measurements.

Experimental Details

The physical arrangement of the magnetic susceptometer for the CfCl_3 measurements was the same as described in Chapter II. Details of the preparation of the CfCl_3 samples are given in Appendix C. The relatively low melting point of CfCl_3 (545°C) allows preparation of the trichloride, conversion of the polycrystalline material between structural forms, and growth of a single crystal all to be carried out on one sample of material in a sealed quartz capillary. This method of processing reduces the possibility of sample contamination and changes in impurity content. Repeated heating of the samples can, however, lead to chemical reactions with the capillary walls.

The polycrystalline samples are described in Table VII-1. Two different preparations of polycrystalline material (designated 1 and 2) were studied in both crystal forms. It was possible to convert the same material back and forth several times between the two crystal structures. The initially prepared hexagonal materials were determined from powder X-ray analyses to be microcrystalline, while the samples after melting were macrocrystalline. Attempts were made to obtain samples of LaCl_3 containing about 10 percent Cf in order to eliminate cooperative magnetic behavior. These preparations led to multiphase samples, however, possibly because of the differences in melting points of CfCl_3 and LaCl_3 (545°C vs. 862°C) and possibly because of chemical reactions with the walls of the quartz capillary.

⁵Carnall and Crosswhite.

Table VII-1. Summary of the polycrystalline CfCl₃ samples.

Sample designation	Crystal structure	Mass of Cf (μ g)	μ_{eff} (μ_B) (100 < T < 340 K)	θ_D (K)	T _N (K)
1-1	hex	12.3	9.9	-11.0	8
1-2	ortho	12.3	10.1	-47.4	11
1-3	hex	12.3	10.1	-20.5	7
2-1	hex	19.5	10.2	-10.7	a
2-2	ortho	19.5	10.3	-25.8	13
2-3	hex	19.5	10.3	-13.1	8
2-4	ortho	19.5	10.4	-35.2	a

^aNot determined.

The single-crystal hexagonal samples are described in Table VII-2. Three preparations of material (designated A, B, and C) were measured at various orientations to the applied magnetic field. Two different methods were used to provide different orientations of the c-axis of the samples with respect to the magnetic field. Preparation A was measured initially in polycrystalline form as preparation 2. A single crystal was then grown and measured in the capillary in its as-grown orientation (sample A-1). The axis of the sample capillary is always parallel to the direction of the magnetic field in the susceptibility meter. The crystal was then broken out of the capillary (with some loss of material) and encapsulated in polyethylene to allow measuring the crystal at angles closer to the perpendicular (sample A-2) or parallel (sample A-3) orientation. The encapsulated material degraded, however, and only the measurements on A-2 were usable. The degradation was probably due to the absorption of water through a break in the polyethylene coating.

All measurements on preparations B and C were performed while the

Table VII-2. Summary of the hexagonal single-crystal CfCl_3 samples.

Sample designation	Mass of Cf (μg)	Orientation ^a	Mounting method
A-1 ^b	19.5	27.5°	capillary
A-2 ^c	14.0	82.3°	polyethylene
A-3 ^c	14.0	12.8°	polyethylene
B-1	221	14.2°	capillary
C-1	17.5	67.5°	capillary
C-2	17.5	8.4°, 16.7° ^d	capillary

^aAngle between c-axis and magnetic field.

^bMeasured as polycrystalline preparation 1 before being converted to a single crystal.

^cSame crystal as A-1, but removed from its quartz capillary and encapsulated in polyethylene.

^dSample consisted of two separate crystals.

materials were in their capillaries. After measuring crystal C-1, it was possible to remelt the material and grow another single-crystal sample (C-2) with a different orientation relative to the capillary. Sample C-2 was, however, composed of two separate crystals with the orientations of the c-axes differing by about 8° and with an average orientation of about 12°. Since the angular dependence of the susceptibility is very slight for near-parallel orientations (see equation III-10), the spread in the angular orientation of sample C-2 does not significantly affect its susceptibility. All crystals grown from preparation B had the same orientation relative to the capillary.

Although single crystals with the orthorhombic structure have been grown,⁶ none were prepared for this study. Interpretation of the magnetic

⁶J. H. Burns *et al.*, J. Inorg. Nucl. Chem. **35**, 1171 (1973).

measurements on single crystals of the orthorhombic form would be difficult because of the low crystal symmetry and lack of spectroscopically-determined crystal field splitting information.

Results of the Magnetic Measurements

Polycrystalline Samples

Inverse magnetic susceptibility curves for the polycrystalline samples are shown in Figure VII-1. A summary of the results of the measurements on all the samples is given in Table VII-1. As determined from a linear fit of the data to the Curie-Weiss law in the temperature range from 100 to 340 K, both the hexagonal and orthorhombic crystal forms have the same effective paramagnetic moment, $10.2 \pm 0.2 \mu_B$. The Weiss constants for this temperature range are -13 ± 5 K for the hexagonal form and -37 ± 10 K for the orthorhombic form. The relatively large variation in the θ_p values from sample to sample may be due to a preferred crystal orientation in the macrocrystalline samples, combined with the anisotropy of the susceptibility.

The magnetic susceptibility curves for the polycrystalline samples below 20 K are shown in Figure VII-2. They indicate that both crystal structures undergo antiferromagnetic ordering. The ordering temperatures are 7 ± 1 K and 13 ± 2 K for the hexagonal and orthorhombic forms, respectively. The susceptibility curves and the magnetization curves at 4.4 K (Figure VII-3) indicate that both forms exhibit metamagnetic behavior. The antiferromagnetic ordering disappears at magnetic fields above about 10 kilogauss for the hexagonal form and about 20 kilogauss for the orthorhombic form. At 4.4 K, the magnetization of the hexagonal form approaches a saturation moment of about $6.5 \mu_B$ per atom at magnetic fields well below 50 kG. The magnetization

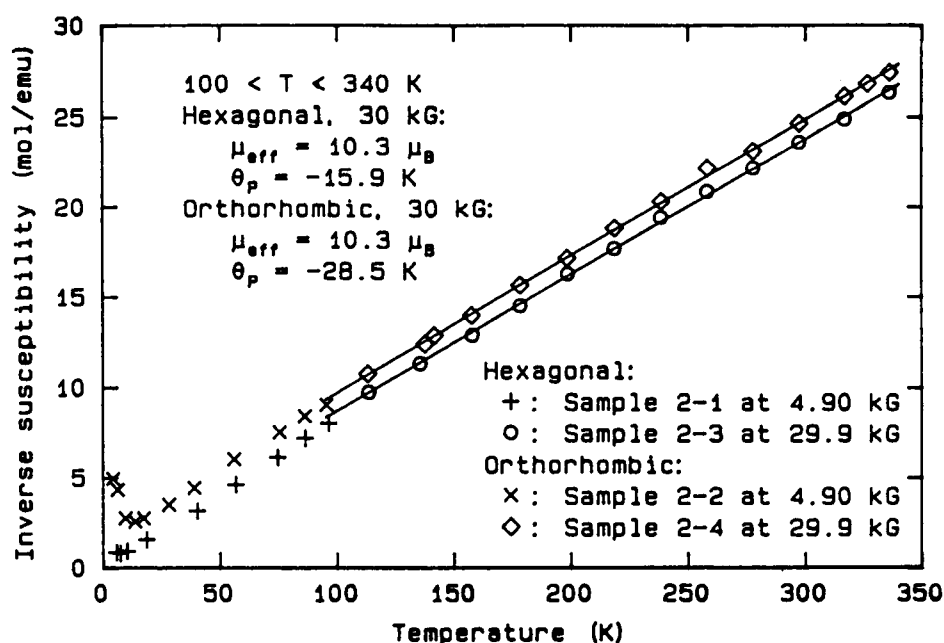


Figure VII-1. Inverse magnetic susceptibility of polycrystalline CfCl_3 in both the hexagonal and orthorhombic crystal structures.

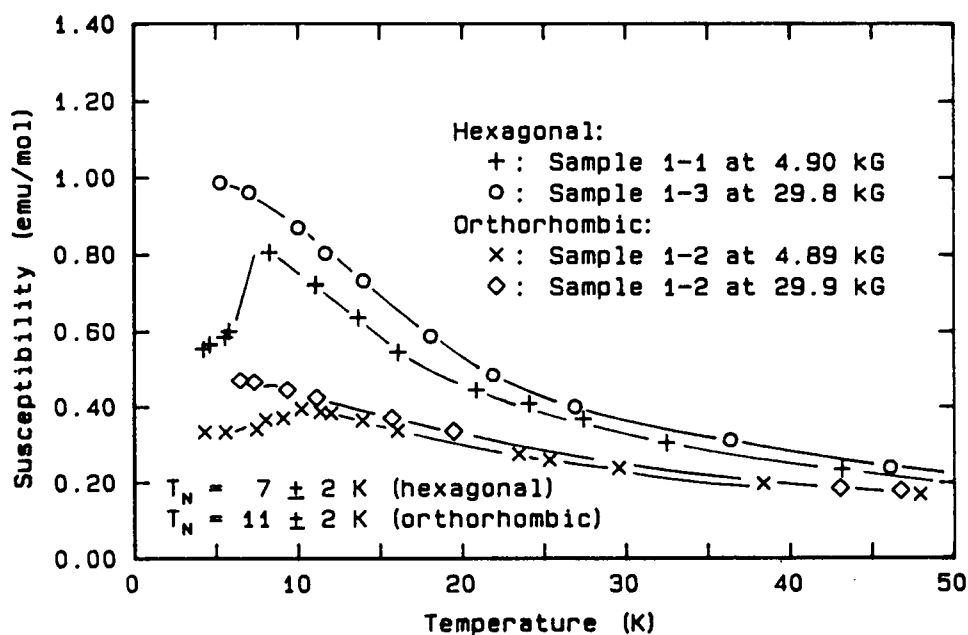


Figure VII-2. Magnetic susceptibility of polycrystalline CfCl_3 below 20 K in both the hexagonal and orthorhombic crystal structures.

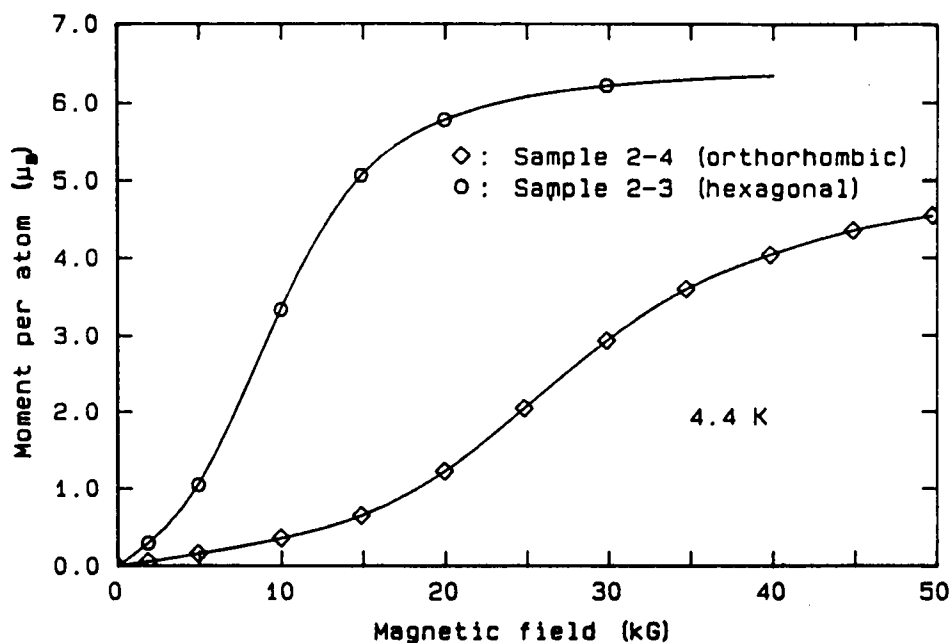


Figure VII-3. Magnetization as a function of magnetic field at 4.4 K for polycrystalline CfCl_3 in both the hexagonal and orthorhombic crystal structures.

curve for the orthorhombic form, however, is still increasing at 50 kG, and appears to saturate at a somewhat lower moment value than does the hexagonal form. Demagnetizing effects in the samples are relatively small. If the polycrystalline samples are assumed to be roughly spherical, with $D = 1/3$, then the internal field is reduced by about 2 kilogauss at magnetizations equivalent to $6 \mu_B$ per atom.

Single-Crystal Samples

The results of the magnetic measurements on the hexagonal single crystals are shown in Figures VII-4 to VII-6. The inverse susceptibility curves clearly show anisotropy in the susceptibility. As noted in Chapter III, the axial symmetry of the hexagonal structure allows the orientation dependence of the susceptibility to be expressed in terms of susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the c-axis. For preparation A, $\chi_{\parallel}$ and $\chi_{\perp}$ were

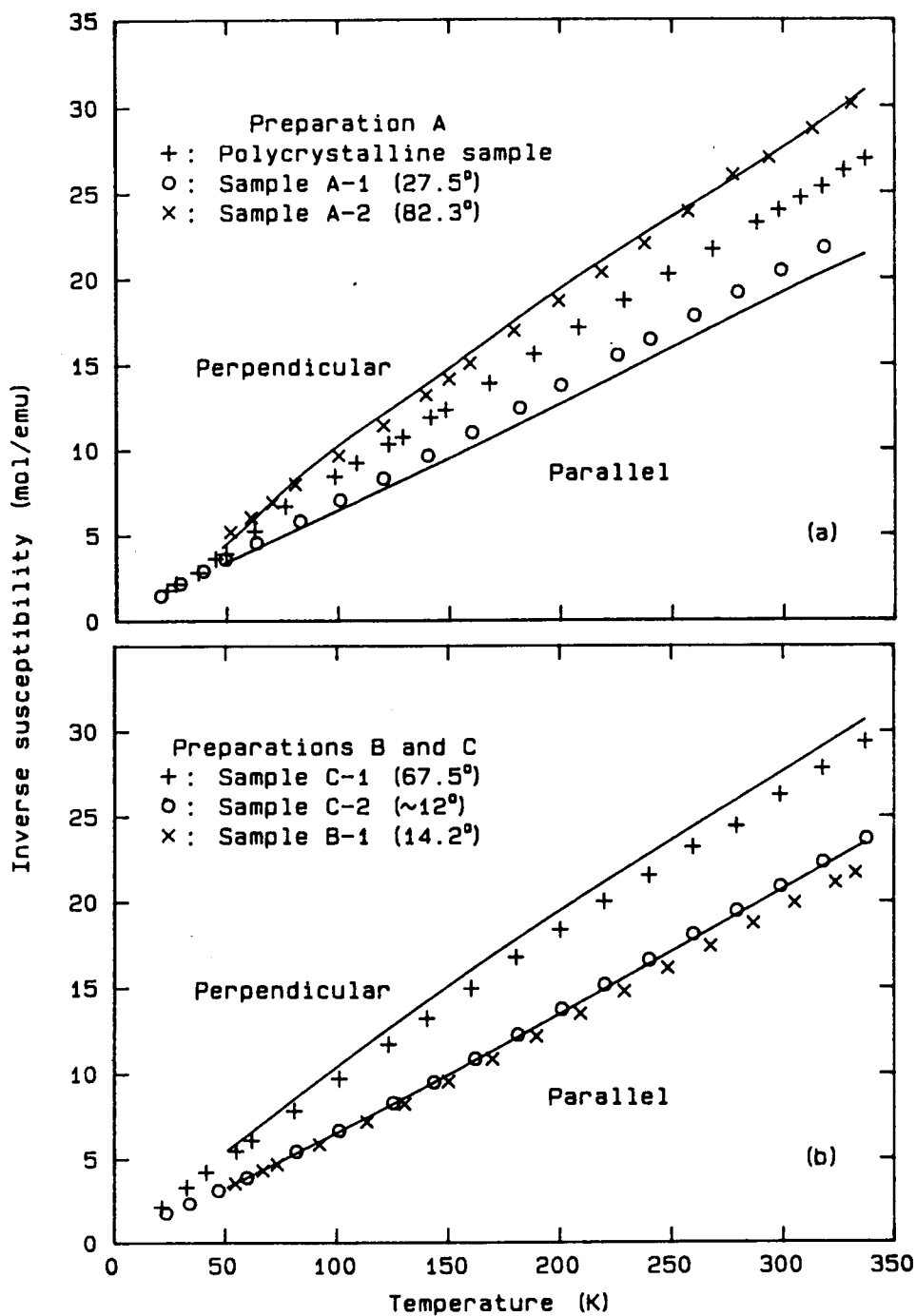


Figure VII-4. Inverse magnetic susceptibility of hexagonal single-crystal CfCl_3 . The solid lines in (a) show the parallel and perpendicular susceptibilities and are determined from the data for the polycrystalline sample and sample A-1 using equation (VII-1) from the text. The solid lines in (b) are determined from the data for samples C-1 and C-2 using equation (VII-2).

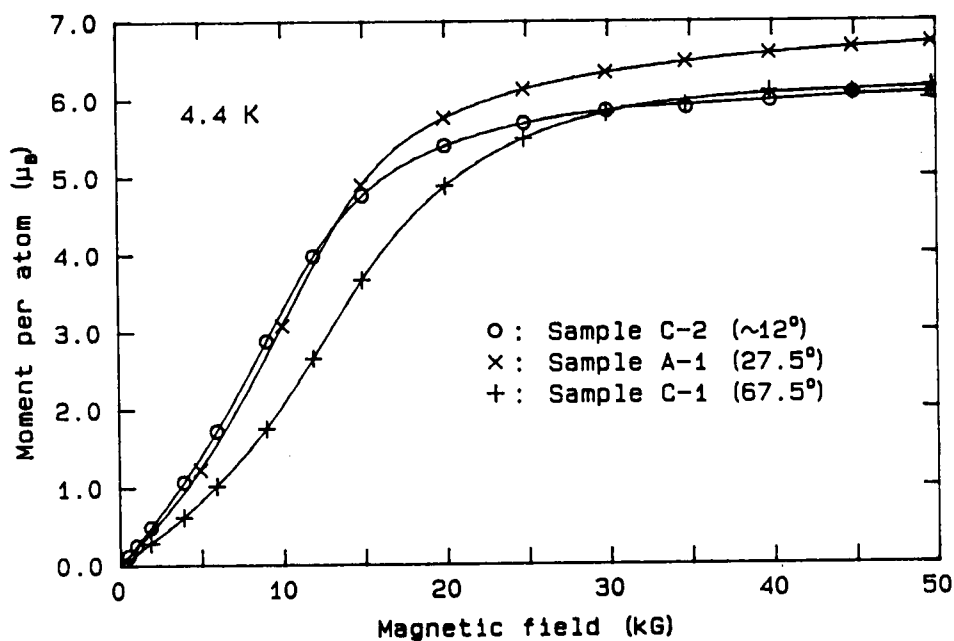


Figure VII-5. Magnetization of hexagonal single-crystal CfCl_3 at 4.4 K for various orientations of the c-axis with respect to the applied magnetic field.

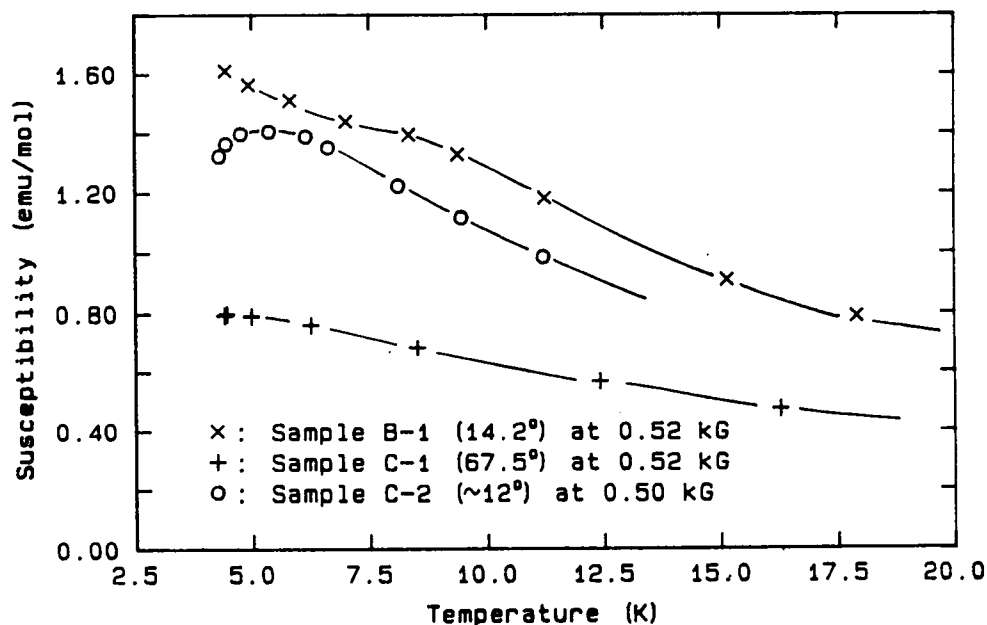


Figure VII-6. Magnetic susceptibility of hexagonal single-crystal CfCl_3 below 20 K.

determined from the measured polycrystalline susceptibility, χ_P , and the single-crystal susceptibility at one angle θ , χ_θ . The susceptibilities were calculated using

$$\chi_{\parallel} = \frac{\sin^2\theta \chi_P - 2/3 \chi_\theta}{1/3 \sin^2\theta - 2/3 \cos^2\theta}$$

$$\text{and } \chi_{\perp} = \frac{\cos^2\theta \chi_P - 1/3 \chi_\theta}{2/3 \cos^2\theta - 1/3 \sin^2\theta}, \quad (\text{VII-1})$$

which are derived from equations III-9 and III-10. The solid lines of Figure VII-4(a) show the results of the calculation. Similarly for preparation C, $\chi_{\parallel}$ and $\chi_{\perp}$ were calculated from two crystal orientations θ and θ' from

$$\chi_{\parallel} = \frac{\sin^2\theta \chi_{\theta'} - \sin^2\theta' \chi_\theta}{\cos^2\theta' \sin^2\theta - \sin^2\theta' \cos^2\theta}$$

$$\text{and } \chi_{\perp} = \frac{\cos^2\theta \chi_{\theta'} - \cos^2\theta' \chi_\theta}{\sin^2\theta' \cos^2\theta - \cos^2\theta' \sin^2\theta}. \quad (\text{VII-2})$$

The results of the calculation for preparation C are shown in Figure VII-4(b). The $\chi_{\perp}$ determined in this manner for preparations A and C are in good agreement and are consistent with the nearly-perpendicular measurement of sample A-2. There is, however, considerable discrepancy in the parallel susceptibilities determined from preparations A and C. The results of measurements of preparation B are more in line with the results of A than with those of C. This discrepancy may be an indication of the presence in the samples of undetected crystal inclusions or of impurities due to chemical reactions with the quartz capillary walls.

Magnetization curves for the single-crystal samples at 4.4 K in magnetic fields up to 50 kilogauss are shown in Figure VII-5. The metamagnetic behavior is clearly evident, with the antiferromagnetic ordering disappearing at fields above about 10 kilogauss. There is little variation of the saturation moment with crystal orientation, although orientations closer to the parallel

orientation saturate at slightly lower magnetic fields. The single-crystal samples were conical in shape with the base diameter about equal to the height and were oriented with the cone axis parallel to the magnetic field. With this geometry and orientation, the demagnetization factor D is estimated to be about $1/2$, or slightly greater than that of a sphere. At sample magnetizations equivalent to $6 \mu_B$ per atom, the internal field is reduced by approximately 3 kilogauss when $D = 1/2$.

The indication of antiferromagnetic ordering by the presence of a maximum in the magnetic susceptibility was not as pronounced in the single-crystal samples as it was in the polycrystalline samples (see Figure VII-6). Only one sample (Sample A-1 with a 27.5° orientation) exhibited a maximum above 4.4 K at 5 kilogauss. The other samples, with orientation angles both smaller and larger than that of A-1, either had no maximum above 4.4 K or had a maximum only at fields below 0.5 kilogauss. These results indicate that the field and temperature dependencies of the antiferromagnetic ordering may be quite sensitive to subtle variations from sample to sample such as stress, crystallinity and impurity content. From the two measurements on preparation C at 12° and 67.5° , where there should be little impurity change, the indication is that the antiferromagnetic ordering is weaker at larger orientation angles. At 67.5° , no maximum was observed above 4.4 K at any magnetic field, whereas at 12° , a maximum was evident at about 6 K and 0.5 kilogauss.

Interpretation of the Magnetic Measurements

Polycrystalline Samples

The effective paramagnetic moments measured for the polycrystalline samples of both crystal structures of CfCl_3 are in excellent agreement with the

intermediate coupling value. The values of the Weiss constant, θ_p , for the polycrystalline samples reflect the influence of both cooperative magnetic effects and crystal field splitting. For the orthorhombic form, deviation from the high temperature Curie-Weiss behavior occurs with decreasing temperature at about 100 K, whereas for the hexagonal structure the deviation begins at a temperature of about 60 K. This indicates that the crystal field splitting in the orthorhombic form may be somewhat greater than that in the hexagonal form. The broadening of the major optical absorption envelopes in the room temperature spectrum of the orthorhombic form relative to the hexagonal form⁷ may also indicate a greater total crystal field splitting in the former. Therefore, the larger magnitude of the θ_p value for the orthorhombic structure is consistent with the observed higher antiferromagnetic transition temperature and the possibility of greater crystal field splitting.

Crystal Field Anisotropy

The symmetry of the californium ion sites in hexagonal CfCl_3 is C_{3h} , and the five crystal field parameters required are B_0^2 , B_0^4 , B_0^6 , $\text{Re}(B_6^6)$ and $\text{Im}(B_6^6)$. The symmetry is so close to D_{3h} , for which B_6^6 is real, that the imaginary part of B_6^6 is usually ignored in this crystal structure. From optical absorption measurements, Carnall and Crosswhite⁸ have determined the crystal field parameters listed in Table VII-3. The splitting of the $J = 15/2$ ground state manifold into eight Kramer's doublets by the crystal field is shown in Figure VII-7, and the symmetry of the wavefunctions of these levels is shown in Table III-8, page 45. The crystal field can mix different J values up to

⁷Peterson *et al.*

⁸Carnall and Crosswhite.

Table VII-3. Crystal field parameters of hexagonal CfCl_3 .

Source of parameters	B_0^2	B_0^4	B_0^6 (cm^{-1})	B_6^6	N_V^a	λ^b (mol/emu)
Magnetic susceptibility ^c	510 ± 100	-1020 ± 200	-610 ± 400	1460 ± 1000	2600 ± 1300	-1.1 ± 0.4
Optical absorption ^d	476 ± 36	-1108 ± 73	-1367 ± 79	963 ± 63	2430 ± 150	-1.2 $\pm 0.3^e$
Dy^{3+} in LaCl_3^f (absorption)	182	-311	-371	271	650	—

^aAuzel scalar crystal field parameter (see equation III-6).

^bMolecular field constant.

^cAverage for preparations A and C.

^dW. T. Carnall and H. M. Crosswhite, Argonne National Laboratory Report No. ANL-84-90, 1985 (unpublished), p. 30.

^eDetermined by calculating the magnetic susceptibility from the optical absorption crystal field parameters and comparing with the measured susceptibility.

^fJ. D. Axe and G. H. Dieke, J. Chem. Phys. 37, 2364 (1962).

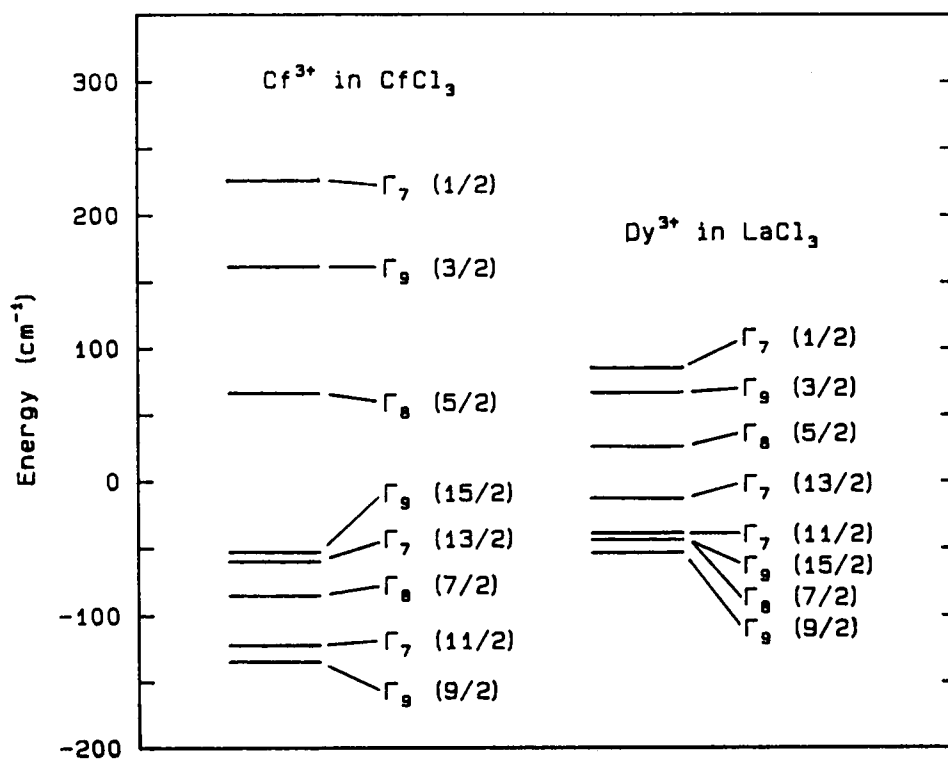


Figure VII-7. Crystal field splitting of Cf^{3+} and Dy^{3+} in an hexagonal crystal field. See Table VII-3 for the crystal field parameters and references. The J_z value that contributes most to each level is indicated in parenthesis.

$\Delta J = 6$, but since the magnitude of the crystal field splitting is relatively small, J mixing is not important for the ground state of CfCl_3 . That is, inclusion of J mixing changes the total splitting of the ground state manifold by only 10 cm^{-1} out of 360 cm^{-1} . Furthermore, the contribution to the ground state wavefunctions by the mixed J states is less than one percent.

If a molecular field model (see equation III-16) is used to account for the influence of cooperative magnetic effects on the magnetic susceptibility of the hexagonal crystal form of CfCl_3 above the ordering temperature, then the experimental magnetic susceptibility data can be fit with five parameters: B_0^2 , B_0^4 , B_0^6 , B_6^6 and λ . The results of parametric fits of the magnetic susceptibility data for temperatures greater than 50 K, allowing all five parameters to vary during the fitting process, are summarized in Table VII-3 and Figure VII-8. The resulting crystal field parameters are in reasonable agreement with the parameters determined from the analysis of optical absorption spectra. The uncertainties in the magnetically-determined parameters are, however, quite large, especially for the sixth order parameters, and are due primarily to variations in the results from sample to sample. If the four crystal field parameters are fixed at the spectroscopically-determined values, then the molecular field constant, as determined from a fit to the susceptibility data, is $-1.2 \pm 0.3 \text{ mol/emu}$. In Figure VII-7 the crystal field splitting in CfCl_3 is compared with the splitting of dysprosium doped into LaCl_3 (pure DyCl_3 is monoclinic). The scalar crystal field parameters listed in Table VII-3 show that the crystal field in CfCl_3 is approximately 3.5 times greater than that in DyCl_3 . This is roughly in line with the larger $\langle r^k \rangle$ values of Cf^{3+} relative to those of Dy^{3+} (see Table III-5, page 40).

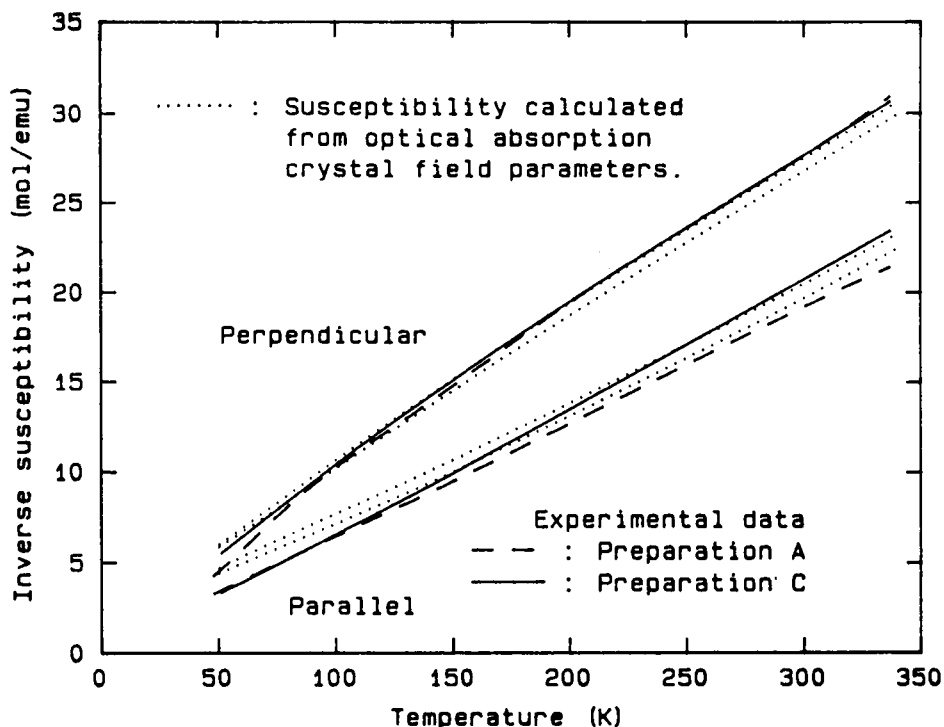


Figure VII-8. Comparison of the experimentally measured anisotropy in the magnetic susceptibility with the anisotropy calculated from optical absorption crystal field parameters. The calculated curves (drawn as double lines to show the uncertainty in the crystal field parameters) have been shifted to correspond to a molecular field constant that best matches the calculated curves and the magnetic data.

The angular dependence of the magnetization at 4.4 K can be compared with the magnetization calculated from the ground state crystal field wavefunctions. The moment per atom as a function of θ , the angle between the c-axis and the magnetic field, is calculated as in equation IV-3. At 4.4 K and 50 kilogauss, only the ground state is significantly populated thermally and therefore only its moment need be considered. A comparison of the measured moments at 4.4 K and 50 kilogauss with the values calculated using the optically-determined crystal field parameters is shown in Figure VII-9. At zero magnetic field, the ground state is a Γ_9 (see Figure VII-7) that is made up 97% by the $J_z = \pm 9/2$ state, and the first excited level consists principally of

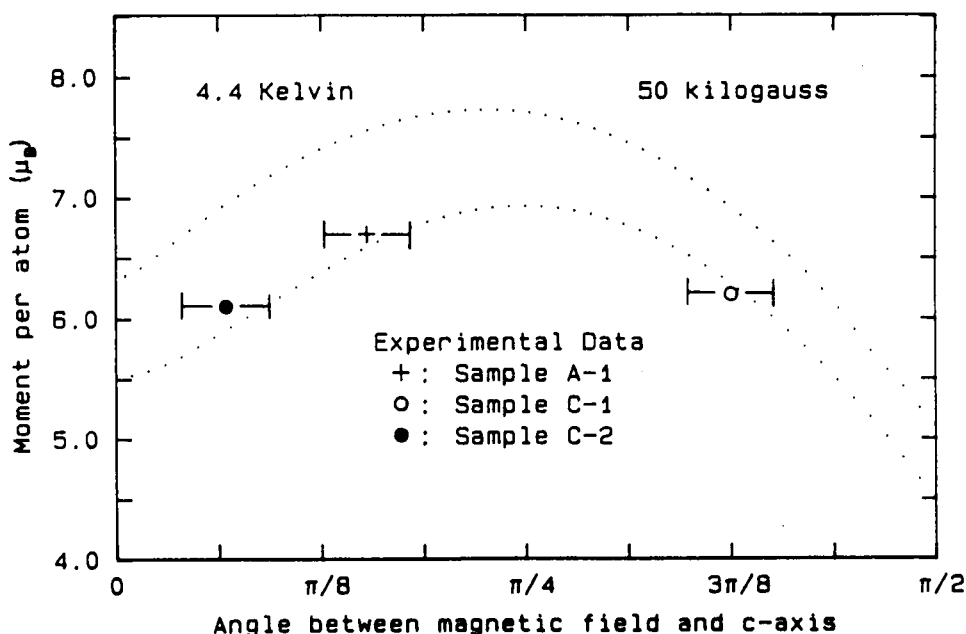


Figure VII-9. Magnetic moment per atom of californium at 50 kilogauss and 4.4 K as a function of the orientation of the hexagonal CfCl_3 single-crystal with respect to the magnetic field. The dotted lines indicate the moments that are predicted by the optical absorption crystal field parameters. The two lines show the uncertainties in the moment values due to uncertainties in the crystal field parameters.

the $J_z = \pm 11/2$ state. For nonparallel orientations, the magnetic field can mix these states, resulting in first an increase, and then a decrease in the moment of the ground state as θ increases. For these calculations, J mixing has a noticeable effect on the composition of the ground state wavefunctions and was therefore included. The moment values shown in Figure VII-9 were calculated assuming no molecular field. If a molecular field is considered, the experimental data fit the calculated curves reasonably well for values of the molecular field constant between -0.5 and $+0.1$ mol/emu.

Magnetic Ordering

The magnetic ordering of hexagonal CfCl_3 can be compared to the ordering that is observed in the light lanthanide trichlorides (cerium through

gadolinium) which also exist in the UCl_3 -type hexagonal form. GdCl_3 orders ferromagnetically at 2.2 K while the other trichlorides exhibit complex ordering behavior at even lower temperatures.⁹ A number of different magnetic structures have been proposed for the lanthanide trichlorides based on analyses considering dipole-dipole interactions and nearest- and next-nearest-neighbor exchange interactions.^{10,11} The antiferromagnetic ordering temperature for CfCl_3 , in comparison, is somewhat higher at about 7 K. This is consistent with the possibilities for larger exchange interactions due to the greater radial extension of the californium wavefunctions and for larger dipole-dipole interactions due to the greater moment of californium. The antiferromagnetic coupling in CfCl_3 at this temperature, however, seems to be relatively weak since it is destroyed by modest magnetic fields.

⁹J. C. Eisenstein *et al.* Phys. Rev. **137**, 1886 (1965).

¹⁰A. T. Skjeltorp, J. Appl. Phys. **49**, 1567 (1978).

¹¹R. A. Hunt, J. Phys. C **4**, 2572 (1971).

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The results of all the magnetic measurements on californium metal and compounds are summarized in Table VIII-1. In those cases where the strength of the crystal field could be estimated from the magnetic measurements or could be extrapolated from lanthanide or light actinide values, the Auzel crystal field strength is also listed.

The following general conclusions can be drawn from these measurements of californium's magnetic properties:

- All of the materials studied exhibit Curie-Weiss behavior at sufficiently high temperatures (generally above about 100 K). The effective paramagnetic moments are consistent with an intermediate coupling model of the californium ground state for which the total angular momentum J is a good quantum number.

- The crystal fields in californium compounds are in general several times greater than the crystal fields in the corresponding lanthanide compounds. This is consistent with the greater radial extension of $5f$ electrons compared to the radial extension of $4f$ electrons.

- The magnetic ordering temperature of Cf metal (like Cm and Bk metal) is lower than the ordering temperature of its lanthanide homologue, Dy metal. The strength of the indirect exchange interaction is therefore apparently weaker in the heavy actinides than in the heavy lanthanides.

- The antiferromagnetic ordering temperatures of the californium oxides and the trichloride are in general slightly higher than the ordering temperatures of the corresponding compounds of the lanthanides. Larger

Table VIII-1. Summary of the magnetic measurements on californium in the solid state.

Crystal structure	Eff. para. moment, $\mu_{\text{eff}} (\mu_B)^a$		Weiss const., θ_p (K) ^a		Néel temp. (K)	Cryst. field strength ^d (cm ⁻¹)
	Theory ^b	Exper.	Total	Cryst. field contribution ^c		
metal	10.2	9.7 ± 0.2	41 ± 3	-2	51 ± 2 ^e	700, 1300 ^f
Cf ₂ O ₃	10.2	10.2 ± 0.2	-80 ± 15	g	8 ± 2	g
Cf ₂ O ₃	10.2	9.9 ± 0.2	-115 ± 15	-35	22 ± 2	23000, 16000 ^h
Cf ₇ O ₁₂	9.8	9.4 ± 0.2	-95 ± 15	g	8 ± 2	g
CfO ₂	9.3	9.2 ± 0.2	-70 ± 10	-10	7 ± 2	4800
BaCfO ₃	9.3	9.2 ± 0.2	-210 ± 20	g	7 ± 2	g
CfN	10.2	10.1 ± 0.2	-45 ± 5	-12	25 ± 5	7100
CfAs	10.2	10.0 ± 0.2	-22 ± 5	-7	17 ± 2	2400
CfSb	10.2	10.2 ± 0.2	-15 ± 3	-7	20 ± 3	2400
CfCl ₃	10.2	10.2 ± 0.2	-13 ± 5	-5	7 ± 2	2430
CfCl ₃	10.2	10.2 ± 0.2	-35 ± 10	g	13 ± 2	g

^aThe applicable temperature ranges are shown on the inverse susceptibility plots for the individual compounds.

^bBased on intermediate coupling model, see Table III-9 (page 56).

^cEstimated contribution of the crystal field to θ_p .

^dAuzel scalar crystal field parameter, see equation III-6.

^eFerromagnetic Curie temperature.

^fFor the D_{3h} and D_{3d} sites, respectively.

^gNot estimated.

^hFor the C₂ and C_{3i} sites, respectively.

ⁱCubic perovskite structure.

exchange effects are to be expected because of the greater radial extension of the $5f$ electrons.

- Magnetic ordering in the semi-metallic californium monopnictides is similar, in terms of ordering temperatures and variation with the metal-to-metal distance, to the magnetic ordering in the lanthanide monopnictides. This may indicate that the relative strengths of the various exchange interactions (RKKY, superexchange and direct exchange) are similar in the californium monopnictides and lanthanide monopnictides.

All of the experimental results of this work can certainly be improved upon by additional, more detailed magnetic measurements. There are a number of unresolved points, however, that warrant special attention and additional study:

- The magnetic susceptibility of bcc Cf_2O_3 should be measured again to resolve the question of the existence of antiferromagnetic ordering at 22 K.

- Additional magnetic studies of californium doped into Y_2O_3 should be performed along with optical absorption studies of the same material to provide more details about the crystal field.

- A reexamination of BaCfO_3 may resolve the question of whether the behavior of the magnetic susceptibility in the temperature range below 100 K is due to crystal fields or to cooperative magnetic effects.

- More detailed magnetization measurements on the californium monopnictides should be carried out to more completely map out the temperature and magnetic field dependencies of the magnetic ordering.

- The determination of the magnetic structure of californium metal would be very useful in assessing the relative importance of the various types of magnetic interactions in the metal. Sufficient quantities of the metal to

allow neutron diffraction studies will probably not be available in the near (or distant) future, however. Single-crystal curium metal will eventually be studied in detail by neutron diffraction, and those results will shed some light on all of the dhcp heavy actinide metals.

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APPENDIXES

APPENDIX A

CALCULATION OF MATRIX ELEMENTS

The calculation of the electronic energy levels and magnetic properties of an atom involves the evaluation of matrix elements of the Hamiltonian of the atom. The important contributions to the Hamiltonian are the electron-electron coulomb interaction energy ($\mathcal{H}_{es}$), spin-orbit energy ($\mathcal{H}_{so}$), crystalline electric field energy ($\mathcal{H}_{cf}$), and the energy of interaction with an external magnetic field ($\mathcal{H}_Z$). The methods used to calculate the matrix elements of these terms of the Hamiltonian within the basis of LS coupled atomic states are described in this appendix.

Coulomb Interaction

The matrix elements of $\mathcal{H}_{es}$ for an f^n configuration can be written

$$\langle \alpha LS | \mathcal{H}_{es} | \alpha' L' S' \rangle = \delta_{S,S'} \delta_{L,L'} \sum_{k=0}^3 e_k E^k. \quad (\text{A-1})$$

The e_k angular parts of the matrix elements can be calculated in a step-wise manner using an expression of Racah,¹

$$\begin{aligned} e_k(f^n; \alpha \alpha' LS) &= \frac{n}{n-2} \sum_{\bar{\alpha} \bar{\alpha}' \bar{L} \bar{S}} (f^n; \alpha LS \{ | f^{n-1}; \bar{\alpha} \bar{L} \bar{S} \rangle \\ &\times e_k(f^{n-1}; \bar{\alpha} \bar{\alpha}' \bar{L} \bar{S}) (f^{n-1}; \bar{\alpha}' \bar{L} \bar{S} \{ | f^n; \alpha' LS \rangle). \end{aligned} \quad (\text{A-2})$$

The $(f^n; \alpha LS \{ | f^{n-1}; \bar{\alpha} \bar{L} \bar{S} \rangle$ are coefficients of fractional parentage. The coefficients of fractional parentage are used to construct the correctly anti-symmetrized LS coupled states of the f^n configuration from product

¹G. Racah, Phys. Rev. **76**, 1352 (1949).

states of single-electron wavefunctions and states of the f^{n-1} configuration. The coefficients of fractional parentage used in the calculations of this work are those tabulated by Nielson and Koster.² The e_k 's for the f^3 to f^7 configurations are calculated using equation A-2, starting with values for f^2 given by Nielson and Koster.³ The matrix elements for the conjugate f^{14-n} configuration are identical to those for the f^n configuration except for an additive constant.

Spin-Orbit Interaction

The spin-orbit matrix elements can be written as⁴

$$\begin{aligned} \langle f^n; \alpha LS, JM | \mathcal{H}_{so} | f^n; \alpha' L' S', JM \rangle &= \zeta (-1)^{J+L+S'} \left\{ \begin{matrix} L & L' & 1 \\ S' & S & J \end{matrix} \right\} \\ &\times \langle f^n; \alpha LS | \sum_{i=1}^N (\mathbf{s}_i \cdot \mathbf{l}_i) | f^n; \alpha' L' S' \rangle, \end{aligned} \quad (\text{A-3})$$

where ζ is the spin-orbit parameter. The term with six arguments in curly brackets is a 6- j symbol. The matrix element on the right-hand side of the equation can be expressed in terms of the reduced matrix element of V^{11} , a double irreducible tensor operator

$$\langle f^n; \alpha LS | \sum_{i=1}^N (\mathbf{s}_i \cdot \mathbf{l}_i) | f^n; \alpha' L' S' \rangle = \sqrt{84} \langle f^n; \alpha LS | V^{11} | f^n; \alpha' L' S' \rangle. \quad (\text{A-4})$$

The reduced matrix elements of V^{11} are evaluated with the aid of

²C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (M.I.T., Cambridge MA, 1963), pp. 6-52.

³*Ibid.*, p. 54.

⁴B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965) p. 38.

coefficients of fractional parentage,⁵

$$\begin{aligned} \langle f^n; \alpha LS | V^{11} | f^n; \alpha' L' S' \rangle &= n \sqrt{3/2} (-1)^L [(2L+1)(2L'+1)(2S+1)(2S'+1)]^{\frac{1}{2}} \\ &\times \sum_{\alpha \bar{L} \bar{S}} (-1)^{\bar{L} + \bar{S} + S + 3/2} \left\{ \begin{matrix} 3 & 3 & 1 \\ L & L' & \bar{L} \end{matrix} \right\} \left\{ \begin{matrix} \frac{1}{2} & \frac{1}{2} & 1 \\ S & S' & \bar{S} \end{matrix} \right\} \\ &\times (f^n; \alpha LS \{ | f^{n-1}; \alpha \bar{L} \bar{S} \} (f^{n-1}; \alpha \bar{L} \bar{S}) | f^n; \alpha' L' S'). \end{aligned} \quad (A-5)$$

The reduced matrix elements for the conjugate f^{14-n} configuration are identical to those for the f^n configuration except for a change in sign.

Crystal Field Interaction

If the crystal field interaction is expressed in the form

$$\mathcal{H}_{cf} = \sum_{k, q} B_q^k \left[\frac{4\pi}{2k+1} \right]^{\frac{1}{2}} Y_q^k, \quad (A-6)$$

then the matrix elements can be written in terms of the matrix elements of U_q^k , an irreducible tensor operator,⁶

$$\begin{aligned} \langle f^n; \alpha LS, JM | \mathcal{H}_{cf} | f^n; \alpha' L' S', J' M' \rangle &= \\ -7 \sum B_q^k \left[\begin{matrix} 3 & k & 3 \\ 0 & 0 & 0 \end{matrix} \right] \langle f^n; \alpha LS, JM | U_q^k | f^n; \alpha' L' S', J' M' \rangle. \end{aligned} \quad (A-7)$$

The term with six arguments in straight brackets is a 3- j symbol. The matrix elements of U_q^k are calculated from the reduced matrix elements of U^k ,

⁵R. D. Cowan, *The Theory of Atomic Structure and Spectra* (Univ. of Calif., Berkeley, 1981), p. 320.

⁶S.-K. Chan and D. J. Lam, in *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), Vol. I, p. 16.

$$\begin{aligned}
\langle f^n; \alpha LS, JM | U^k | f^n; \alpha' L' S', J' M' \rangle = \\
(-1)^{k+S+L'+2J-M} [(2J+1)(2J'+1)]^{\frac{1}{2}} \left\{ \begin{matrix} L & J & S \\ J' & L' & k \end{matrix} \right\} \\
\times \left[\begin{matrix} J & k & J' \\ -M & q & M' \end{matrix} \right] \langle f^n; \alpha LS | U_q^k | f^n; \alpha' L' S' \rangle. \quad (A-8)
\end{aligned}$$

The reduced matrix elements are calculated from

$$\begin{aligned}
\langle f^n; \alpha LS | U^k | f^n; \alpha' L' S' \rangle = \delta_{S,S'} [(2L+1)(2L'+1)]^{\frac{1}{2}} \\
\times \sum_{\bar{\alpha} \bar{L} \bar{S}} (f^n; \alpha LS | \{ f^{n-1}; \bar{\alpha} \bar{L} \bar{S} \} (f^{n-1}; \bar{\alpha} \bar{L} \bar{S}) | f^n; \alpha' L' S') \\
\times (-1)^{\bar{L}+k+3+L} \left\{ \begin{matrix} 3 & L & \bar{L} \\ L' & 3 & k \end{matrix} \right\}. \quad (A-9)
\end{aligned}$$

The matrix elements of conjugate configurations have opposite signs for even k .

Zeeman Interaction

Matrix elements of the interaction between the applied magnetic field and the magnetic moment of the atom are required for susceptibility calculations. Since the energy of interaction is $\mathbf{H} \cdot \boldsymbol{\mu}$, the matrix elements of $\boldsymbol{\mu}$ are needed. If the magnetic field is applied along the z -direction, then χ_z or $\chi_{||}$ is calculated from the matrix elements of μ_z which are evaluated from⁷

$$\begin{aligned}
\langle \alpha LS, JM | \mu_z | \alpha LS, JM \rangle &= M g(LSJ) \\
\text{and } \langle \alpha LS, JM | \mu_z | \alpha LS, (J-1)M \rangle &= (J^2 - M^2)^{\frac{1}{2}} f(LSJ)/2, \quad (A-10)
\end{aligned}$$

where $g(LSJ)$ and $f(LSJ)$ are defined as

⁷Chan and Lam, p. 47.

$$g(LSJ) = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

and $f(LSJ) = \left[\frac{(S+L+J+1)(S+L-J+1)(S+J-L)(L+J-S)}{J^2(2J+1)(2J-1)} \right]^{\frac{1}{2}}. \quad (\text{A-11})$

For crystals with axial symmetry, χ_1 is calculated from the matrix elements of μ_x which are evaluated using

$$\langle \alpha LS, JM | \mu_x | \alpha LS, J(M\pm 1) \rangle = [(J\pm M+1)(J\mp M)]^{\frac{1}{2}} g(LSJ)/2$$

and $\langle \alpha LS, JM | \mu_x | \alpha LS, (J-1)M \rangle = \pm [(J\mp M-1)(J\mp M)]^{\frac{1}{2}} f(LSJ)/4.$

(A-12)

APPENDIX B

CRYSTALLOGRAPHIC DATA

The crystallographic data for californium metal and for the californium compounds studied in this work are summarized in the tables of this appendix. The stereographic views of the crystal structures are to be viewed using the "crossed-eyes" method: the left image is viewed with the right eye and the right image is viewed with the left eye.

Table B-1. Crystallography of californium metal.^a

Double hexagonal close-packed structure

Space group: D_{6h}^4 ($P6_3/mmc$)

Californium atoms per unit cell: 4

Lattice parameters:

$a = 4.00 \text{ \AA}$ (divalent), $3.38 \text{ \AA}$ (trivalent)

$c = 12.80 \text{ \AA}$ (divalent), $11.04 \text{ \AA}$ (trivalent)

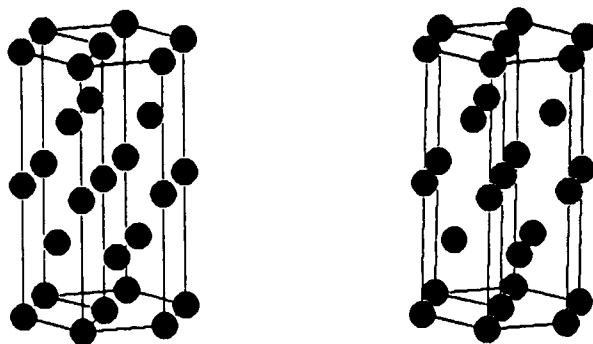
Two non-equivalent californium sites -

(1) B and C layers, D_{3h} site symmetry.

(2) A layers, D_{3d} site symmetry.

Cf-Cf distance:

$4.00 \text{ \AA}$ (divalent), $3.38 \text{ \AA}$ (trivalent)



A-B-A-C sequence of close-packed layers

Table B-1. (continued)

Face-centered cubic close-packed structure

Space group: O_h ($Fm\bar{3}m$)

Californium atoms per unit cell: 4

Lattice parameter:

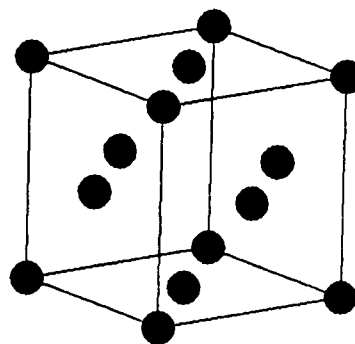
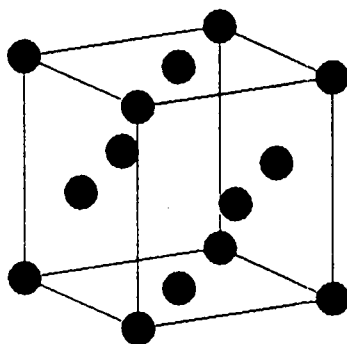
$a = 5.74 \text{ \AA}$ (divalent)

$a = 4.78 \text{ \AA}$ (trivalent)

O_h site symmetry.

Cf-Cf distance:

$4.06 \text{ \AA}$ (divalent), $3.38 \text{ \AA}$ (trivalent)



A-B-C sequence of close-packed layers

^aR. G. Haire in *Chemistry of the Actinide Elements*, edited by J. J. Katz *et al.* (Chapman and Hall, New York, 1986), Vol. 2, p. 1036.

Table B-2. Crystallography of CfO_2 .^a

Face-centered cubic (CaF_2 -type) structure

Space group: $\text{O}_h^{\bar{5}}$ ($\text{Fm}3\text{m}$)

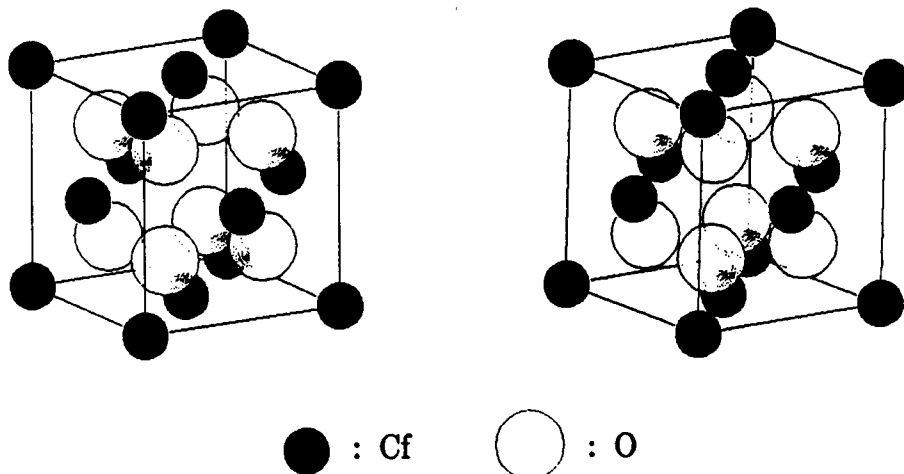
Formula units per unit cell: 4

Lattice parameter;
 $a = 5.31 \text{ \AA}$

Coordination number = 8, O_h site symmetry.

Eight oxygens located at corners of a cube at a distance
of $2.30 \text{ \AA}$ from the californium.

Cf-Cf distance: $3.76 \text{ \AA}$



^aR. P. Turcotte and R. G. Haire, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 267.

Table B-3. Crystallography of Cf_7O_{12} .^a

Rhombohedral (Tb_7O_{12} -type) structure

Space group: C_{3i}^2 ($R\bar{3}$)

Formula units per unit cell: 1

Lattice parameters:

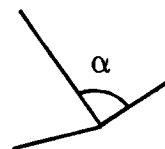
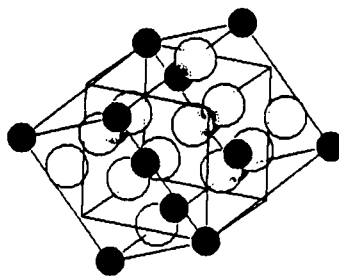
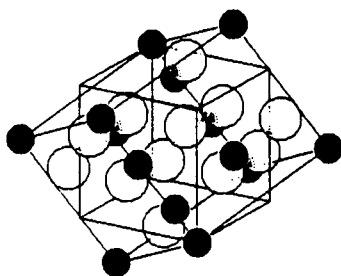
$$a = 6.60 \text{ \AA}$$

$$\alpha = 99.4^\circ$$

Two non-equivalent californium sites -

- (1) Six locations - coordination number = 7, C_3 site symmetry.
Oxygens at corners of distorted cube at average distance of 2.33 Å from californium.
- (2) One location - coordination number = 6, C_{3h} site symmetry.
Six oxygens at corners of distorted cube at average distance of 2.33 Å from californium. Two oxygens missing from body diagonal of cube.

Cf-Cf distance: 3.81 Å



● : Cf

○ : O

The relationship to the CfO_2 structure is shown by the inset cube.

^aR. P. Turcotte and R. G. Haire, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 267.

Table B-4. Crystallography of Cf_2O_3 .^a

Body-centered cubic (C-type rare earth sesquioxide) structure

Space group: T_h^7 (Ia3)

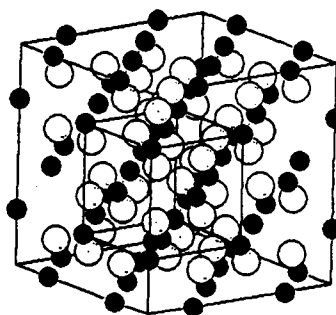
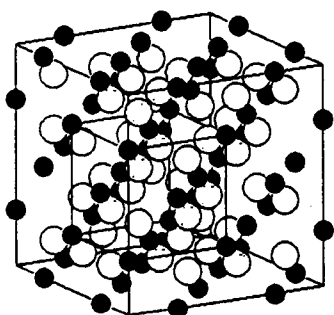
Formula units per cell: 16

Lattice parameter:
 $a = 10.83 \text{ \AA}$

Two non-equivalent californium sites -

- (1) 24 locations - coordination number = 6, C_2 site symmetry.
Six oxygens at corners of slightly distorted cube at average distance of $2.35 \text{ \AA}$ from californium. Two oxygens missing from face diagonal of cube.
- (2) 8 locations - coordination number = 6, C_{3i} site symmetry.
Six oxygens at corners of cube at distance of $2.35 \text{ \AA}$ from californium. Two oxygens missing from body diagonal of cube.

Cf-Cf distance: $3.83 \text{ \AA}$



● : Cf ○ : O

The relationship to the CfO_2 structure is shown by the inset cube.

Table B-4. (continued)

Monoclinic (B-Type rare earth sesquioxide) structure

Space group: C_{2h}^3 (C2/m)

Formula units per unit cell: 6

Lattice parameters:

$$a = 14.10 \text{ \AA}$$

$$b = 3.59 \text{ \AA}$$

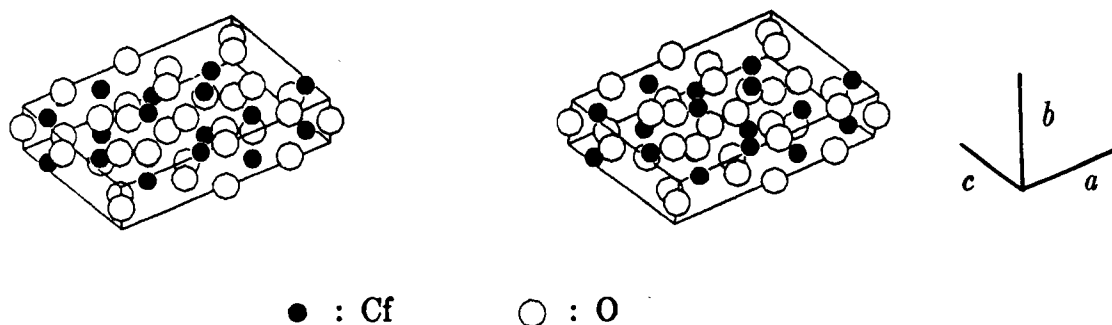
$$c = 8.80 \text{ \AA}$$

$$\beta = 100.2^\circ$$

Three non-equivalent californium sites -

- (1) 4 locations - coordination number = 7, C_3 site symmetry.
Six oxygens octahedrally located at average distance of 2.36 Å from californium. Seventh oxygen at 3.10 Å
- (2) 4 locations - coordination number = 7, C_{1h} site symmetry.
Six oxygens at corners of trigonal prism at average distance of 2.38 Å from californium. Seventh oxygen at 2.78 Å.
- (3) 4 locations - coordination number = 7, C_{1h} site symmetry.
Six oxygens at corners of trigonal prism at average distance of 2.34 Å from californium. Seventh oxygen at 2.74 Å.

Average Cf-Cf distance: 3.77 Å



^aR. P. Turcotte and R. G. Haire, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 267.

Table B-5. Crystallography of BaCfO₃.^a

Pseudo-cubic perovskite-type structure

Space group: O_h¹ (Pm3m)

Formula units per unit cell: 1

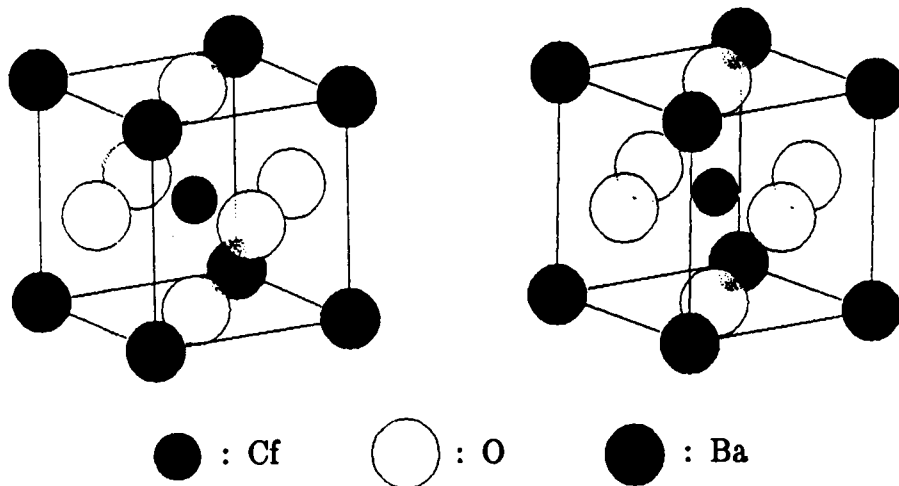
Lattice parameter:

$$a = 4.3 \text{ to } 4.4 \text{ \AA}$$

Coordination number = 6, O_h site symmetry.

Six oxygens octahedrally located at 2.2 Å from californium.

Cf-Cf distance: 4.3 to 4.4 Å



^aR. G. Haire, private communication.

Table B-6. Crystallography of the californium monopnictides.

Face-centered cubic (NaCl-type) structure

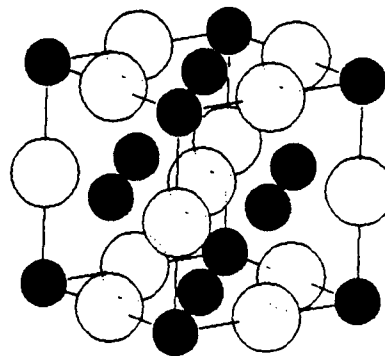
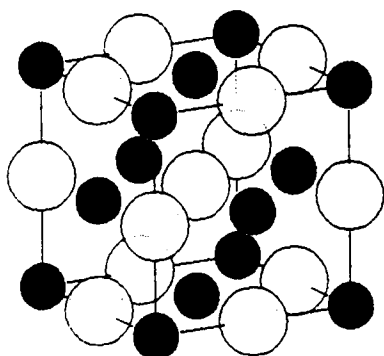
Space group: O_h^F (Fm3m)

Formula units per unit cell: 4

Lattice parameter (a) –
 nitride: 4.9 to 5.0 Å^a
 arsenide: 5.81 Å^b
 antimonide: 6.17 Å^b

Coordination number = 6, O_h site symmetry.
 Pnictogens located octahedrally around californium at
 following distances –
 nitride: 2.5 Å
 arsenide: 2.90 Å
 antimonide: 3.08 Å

Cf–Cf distances –
 nitride: 3.5 Å
 arsenide: 4.11 Å
 antimonide: 4.36 Å



^aR. G. Haire, private communication.

^bD. A. Damien *et al.*, Inorg. Nucl. Chem. Lett. **16**, 537 (1980).

Table B-7. Crystallography of CfCl_3 .^a

Hexagonal (UCl_3 -type) structure

Space group: C_{6h}^2 ($P6_3/m$)

Formula units per unit cell: 2

Lattice parameters:

$$a = 7.38 \text{ \AA}$$

$$c = 4.09 \text{ \AA}$$

Coordination number = 9, C_{3h} site symmetry.

Six chlorines in equilateral prism at $2.82 \text{ \AA}$ from californium. Two chlorines in Cf equatorial plane at $2.92 \text{ \AA}$.

Cf-Cf distance: $4.09 \text{ \AA}$

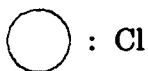
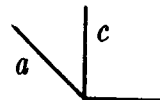
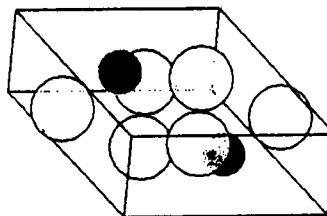
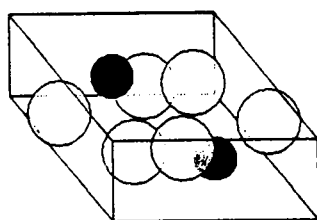


Table B-7. (continued)

Orthorhombic (PuBr₃-type) structure

Space group: D_{2h}^{17} (Cmcm)

Formula units per unit cell: 4

Lattice parameters:

$$a = 3.87 \text{ \AA}$$

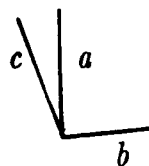
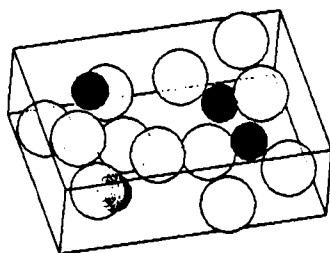
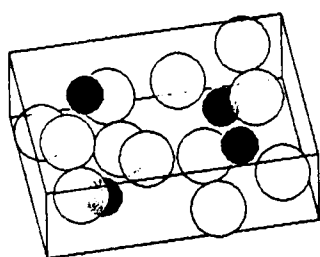
$$b = 11.75 \text{ \AA}$$

$$c = 8.56 \text{ \AA}$$

Coordination number = 8, C_{2v} site symmetry.

Six chlorines in isosceles trigonal prism – two at 2.94 Å and four at 2.81 Å from californium. Two chlorines in Cf equatorial plane at 2.69 Å.

Cf–Cf distance: 3.87 Å



^aJ. H. Burns *et al.*, J. Inorg. Nucl. Chem. **35**, 1171 (1973).

APPENDIX C

SAMPLE PREPARATION

The californium-249 that was used in the samples studied in this work was obtained from the beta-decay of berkelium-249, which has a half-life of 320 days. The berkelium was synthesized in the High Flux Isotope Reactor and chemically separated in the Transuranium Processing Plant facilities at the Oak Ridge National Laboratory (ORNL). The final chemical preparation of the samples was performed in the facilities of the Transuranium Research Laboratory at ORNL by University of Tennessee and ORNL personnel. The preparation and characterization methods are briefly described in this appendix. The special techniques that are required due to the small size and radioactivity of the samples are described in detail in the references. All samples except the CfCl_3 samples were sealed in quartz (fused silica) capillaries under vacuum or helium gas. The CfCl_3 samples were sealed under HCl gas. X-ray, optical absorption and magnetic analyses can all be performed with the samples in quartz capillaries. All of the polycrystalline samples were analyzed by powder X-ray diffraction to confirm crystal structures and lattice parameters.

Californium metal¹ is obtained by reducing californium sesquioxide with lanthanum metal. The californium metal is then distilled and condensed on a tantalum surface from which it is scraped.

The starting material for making the californium oxides² is californium

¹R. G. Haire, in *Actinides in Perspective*, edited by N. M. Edelstein (Pergamon, New York, 1982), p. 334.

²R. P. Turcotte and R. G. Haire, in *Transplutonium Elements 1975*, edited by W. Müller and R. Lindner (North-Holland, Amsterdam, 1976), p. 267.

oxalate. The body-centered cubic Cf_2O_3 is made by calcining the oxalate and then reducing it at 900–950°C in hydrogen, carbon monoxide or in a vacuum. Heating to 1100–1400°C produces the monoclinic form which is retained at lower temperatures. Cf_7O_{12} is formed by heating californium oxalate in oxygen. BaCfO_3 is prepared by calcining mixed nitrate salts of barium and californium, followed by treatment in oxygen. The californium dioxide samples that were measured in this work were originally prepared as BkO_2 and had radioactively decayed to CfO_2 .

The californium monpnictides³ are formed by heating californium metal with excess pnictogen in a quartz capillary. The excess pnictogen in the antimonide and arsenide samples is sublimed from the sample and condensed in another part of the capillary.

Californium trichloride⁴ is obtained by the hydrochlorination of small solid chunks of CfO_{2-x} . The crystal structure can be determined either from powder X-ray diffraction measurements or from optical absorption measurements. The orthorhombic crystal structure is obtained by rapidly quenching the CfCl_3 from the melt (melting point = 545°C). Annealing the material at just below the melting point converts it to the hexagonal structure. Single crystals with the hexagonal structure can be grown using a modified Bridgeman method. The CfCl_3 sample is melted in the end of a quartz capillary in a furnace with a shallow temperature gradient. Starting with an unmelted seed in the tip of the capillary, the furnace is slowly cooled and the crystal grows as the liquid–solid interface slowly traverses the sample. Small orthorhombic crystals can be prepared by rapid quenching from the

³D. A. Damien *et al.*, *Inorg. Nucl. Chem. Lett.* **16**, 537 (1980).

⁴J. P. Young *et al.*, *J. Radioanal. Chem.* **43**, 479 (1978).

melt, but none were studied in this work. Precession X-ray camera techniques are used to determine the orientation of the single crystals.

The following persons are acknowledged for their work in the preparation of the samples used in this study:

- R. G. Haire (ORNL) for the preparation of all the raw californium materials that were used in all samples, and for the final preparation and X-ray characterization of the metal and oxide samples;

- D. A. Damien (currently at CEA, Bruyères le Châtel, France) and J. R. Peterson (University of Tennessee) for the preparation and X-ray characterization of the pnictide samples;

- J. R. Peterson and W. R. Wilmarth (U. of Tenn.) for the preparation and characterization by X-rays and optical absorption of the polycrystalline californium trichloride samples.

- R. C. Hart (U. of Tenn.) and S. E. Nave (U. of Tenn.) for the growth and X-ray characterization of the single-crystal samples of hexagonal californium trichloride.

VITA

James Reese Moore was born on August 15, 1951 and was raised in the town of Rotterdam, near Schenectady, New York. He attended Cornell University and received a B.S. degree in engineering physics in August 1973 and a Master's of Engineering degree in nuclear engineering in August 1974. He married the former Mary Anne Kozilsky in June 1973.

From 1974 through 1981 Mr. Moore was employed as a design engineer at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. He was involved with the design of experimental equipment for plasma confinement and superconducting magnet research.

In September 1981 Mr. Moore began graduate work in physics at the University of Tennessee at Knoxville. His first year of studies was supported by a University of Tennessee fellowship. Subsequent study and research were supported by research assistantships financed by U.S. Department of Energy contracts. He received a Ph.D. in physics in March 1988. Since 1982, Mr. Moore has been involved in research at the Transuranium Research Laboratory of the Oak Ridge National Laboratory concerning the magnetic properties of the transplutonium elements.