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Magnetic and electronic properties of $Eu_4Sr_4Ga_{16}Ge_{30}$

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Magnetization, static and ac magnetic susceptibility, nuclear forward scattering, and electrical resistivity measurements have been performed on polycrystalline $Eu_4Sr_4Ga_{16}Ge_{30}$, 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 $Eu_8Ga_{16}Ge_{30}$ and $Eu_6Sr_2Ga_{16}Ge_{30}$. The ferromagnetic ordering of these Eu-containing clathrates is substantially altered by the incorporation of strontium, as compared to $Eu_8Ga_{16}Ge_{30}$. Ferromagnetism, accompanied by a relatively large negative magnetoresistance, is observed below 15 and 20 K in $Eu_4Sr_4Ga_{16}Ge_{30}$ and $Eu_6Sr_2Ga_{16}Ge_{30}$, respectively. An effective magnetic moment of 7.83 μ_B per Eu ion is observed above 30 K for $Eu_4Sr_4Ga_{16}Ge_{30}$, a moment which is close to the free-ion moment of 7.94 μ_B per europium(II) ion.

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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.[1] 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 $M_8Ga_{16}Ge_{30}$ clathrates where M represents alkali or alkali-earth ions.[1,2] 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_{24}.

To date, with the exception of europium, type I clathrates with lanthanides inside the polyhedra have not been synthesized.[3] The europium type I clathrates are of special interest because they contain magnetic divalent europium ions.[4–8] 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.[4,5] Further, it has been shown that $Eu_8Ga_{16}Ge_{30}$ possesses a high Curie temperature of ~35 K and a relatively large negative magnetoresistance with a magnitude of 10% near its Curie temperature.[5–7] In $Eu_8Ga_{16}Ge_{30}$ the magnetic moment is localized on the europium(II) ions and magnetic susceptibility measurements[5] on a single crystal of $Eu_8Ga_{16}Ge_{30}$ have yielded an effective magnetic moment, μ_{eff}, of 8.13 μ_B per europium(II) ion, a moment which is close to the free-ion moment of 7.94 μ_B per europium(II) ion. The corresponding magnetization[5] saturates in fields above ~1.5 T at 5 K with a moment of 7.3 μ_B per europium(II) ion. Because of the large 5.23 Å Eu-Eu separation in $Eu_8Ga_{16}Ge_{30}$, 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 $Eu_8Ga_{16}Ge_{30}$ by altering the carrier concentration have been unsuccessful to date.[5] The reason for these failures has been recently unraveled.[9] The RKKY coupling constant has been calculated as a function of the charge carrier concentration, n, in $Eu_8Ga_{16-x}Ge_{30+x}$ 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 $Eu_8Ga_{16-x}Ge_{30+x}$ clathrates.

More complex europium containing type I clathrate compounds, i.e., $Eu_2Ba_6Al_8Si_{36}$, $Eu_2Ba_6Cu_4Si_{42}$, and $Eu_2Ba_6Cu_4Si_{38}Ga_4$, have been synthesized; the europium in these compounds was found to fully occupy the E_{20} dodecahedral polyhedra.[10] 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 μ_{eff} values of 7.82, 8.02, and 7.53 μ_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 $Eu_8Ga_{16}Ge_{30}$ by partially substituting strontium(II) for europium(II) to form polycrystalline $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_4Sr_4Ga_{16}Ge_{30}$ are compared with those for $Eu_6Sr_2Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$.

Polycrystalline $Eu_8Ga_{16}Ge_{30}$, $Eu_6Sr_2Ga_{16}Ge_{30}$, and

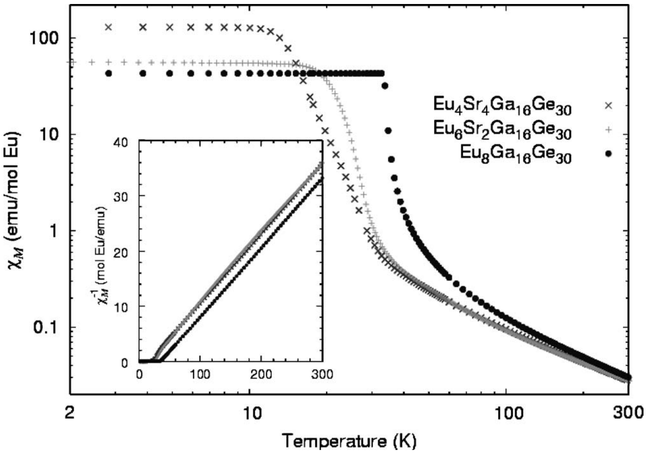

FIG. 1. The temperature dependence of the molar magnetic susceptibility of $Eu_4Sr_4Ga_{16}Ge_{30}$ (× symbols) $Eu_6Sr_2Ga_{16}Ge_{30}$ (+ symbols), and $Eu_8Ga_{16}Ge_{30}$ (filled circles). Inset: The temperature dependence of the inverse molar susceptibility of $Eu_4Sr_4Ga_{16}Ge_{30}$, $Eu_6Sr_2Ga_{16}Ge_{30}$, and $Eu_8Ga_{16}Ge_{30}$.

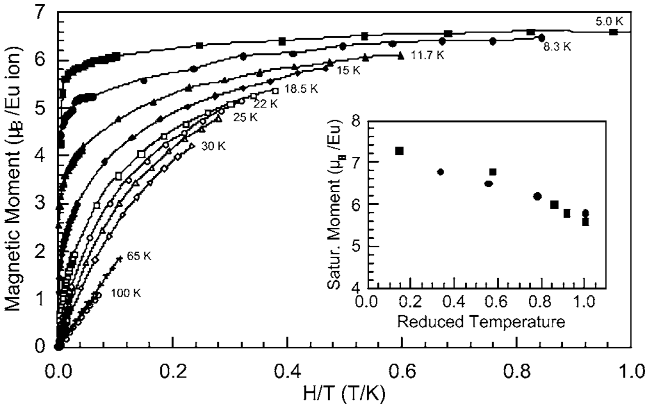

FIG. 2. The magnetic moment per europium(II) ion in $Eu_4Sr_4Ga_{16}Ge_{30}$ obtained at several temperatures between 5 (top) and 100 (bottom) K in applied fields of up to 7 T as a function of applied field divided by temperature. Inset: The saturation moment per europium(II) ion in $Eu_8Ga_{16}Ge_{30}$, squares, and $Eu_4Sr_4Ga_{16}Ge_{30}$, circles, as a function of reduced temperature.

$Eu_4Sr_4Ga_{16}Ge_{30}$ 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 metallographic analysis on polished surfaces. Refinement of synchrotron powder diffraction patterns revealed for $Eu_4Sr_4Ga_{16}Ge_{30}$ a stoichiometry of $Eu_{3.47(3)}Sr_{4.53(3)}Ga_{14.48(13)}Ge_{31.52(13)}$ with a 76% preferential europium occupation of the 2*a* 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 $Eu_{8-x}Sr_xGa_{16}Ge_{30}$ 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 $Eu_8Ga_{16}Ge_{30}$, $Eu_6Sr_2Ga_{16}Ge_{30}$, and $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $1\times2\times4$ 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 line[11] ID22n at the European Synchrotron Radiation Facility in Grenoble, France. In this experiment the intensity of elastic coherent nuclear forward scattering[12] is detected[13] by an avalanche photodiode. This scattering process should not be confused with the incoherent nuclear inelastic scattering[14,15] that may also be measured at the same beam line.

The magnetic susceptibility of $Eu_4Sr_4Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ 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 $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 behavior of $Eu_4Sr_4Ga_{16}Ge_{30}$. In addition to the above compounds, we also measured the magnetization of $Eu_6Sr_2Ga_{16}Ge_{30}$ between 0 and 2.5 T at 2 K (not shown), which yielded a saturation moment of 7 μ_B per Eu.

In order to compare the magnetic behavior of $Eu_4Sr_4Ga_{16}Ge_{30}$ with those of $Eu_8Ga_{16}Ge_{30}$ and $Eu_6Sr_2Ga_{16}Ge_{30}$, 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 $Eu_{8-x}Sr_xGa_{16}Ge_{30}$ with x=0, 2, and 4, respectively. Further, the low field magnetic susceptibility measurements indicate that the ferromagnetic transition is extremely sharp in $Eu_8Ga_{16}Ge_{30}$, and much smoother in $Eu_6Sr_2Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$. A fit of the susceptibility just above the critical temperature with the $\chi \sim (T-T_c)^\gamma$ power law yields a critical exponent, $\gamma=-1.2$ for $Eu_8Ga_{16}Ge_{30}$, close to the typical value of −1.3 to −1.4.[17] For $Eu_6Sr_2Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$, this critical exponent is not unambiguously determined, but it is larger than for $Eu_8Ga_{16}Ge_{30}$.

The temperature dependence of the magnetic susceptibility and the magnetization curves obtained for $Eu_4Sr_4Ga_{16}Ge_{30}$ are indicative of its complex magnetic interactions. Further, the similarity of saturation behavior of $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_8Ga_{16}Ge_{30}$ the magnetic order occurs through an RKKY interaction.[5,9] In $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_4Sr_4Ga_{16}Ge_{30}$.

The real, χ', and imaginary, χ'', components of the ac susceptibility, $\chi_{ac}=\chi'-i\chi''$, of $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_4Sr_4Ga_{16}Ge_{30}$. 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 $Eu_4Sr_4Ga_{16}Ge_{30}$ sample. It should be noted that the increase in χ'' coincides, as expected, with an increase in χ'.

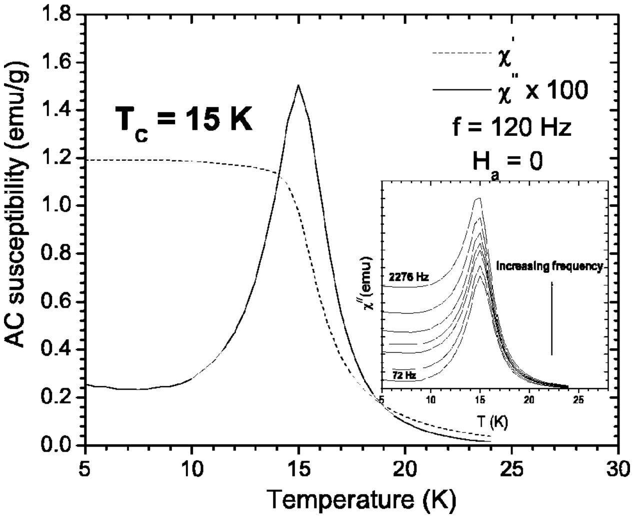

FIG. 3. The real, χ', and imaginary, χ'', portions of the ac susceptibility of $Eu_4Sr_4Ga_{16}Ge_{30}$ obtained at a frequency of 120 Hz. Inset: The dependence of χ'' on frequency between 72 and 2275 Hz.

Several ac susceptibility measurements on $Eu_4Sr_4Ga_{16}Ge_{30}$ have been made at different frequencies, as is shown in the inset of Fig. 3, and no change in χ'' and T_C is observed with frequency, at least between 72 and 2275 Hz. However, increasing the frequency did result in larger energy losses at and below 15 K. Dynamical measurements such as ac susceptibility can be affected by losses due to Eddy currents. Higher energy losses due to an increase in frequency, as shown in the inset of Fig. 3, may be due to contributions from Eddy currents because our specimen exhibits metallic conduction (see below). Further, the randomness between Sr and Eu in the lattice sites can result in more pinning of the domain walls and yield a larger energy loss. Finally, it should be noted that the χ' values obtained at different frequencies showed no significant changes with respect to the dashed curve taken at 120 Hz in Fig. 3.

To further investigate the magnetic properties of $Eu_4Sr_4Ga_{16}Ge_{30}$ below 50 K nuclear forward scattering measurements have been carried out with the europium-151 nuclide. The europium-151 nuclear forward scattering intensity has been measured as a function of temperature between 10 and 50 K for both $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ with ~100 mg of both samples. The measured intensities (see Fig. 4) exhibit a sharp increase upon heating at the ordering temperatures of ~35 and ~15 K for $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$, respectively. The origin of this increase in the scattering intensity can be understood as follows. In the low temperature ferromagnetic phase, the magnetic hyperfine interaction completely removes the degeneracy of the europium-151 nuclear ground and excited states. As the temperature increases, the europium(II) hyperfine field decreases and, hence, the splitting in the nuclear levels is reduced. Finally, in the paramagnetic phase, above T_C, the europium-151 nuclear states are fully degenerate. This gradual decrease in the splitting of the nuclear energy levels yields a strong increase in the nuclear forward scattering cross section, an increase that reveals the magnetic ordering temperature. The resulting value of T_C obtained for $Eu_4Sr_4Ga_{16}Ge_{30}$ is in good

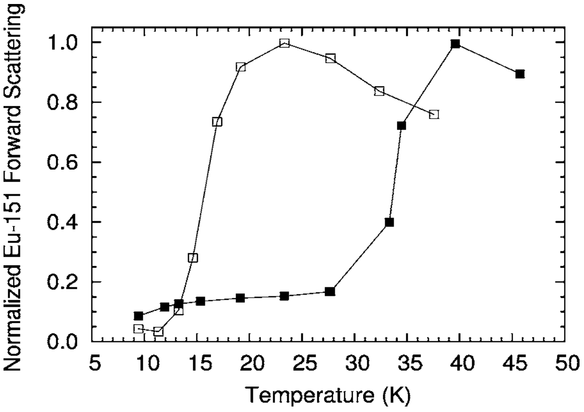

FIG. 4. The europium-151 nuclear forward scattering intensity for both $Eu_4Sr_4Ga_{16}Ge_{30}$, open squares, and $Eu_8Ga_{16}Ge_{30}$, closed squares. The intensities are normalized to their respective maximum. The error bars are approximately the size of the data points.

agreement with the value obtained from the maximum in χ'' discussed above.

In order to determine whether or not $Eu_4Sr_4Ga_{16}Ge_{30}$ is metallic, temperature dependent electrical resistivity measurements have been carried out. The temperature dependence of the electrical resistivity, ρ, of $Eu_4Sr_4Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$, obtained in a zero applied magnetic field ($H_a = 0\ T$), is shown in Fig. 5. The room temperature resistivities for polycrystalline samples of $Eu_4Sr_4Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ are 0.83 and 0.6 mΩ cm, respectively. In spite of possible scattering between the grains in the polycrystalline sample, similar values of 0.48 and 0.6 mΩ cm have been observed in single crystalline[5] and polycrystalline[7] $Eu_8Ga_{16}Ge_{30}$. Further, a recent study[18] of the transport properties of type I and type VIII $Eu_8Ga_{16-x}Ge_{30+x}$ clathrates reported 2 K resistivities of between 0.299 and 0.894 mΩ cm. Nonetheless, the temperature dependent resistivities of the polycrystalline samples of $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ indicate that both display metallic behavior above 70 K, and hence are heavily doped compounds. Below 40 and 30 K for $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$, 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 $Eu_8Ga_{16}Ge_{30}$ clathrates. Such anomalies are usually observed at the onset of magnetic ordering and are no doubt associated with the ferromagnetic ordering of $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ 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.

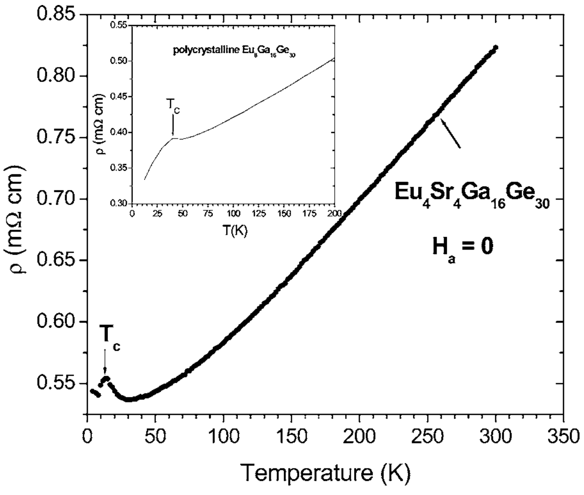

FIG. 5. The temperature dependence of the resistivity of $Eu_4Sr_4Ga_{16}Ge_{30}$. All data indicates the Curie temperature. The inset shows the resistivity of $Eu_8Ga_{16}Ge_{30}$ to compare. All data have been collected with a zero applied magnetic field.

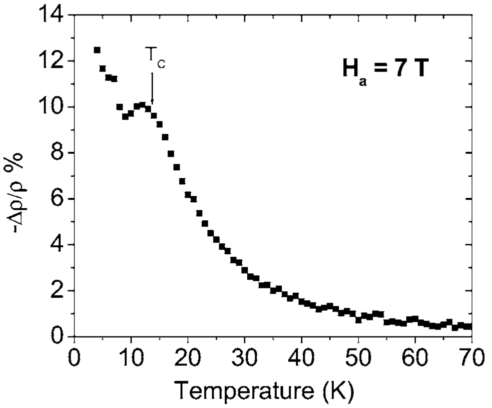

FIG. 6. The temperature dependence of the negative magnetoresistance of $Eu_4Sr_4Ga_{16}Ge_{30}$ obtained in an applied field of 7 T.

The percentage change in the magnetoresistance of $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 ρ_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 $Eu_8Ga_{16}Ge_{30}$ and is observed herein for $Eu_4Sr_4Ga_{16}Ge_{30}$, 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 $Eu_4Sr_4Ga_{16}Ge_{30}$ has the same magnitude and sign as that observed both for our polycrystalline $Eu_8Ga_{16}Ge_{30}$, and for single crystalline[5] $Eu_8Ga_{16}Ge_{30}$. 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 $Eu_4Sr_4Ga_{16}Ge_{30}$ 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 $Eu_4Sr_4Ga_{16}Ge_{30}$, have been presented elsewhere.[19]

Thus, the substitution of europium by strontium in $Eu_8Ga_{16}Ge_{30}$ to form $Eu_4Sr_4Ga_{16}Ge_{30}$ decreases the Curie temperature from 35 to 15 K. An effective magnetic moment of 7.83 μ_B per europium(II) ion is obtained from the temperature dependence of the magnetic susceptibility of $Eu_4Sr_4Ga_{16}Ge_{30}$, an effective moment that is close to the free-ion moment of 7.94 μ_B. The magnetization curves obtained 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 μ_B, a moment that is smaller than the expected 7 μ_B.

Because of the large separation between the 4*f* moments, it is well known[5,7,9,18] that the magnetic interactions in $Eu_8Ga_{16}Ge_{30}$ arise from the RKKY mechanism. The average Eu(II)-Eu(II) separation in $Eu_8Ga_{16}Ge_{30}$ is approximately 5.2 Å. Because this distance is so large, direct exchange between the localized europium(II) 4*f* moments can be ruled out as the mechanism for the ferromagnetism. However, indirect exchange via the RKKY mechanism is certainly possible due to the long range of the charge carriers. Interestingly, from calculations using the exchange Hamiltonian in the RKKY formalism, and the carrier concentrations from the Hall constants at the Curie temperature, Paschen *et al.*[7] determined that ferromagnetism existed within either a Eu-Eu distance of 6.5 Å in the type I clathrate, $Eu_8Ga_{16}Ge_{30}$, with a Curie temperature of ~35 K or a Eu-Eu distance of 10 Å in the type VIII clathrate with a Curie temperature of ~10 K. This difference in Curie temperatures of the type I and type VIII $Eu_8Ga_{16}Ge_{30}$ clathrates has recently been reexamined[9,18] and explained in terms of the different effective masses of the charge carriers. In $Eu_4Sr_4Ga_{16}Ge_{30}$, the average Eu-Eu separation is ~10 Å, a separation which is similar to that in the type VIII clathrate[7] and the RKKY exchange interaction leads to a similar Curie temperature of 15 K.

As far as we can determine, the magnetic properties of only a few europium containing clathrates have been studied to date.[5,7,9,10,18,20] For the compounds studied, magnetic susceptibility measurements revealed divalent europium ions with μ_{eff} values close to the free ion value of 7.94 μ_B. In contrast, the ordering temperatures were reported to vary from 4 K in $Eu_2Ba_6Cu_4Si_{38}Ga_4$ to 35 K in type I $Eu_8Ga_{16}Ge_{30}$. This wide variation[7,9,18] results from the combined influence of the Eu-Eu separation and the effective mass of the charge carrier. Among $Eu_2Ba_6Al_8Si_{36}$, $Eu_2Ba_6Cu_4Si_{42}$, and $Eu_2Ba_6Cu_4Si_{38}Ga_4$, clathrates in which all the divalent europium ions occupy the dodecahedral cages and are ~10.4 Å apart, $Eu_2Ba_6Al_8Si_{36}$ is unique because of its high Curie temperature[10] of 32 K and, as a consequence, this compound deserves more extensive study. $Eu_4Ga_8Ge_{16}$ exhibits[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.

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[1] G. S. Nolas in *Chemistry, Physics, and Materials Science of Thermoelectric Materials, Beyond Bismuth Telluride*, edited by M. G. Kanatzidis, S. D. Mahanti, and T. P. Hogan (Kluwer Academic/Plenum, 2003), p. 107.

[2] See, for example, G. S. Nolas, G. A. Slack, and S. B. Schujman in *Semiconductors and Semimetals*, edited by T. M. Tritt (Academic Press, 2001), Vol. 29, p. 255.

[3] V. Pacheco, W. Carrillo-Cabrera, V. H. Tran, S. Paschen, and Y. Grin, Phys. Rev. Lett. **87**, 099601 (2001); T. Kawaguchi, K. Tanigaki, and M. Yasukawa, *ibid.* **87**, 099602 (2001), and references therein.

[4] J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack, Phys. Rev. Lett. **82**, 779 (1999).

[5] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, and D. Mandrus, Phys. Rev. B **63**, 245113 (2001).

[6] B. C. Chakoumakos, B. C. Sales, and D. G. Mandrus, J. Am. Ceram. Soc. **322**, 127 (2001).

[7] S. Paschen, W. Carrillo-Cabrera, A. Bentien, V. H. Tran, M. Baenitz, Y. Grin, and F. Steglich, Phys. Rev. B **64**, 214404 (2001).

[8] Y. Zhang, P. L. Lee, G. S. Nolas, and A. P. Wilkinson, Appl. Phys. Lett. **80**, 2931 (2002).

[9] V. Pacheco, A. Bentien, W. Carrillo-Cabrera, S. Paschen, F. Steglich, and Yu. Grin, Phys. Rev. B **71**, 165205 (2005).

[10] Y. Mudryk, P. Rogl, C. Paul, S. Berger, E. Bauer, G. Hilscher, C. Godart, and H. Noël, J. Phys.: Condens. Matter **14**, 7991 (2002).

[11] http://www.esrf.fr/exp_facilities/ID18/

[12] A. I. Chumakov and W. Sturhahn, Hyperfine Interact. **123/124**, 781 (1999).

[13] O. Leupold, A. I. Chumakov, E. E. Alp, W. Sturhahn, and A. Q. R. Baron, Hyperfine Interact. **123/124**, 611 (1999).

[14] W. Sturhahn, J. Phys.: Condens. Matter **16**, S497 (2004).

[15] G. J. Long, R. P. Hermann, F. Grandjean, E. E. Alp, W. Sturhahn, C. E. Johnson, D. E. Brown, O. Leupold, and R. Rüffer, Phys. Rev. B **71**, 140302(R) (2005).

[16] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), Chap. 15.

[17] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Thomson, 1976), Chap. 33, p. 699.

[18] A. Bentien, V. Pacheco, S. Paschen, Yu. Grin, and F. Steglich, Phys. Rev. B **71**, 165206 (2005).

[19] C. K. Yang, J. Zhao, and J. P. Lu, Phys. Rev. B **70**, 073201 (2004).

[20] M. Kataoka, Phys. Rev. B **63**, 134435 (2001).

[21] M. Christensen, J. D. Bryan, H. Birkedal, G. D. Stucky, B. Lebech, and B. B. Iversen, Phys. Rev. B **68**, 174428 (2003).