Magnetic and electronic properties of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$

G.T. Woods
J. Martin
M. Beekman
Raphaël P. Hermann
Fernande Grandjean

See next page for additional authors

Follow this and additional works at: https://trace.tennessee.edu/utk_matepubs

Part of the Materials Science and Engineering Commons

Recommended Citation

This Article is brought to you for free and open access by the Engineering -- Faculty Publications and Other Works at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Faculty Publications and Other Works -- Materials Science & Engineering by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.
Authors

This article is available at TRACE: Tennessee Research and Creative Exchange: https://trace.tennessee.edu/utk_matepubs/3
Magnetic and electronic properties of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$

G. T. Woods,$^1$ J. Martin,$^1$ M. Beekman,$^1$ Raphaël P. Hermann,$^{2,3}$ Fernande Grandjean,$^2$ V. Keppens,$^3$ O. Leupold,$^4$ Gary J. Long,$^5$ and G. S. Nolas$^{1,*}$  

$^1$Department of Physics, University of South Florida, Tampa, Florida 33620, USA  
$^2$Department of Physics, B5, University of Liège, B-4000 Sart-Tilman, Belgium  
$^3$Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37966, USA  
$^4$European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France  
$^5$and the Deutsches Elektronen Synchrotron, Notkestrasse 85, D-22607 Hamburg, Germany  

$^*$Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65409-0010, USA

(Received 18 March 2005; revised manuscript received 9 January 2006; published 1 May 2006)

Magnetization, static and ac magnetic susceptibility, nuclear forward scattering, and electrical resistivity measurements have been performed on polycrystalline Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, a type I clathrate that has divalent strontium and europium ions encapsulated within a Ga-Ge framework. These data are compared with those of type I clathrates Eu$_8$Ga$_{16}$Ge$_{30}$ and Eu$_6$Sr$_2$Ga$_{16}$Ge$_{30}$. The ferromagnetic ordering of these Eu-containing clathrates is substantially altered by the incorporation of strontium, as compared to Eu$_8$Ga$_{16}$Ge$_{30}$. Ferromagnetism, accompanied by a relatively large negative magnetoresistance, is observed below 15 and 20 K in Eu$_6$Sr$_2$Ga$_{16}$Ge$_{30}$ and Eu$_8$Sr$_4$Ga$_{16}$Ge$_{30}$, respectively. An effective magnetic moment of 7.83 $\mu_B$ per Eu ion is observed above 30 K for Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, a moment which is close to the free-ion moment of 7.94 $\mu_B$ per europium(II) ion.

DOI: 10.1103/PhysRevB.73.174403  
PACS number(s): 75.30.Cr, 75.50.Cc, 72.15.Eb

Clathrates are a class of “open-structured” materials in which molecules, atoms, or ions are completely enclosed within a framework comprised of other atoms or molecules. Many inorganic clathrates have frameworks consisting of group III and IV atoms. A variety of different clathrate compositions are possible, compositions which are of fundamental interest from the perspective of both their bonding and physical properties. They are also of interest as potential thermoelectric materials due to their low thermal conductivity.

There have been many reports on the structural and transport properties of the type I $\text{M}_x\text{Ga}_{16}\text{Ge}_{30}$ clathrates where $\text{M}$ represents alkali or alkali-earth ions. The group III and IV atoms in these clathrates are tetrahedrally bonded into a framework that contains two different types of face sharing polyhedra. The resulting cubic unit cell is made up of two dodecahedral polyhedra, $E_{20}$, and six tetrakaidecahedral polyhedra, $E_{25}$.

To date, with the exception of europium, type I clathrates with lanthanides inside the polyhedra have not been synthesized. The europium type I clathrates are of special interest because they contain magnetic divalent europium ions. They exhibit a relatively high thermopower, a high electrical conductivity, and a very low thermal conductivity, a combination of properties that is atypical of crystalline materials. Further, it has been shown that Eu$_8$Ga$_{16}$Ge$_{30}$ possesses a high Curie temperature of $\sim 35$ K and a relatively large negative magnetoresistance with a magnitude of 10% near its Curie temperature. In Eu$_8$Ga$_{16}$Ge$_{30}$ the magnetic moment is localized on the europium(II) ions and magnetic susceptibility measurements on a single crystal of Eu$_8$Ga$_{16}$Ge$_{30}$ have yielded an effective magnetic moment, $\mu_{\text{eff}}$, of 8.13 $\mu_B$ per europium(II) ion, a moment which is close to the free-ion moment of 7.94 $\mu_B$ per europium(II) ion. The corresponding magnetization saturates in fields above $\sim 1.5$ T at 5 K with a moment of 7.3 $\mu_B$ per europium(II) ion. Because of the large 5.23 Å Eu–Eu separation in Eu$_8$Ga$_{16}$Ge$_{30}$, the occurrence of ferromagnetism below 35 K is believed to result from Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions involving the conduction electrons. However, attempts to alter the Curie temperature of Eu$_8$Ga$_{16}$Ge$_{30}$ by altering the carrier concentration, $n$, in Eu$_8$Ga$_{16}$Ge$_{30}$, specimens and has been found to show only a shallow minimum in the range of $n$ values observed in various preparations of both type I and type VIII Eu$_{4-8}$Ga$_{16-x}$Ge$_{30-x}$ clathrates.

More complex europium containing type I clathrate compounds, i.e., Eu$_2$Ba$_6$Al$_8$Si$_{56}$, Eu$_2$Ba$_6$Cu$_2$Si$_{42}$, and Eu$_2$Ba$_6$Cu$_2$Si$_{15}$Ga$_4$, have been synthesized; the europium in these compounds was found to fully occupy the $E_{20}$ dodecahedral polyhedra. These clathrates also show negative thermopower and magnetic ordering below 32, 5, and 4 K, respectively. Above 50 K the temperature dependence of the inverse magnetic susceptibility yields $\mu_{\text{eff}}$ values of 7.82, 8.02, and 7.53 $\mu_B$, respectively, in good agreement with the free-ion value for the europium(II) ion; the corresponding Curie temperatures are 19.6, 5.5, and 9.7 K, respectively.

Herein we report on the alteration of the magnetic properties of Eu$_8$Ga$_{16}$Ge$_{30}$ by partially substituting strontium(II) for europium(II) to form polycrystalline Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ in which the Eu(II)-Eu(II) separation has increased both as a result of an increase in the cubic lattice parameter and the partial occupation of the cages by strontium. The results for Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ are compared with those for Eu$_6$Sr$_2$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$.

Polycrystalline Eu$_4$Ga$_{16}$Ge$_{30}$, Eu$_6$Sr$_2$Ga$_{16}$Ge$_{30}$, and
FIG. 1. The temperature dependence of the molar magnetic susceptibility of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ (× symbols) Eu$_6$Sr$_2$Ga$_{14}$Ge$_{30}$ (+ symbols), and Eu$_8$Ga$_{16}$Ge$_{30}$ (filled circles). Inset: The temperature dependence of the inverse molar susceptibility of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, Eu$_6$Sr$_2$Ga$_{14}$Ge$_{30}$, and Eu$_8$Ga$_{16}$Ge$_{30}$.

Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ have been synthesized as previously reported.4,8 X-ray diffraction and electron-beam microprobe analyses revealed only the type I clathrate phase, with homogeneous compositions within the polycrystalline grains. Hot pressing resulted in dense pellets with an average grain size of ~10 μm, as determined by optical metallocraphic analysis on polished surfaces. Refinement of synchrotron powder diffraction patterns revealed for Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ a stoichiometry of Eu$_{13.47(3)}$Sr$_{4.53(3)}$Ga$_{14.48(13)}$Ge$_{31.52(13)}$ with a 76% preferential europium occupation of the 2a crystallographic sites.8

All the magnetic susceptibility and magnetization measurements have been performed with a Quantum Design Physical Properties Measurement System (PPMS). The temperature dependence of the magnetic susceptibility was measured in a 1 T magnetic field and the magnetization was measured at several temperatures between 2 and 100 K in fields up to 7 T. Furthermore, for the Eu$_{6-x}$Sr$_x$Ga$_{14}$Ge$_{30}$ samples, with x = 0, 2, and 4, the magnetic susceptibility has been measured in a low field of 0.01 T with the vibrating sample magnetometer option of a Quantum Design PPMS (see Fig. 1). The measured susceptibilities have been corrected for the sample geometry, which differed from the geometry of the nickel standard. The magnetic susceptibility of Eu$_6$Ga$_{16}$Ge$_{30}$, Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, and Eu$_8$Sr$_2$Ga$_{14}$Ge$_{30}$ was corrected for its ~64.3, ~83.3, ~121.5 × 10$^{-6}$ emu/mol Eu diamagnetic susceptibility, respectively, a correction that has been obtained from Pascal constants.7 The ac susceptibility has been measured with nearly zero dc field and at frequencies between 72 and 2275 Hz.

Parallelepiped shaped samples with 1 × 2 × 4 mm$^3$ dimensions were cut from the dense polycrystalline pellets and have been used for four-probe resistivity measurements. The electrical resistivity has been measured between 4 and 300 K by using a Quantum Design PPMS. A precise mask was fabricated in order to nickel plate the sample at precise points in order to solder the four 0.0025 cm diameter copper leads used for the resistivity measurements. The magnetoresistance has been measured in fields of up to 7 T in the same configuration used for the zero-field resistivity measurements.

The europium-151 nuclear forward scattering measurements have been carried out on beam line11 ID22n at the European Synchrotron Radiation Facility in Grenoble, France. In this experiment the intensity of elastic coherent nuclear forward scattering12 is detected13 by an avalanche photodiode. This scattering process should not be confused with the incoherent nuclear inelastic scattering14,15 that may also be measured at the same beam line.

The magnetic susceptibility of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$ has been measured between 2 and 300 K in an applied field of 1 T. The inverse molar susceptibility is linear down to ~30 K and the slope obtained between 50 and 300 K yields a Weiss temperature of 19.2 K, a Curie constant, C, of 7.65 K/(mol Eu/emu), and an effective magnetic moment, μ$_{eff}$, of 7.83 μ$_B$. This moment, which agrees very well with the expected europium(II) spin-only magnetic moment of 7.94 μ$_B$, is essentially constant above ~60 K.

The magnetization of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ has been measured at several temperatures between 5 and 100 K in applied fields of up to 7 T. The moment per europium(II) ion is shown as a function of the applied field divided by the temperature in Fig. 2. As expected for a paramagnetic compound, at 65 and 100 K the magnetization increases linearly with applied field. At lower temperatures and higher applied fields the magnetization approaches saturation and at 5 K saturates at 6.7 μ$_B$, a moment which is somewhat below the expected saturation moment of 7 μ$_B$. Figure 2 also indicates that the curves above the Curie temperature do not coincide as would be expected from a simple paramagnetic compound whose magnetic moment follows a Brillouin curve.16 In the inset in Fig. 2, the extrapolated saturation magnetic moment of Eu$_4$Ga$_{16}$Ge$_{30}$ and Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ at temperatures below their respective Curie temperatures is plotted as a function of reduced temperature. Both compounds show similar saturation behavior. Finally, there was no observable hysteresis between 0 and ±10 Oe in the magnetization, an observation that is consistent with the expected soft ferromagnetic behav-
ior of Eu₄Sr₂Ga₁₆Ge₃₀. In addition to the above compounds, we also measured the magnetization of Eu₆Sr₂Ga₁₆Ge₃₀ between 0 and 2.5 T at 2 K (not shown), which yielded a saturation moment of 7 μB per Eu.

In order to compare the magnetic behavior of Eu₄Sr₂Ga₁₆Ge₃₀ with those of Eu₆Ga₁₆Ge₃₀ and Eu₆Sr₂Ga₁₆Ge₃₀, the magnetic susceptibility of the three compounds was measured between 2 and 300 K in a small applied field of 0.01 T (see Fig. 1). The inverse magnetic susceptibility is linear for the three compounds above ~50 K. Because these measurements needed to be corrected for the sample geometry, they cannot be used for a determination of the paramagnetic moment. However, they allow one to estimate the ferromagnetic ordering temperature and to compare the three susceptibility measurements. The ferromagnetic ordering temperature, T_C, estimated from the intersection of the extrapolated constant susceptibility, at low temperature, and the power law just above the ordering temperature, yields T_C = 33.4, 21, and 13 K for Eu₄−xSrₓGa₁₆Ge₃₀ with x = 0, 2, and 4, respectively. Further, the low field magnetic susceptibility measurements indicate that the ferromagnetic transition is extremely sharp in Eu₆Ga₁₆Ge₃₀ and much smoother in Eu₆Sr₂Ga₁₆Ge₃₀ and Eu₆Sr₂Ga₁₆Ge₃₀. A fit of the susceptibility just above the critical temperature with the χ ~ (T − T_C)^γ power law yields a critical exponent, γ = −1.2 for Eu₆Ga₁₆Ge₃₀, close to the typical value of −1.3 to −1.4.¹⁷

For Eu₆Sr₂Ga₁₆Ge₃₀ and Eu₆Sr₂Ga₁₆Ge₃₀, this critical exponent is not unambiguously determined, but it is larger than for Eu₆Ga₁₆Ge₃₀.

The temperature dependence of the magnetic susceptibility and the magnetization curves obtained for Eu₄Sr₂Ga₁₆Ge₃₀ are indicative of its complex magnetic interactions. Further, the similarity of saturation behavior of Eu₆Ga₁₆Ge₃₀ and Eu₆Sr₂Ga₁₆Ge₃₀ indicates that the origin of the magnetic interactions is similar in both compounds. It has been suggested that because of the large distance of 5.2 Å between the europium(II) ions in Eu₆Ga₁₆Ge₃₀ the magnetic order occurs through an RKKY interaction.⁵,⁹ In Eu₄Sr₂Ga₁₆Ge₃₀ the distance between the europium(II) ions is even larger and the RKKY indirect exchange interaction is certainly the most likely coupling between the europium(II) ions. Because this interaction is oscillating in sign from ferromagnetic to antiferromagnetic as a function of distance from a europium ion with a magnitude and period that depends on the conduction electron density, it is not surprising that both the lattice expansion and the Sr/Eu distribution affects the magnetic properties of Eu₄Sr₂Ga₁₆Ge₃₀.

The real, χ', and imaginary, χ'', components of the ac susceptibility, χ_ac = χ' − iχ'', of Eu₄Sr₂Ga₁₆Ge₃₀ have been measured at about zero dc field and a frequency of 120 Hz, as shown in Fig. 3. In this figure χ' has been multiplied by 100 in order to compare with the χ' results. The ordering temperature, T_C, corresponds to the maximum in χ'' at 15 K in the case of Eu₄Sr₂Ga₁₆Ge₃₀. The χ'' susceptibility exhibits a relatively sharp increase starting at ~20 K and then a sudden decrease below 15 K. These sharp changes are characteristic of uniform ferromagnetic exchange interactions and indicate the excellent homogeneity of the polycrystalline Eu₄Sr₂Ga₁₆Ge₃₀ sample. It should be noted that the increase in χ'' coincides, as expected, with an increase in χ'.
agreement with the value obtained from the maximum in $\chi''$ discussed above.

In order to determine whether or not Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ is metallic, temperature dependent electrical resistivity measurements have been carried out. The temperature dependence of the electrical resistivity, $\rho$, of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$, obtained in a zero applied magnetic field ($H_a=0$ T), is shown in Fig. 5. The room temperature resistivities for polycrystalline samples of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$ are 0.83 and 0.6 m$\Omega$ cm, respectively. In spite of possible scattering between the grains in the polycrystalline sample, similar values of 0.48 and 0.6 m$\Omega$ cm have been observed in single crystalline$^5$ and polycrystalline$^7$ Eu$_8$Ga$_{16}$Ge$_{30}$. Further, a recent study$^1$ of the transport properties of type I and type VIII Eu$_8$Ga$_{16}$Ge$_{30}$ clathrates reported 2 K resistivities of between 0.299 and 0.894 m$\Omega$ cm. Nonetheless, the temperature dependent resistivities of the polycrystalline samples of Eu$_8$Ga$_{16}$Ge$_{30}$ and Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ indicate that both display metallic behavior above 70 K, and hence are heavily doped compounds. Below 40 and 30 K for Eu$_8$Ga$_{16}$Ge$_{30}$ and Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, respectively, an anomaly is observed. Similar anomalies have been observed$^5,7,18$ in the temperature dependence of the electrical resistivity of type I and type VIII Eu$_8$Ga$_{16}$Ge$_{30}$ clathrates. Such anomalies are usually observed at the onset of magnetic ordering and are no doubt associated with the ferromagnetic ordering of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ and Eu$_8$Sr$_4$Ga$_{16}$Ge$_{30}$ below 35 and 15 K, respectively. In the latter case, the results shown in Fig. 3 indicate that the anomaly is related to the ferromagnetic ordering. Below 8 K the resistivity increases slightly perhaps because of grain boundary scattering.

The percentage change in the magnetoresistance of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ obtained between 5 and 70 K in an applied field of 7 T is shown in Fig. 6. The magnetoresistance has been calculated with the expression,$\Delta \rho=(\rho_H-\rho_0)/\rho_0$, where $\rho_0$ is the resistivity in zero applied magnetic field. Just below 30 K the magnetoresistance begins to increase significantly and reaches about 10% at 12 K. As has been reported earlier$^5$ for Eu$_8$Ga$_{16}$Ge$_{30}$ and is observed herein for Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, the magnetoresistance changes significantly as the temperature approaches the Curie temperature as a result of magnetic spin disorder scattering. It should be noted that the magnetoresistance near the Curie temperature of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ has the same magnitude and sign as that observed both for our polycrystalline Eu$_8$Ga$_{16}$Ge$_{30}$ and for single crystalline$^5$ Eu$_8$Ga$_{16}$Ge$_{30}$. Below 12 K the magnetoresistance decreases by 1% and then increases up to 12% below 9 K. Because the magnetic moment is localized on the europium(II) ions, the magnetoresistance of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ can be understood as the scattering of $s$ electrons by the localized 4$f$ electrons. Models which describe the scattering of $s$ electrons by localized electrons in systems where both localized moments and high carrier concentrations exist, as is the case for Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, have been presented elsewhere.$^{19}$

Thus, the substitution of europium by strontium in Eu$_8$Ga$_{16}$Ge$_{30}$ to form Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ increases the Curie temperature from 35 to 15 K. An effective magnetic moment of 7.83 $\mu_B$ per europium(II) ion is obtained from the temperature dependence of the magnetic susceptibility of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$, an effective moment that is close to the free-ion moment of 7.94 $\mu_B$. The magnetization curves ob-

![FIG. 5. The temperature dependence of the resistivity of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$. All data indicates the Curie temperature. The inset shows the resistivity of Eu$_8$Ga$_{16}$Ge$_{30}$ to compare. All data have been collected with a zero applied magnetic field.](image1)

![FIG. 6. The temperature dependence of the negative magnetoresistance of Eu$_4$Sr$_4$Ga$_{16}$Ge$_{30}$ obtained in an applied field of 7 T.](image2)
tained at different temperatures up to a field of 7 T do not follow a simple Brillouin behavior for a spin of 7/2. At 5 K and 7 T, the magnetic moment per europium(II) ion saturates at 6.7 $\mu_B$, a moment that is smaller than the expected 7 $\mu_B$.

Because of the large separation between the 4f moments, it is well known\textsuperscript{5,7,9,18} that the magnetic interactions in Eu$_8$Ga$_{16}$Ge$_{30}$ arise from the RKKY mechanism. The average Eu-II-Eu(II) separation in Eu$_8$Ga$_{16}$Ge$_{30}$ is approximately 5.2 Å. Because this distance is so large, direct exchange between the localized europium ions that are separated by 4.12 Å, whereas antiferromagnetic coupling occurs between the chains that are separated by 5.99 Å.

As far as we can determine, the magnetic properties of only a few europium containing clathrates have been studied to date.\textsuperscript{5,7,9,10,18,20} For the compounds studied, magnetic susceptibility measurements revealed divalent europium ions with $\mu_{eff}$ values close to the free ion value of 7.94 $\mu_B$. In contrast, the ordering temperatures were reported to vary from 4 K in Eu$_2$Ba$_6$Cu$_8$Si$_{18}$Ga$_4$ to 35 K in type I Eu$_8$Ga$_{16}$Ge$_{30}$. This wide variation\textsuperscript{7,9,18} results from the combined influence of the Eu-Eu separation and the effective mass of the charge carrier. Among Eu$_2$Ba$_6$Al$_{18}$Si$_{36}$, Eu$_2$Ba$_6$Cu$_8$Si$_{18}$, and Eu$_2$Ba$_6$Cu$_8$Si$_{18}$Ga$_4$, clathrates in which all the divalent europium ions occupy the dodecahedral cages and are $\sim$10.4 Å apart, Eu$_2$Ba$_6$Al$_{18}$Si$_{36}$ is unique because of its high Curie temperature\textsuperscript{10} of 32 K and, as a consequence, this compound deserves more extensive study. Eu$_8$Ga$_{16}$Ge$_{30}$ exhibits\textsuperscript{21} a complex antiferromagnetic structure with a Néel temperature of 8 K, a magnetic structure in which a ferromagnetic coupling occurs along chains of europium(II) ions that are separated by 4.12 Å, whereas antiferromagnetic coupling occurs between the chains that are separated by 5.99 Å.

The authors thank Srikanth Hariharan for access to the PPMS used in the magnetic measurements and Srinath Sanyadanam for useful discussions on the analysis of magnetic data. The European Synchrotron Radiation Facility is acknowledged for provision of synchrotron radiation facilities at the beam line ID22n. G.S.N. and J.M. acknowledge support from the University of South Florida Research and Creative Scholarship Grant Program under Grant No. 1253-938RO. M.B. acknowledges support from the University of South Florida.

---

\textsuperscript{8}Electronic address: gnolas@cas.usf.edu
\textsuperscript{19}http://www.esrf.fr/exp_facilities/ID18/
\textsuperscript{27}C. K. Yang, J. Zhao, and J. P. Lu, Phys. Rev. B 70, 073201 (2004).