Temperature dependence of Eu 4f and Eu 5d magnetizations in the filled skutterudite EuFe$_3$Sb$_{12}$

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The element-specific and shell-specific magnetism of Eu in the filled skutterudite ferrimagnet Eu$_{0.95}$Fe$_4$Sb$_{12}$ has been investigated using Eu M$_{4.5}$- and Eu L$_{2.3}$-edge x-ray magnetic circular dichroism (XMCD) spectroscopy as a function of temperature. Eu L$_3$-edge x-ray absorption spectroscopy shows that Eu is mostly in the divalent state. Eu M$_2$-edge x-ray absorption spectroscopy, measured by electron yield, shows nearly equal fractions of Eu$^{2+}$ and Eu$^{3+}$ states because it probes a significant portion of the surface volume which is dominated by the Eu$^{3+}$ impurity state. Sum-rule analysis of the Eu M$_{4.5}$-edge XMCD spectrum measured at 4.9 K yielded the 4f spin moment of (7.15 ± 0.3)μ$_B$ per Eu$^{3+}$ ion. By comparing the Eu L$_{2.3}$-edge XMCD spectrum in the ferrimagnetic state of Eu$_{0.95}$Fe$_4$Sb$_{12}$ to that of a divalent Eu reference compound, the clathrate Eu$_5$Ga$_{10}$Ge$_{30}$, we show that the 5d spin polarization of Eu in the skutterudite is strongly enhanced by the exchange coupling with the 3d band electrons of Fe, which were shown to have an ordered moment of −0.21μ$_B$/Fe in our earlier Fe L$_{2.3}$ XMCD measurements. The temperature dependence of the magnetic order parameter, determined from the Eu L$_3$-edge XMCD intensity, yields a mean-field-like exponent (∼0.52) in the skutterudite and a three-dimensional Heisenberg-type (∼0.36) exponent in the clathrate.

DOI: 10.1103/PhysRevB.79.014426 PACS number(s): 71.27.+a, 61.05.cj, 75.30.Mb, 75.50.Bb

I. INTRODUCTION

Filled skutterudites RM$_n$X$_{12}$ (R=rare earth; M=Fe, Ru, and Os; and X=Sb and P) have attracted considerable interest because they exhibit a variety of correlated electron phenomena associated with an electronic ground state such as superconductivity, ferromagnetic ordering, antiferromagnetic ordering, and heavy-fermion behavior at low temperatures. The filled skutterudites also have potential, such as thermoelectric materials, due to their large thermopower and lower electrical resistivity. These materials crystallize in the cubic structure (space group Im3) with 2 f.u./unit cell. The rare-earth atoms fill the voids in the skutterudite structure of M$_n$X$_{12}$. The rattling motion of rare-earth atoms in the oversized atomic cages is believed to reduce the thermal conductivity while not significantly altering the electrical conductivity. La Knight-shift measurements in filled skutterudites using $^{139}$La nuclear magnetic resonance (NMR) show strong correlation between the d bands of transition metal and the rattling motion of rare-earth atoms through electron-phonon coupling. $^{125}$Sb nuclear inelastic-scattering measurements in EuFe$_3$Sb$_{12}$ show that the vibrational density of states of Sb is lowered upon the filling of the cages by the rare-earth atoms. The cubic crystal electric field at the rare-earth site plays an important role in determining the electronic ground state and the low-temperature magnetic and transport properties of these compounds. Despite several experimental and theoretical efforts on filled skutterudites, the mechanism of magnetic ordering in these compounds is not well understood, and the nature of magnetic interaction between the rare-earth and transition-metal ions is not clear. Therefore, detailed studies of the element-specific contributions to the total magnetization in magnetically ordered skutterudites are critically important to understand the role played by rare-earth ions, transition-metal ions, and conduction electrons in magnetic and thermal properties.

The valence-band structures of the narrow band-gap semiconductor CoSb$_3$ and related filled skutterudites AFe$_4$Sb$_{12}$ (A=alkali metal, alkaline metal, or rare earth) consist of a manifold of Sb p-Fe 3d-derived states, with the d character concentrated just below the band edge, resulting in 24 valence electrons ($n_v$) per FeSb$_3$ unit, which include Sb s states. While CoSb$_3$ ($n_v$=24) is nonmagnetic, one may expect the d-derived density of states from the M atoms to increase as $n_v$ is further reduced, leading to a Stoner instability toward magnetism. Ferromagnetic order would be anticipated because of the strongly hybridized electronic structure, which is, in fact, observed. While the nonsuperconducting metal LaFe$_4$Sb$_{12}$ ($n_v$=23.75) shows no magnetic ordering, CaFe$_4$Sb$_{12}$, SrFe$_4$Sb$_{12}$, and BaFe$_4$Sb$_{12}$, with $n_v$=23.5, show nearly ferromagnetic metallic behavior, and the $n_v$=23.25 compounds NaFe$_4$Sb$_{12}$ and KFe$_4$Sb$_{12}$ are half-metallic ferromagnets. The $n_v$=23.5 compounds, i.e., skutterudites that are filled with a divalent ion, are interesting because of their borderline ferromagnetic behavior.

The electronic properties of Eu-filled skutterudites are of particular interest because the variation in the Eu valency...
dramatically changes their magnetic properties. The Eu ion can be in a nonmagnetic trivalent state, a magnetic divalent state with a large free-ion-like moment, or in a mixed-valence state with an average moment between 0 and 7. A mixed-valence state for Eu is another way to modify the band filling or and hence alter the magnetic properties of the skutterudite. Similarly, the Eu site occupancy is also very important because it can modify the magnetic properties, such as the total magnetic moment, the transition temperature, Eu 4f–Eu 4f interatomic interaction, and Eu 4f–Fe 3d interatomic interaction.

Figure 1(a) shows the crystal structure of the Eu-filled skutterudite Eu0.95Fe4Sb12. It is nearly metallic and orders ferrimagnetically with a Curie temperature of 85 K. dc magnetization measurements on our polycrystalline specimens, presented in Fig. 2, show that the net magnetic moment of the compound is about 5.1 \mu_B per f.u. at 5 K, similar to that found in single crystals. Eu L3-edge x-ray absorption spectroscopy measurements by Bauer et al. in EuT2Sb12 (T=Fe, Ru, Os) indicated nearly divalent Eu configuration without any change in the Eu2+ population with temperature. Eu Mössbauer spectroscopy measurements and Eu L3-edge x-ray absorption measurements by Grytsiv et al. also indicated that Eu is nearly divalent in Eu0.93Fe4Sb12. 57Fe Mössbauer spectroscopy measurements by Reissner et al. showed that Fe has two different environments in Eu0.88Fe4Sb12. The value of the magnetic moment in Eu0.95Fe4Sb12 is only 73% of the value of a fully saturated Eu2+ ion with seven electrons in the 4f shell, \( L=0, S=7/2 \), and total magnetic moment \( \mu=7\mu_B \). Using Eu M4,5-edge and Fe L2,3 x-ray magnetic circular dichroism (XMCD) spectroscopy, Eu L3-edge x-ray absorption spectroscopy, and local spin-density calculations, we have recently demonstrated that the lower value of the magnetic moment per f.u. in Eu0.93Fe4Sb12 originates from a combination of a small fraction of Eu ions having a nominal 3+ valence and the ferrimagnetic alignment of a \( 7\mu_B \) moment per Eu2+ site and a \(-0.21\mu_B \) moment per Fe site.

Polarization-dependent x-ray absorption is a powerful tool for element-specific magnetization measurements in transition metal and rare earth containing ferromagnets. XMCD measurements can give an insight into the temperature and magnetic field dependence of element- and shell-specific magnetic moments. In this paper, we report the temperature dependence of the 4f and 5d electron magnetizations of Eu from Eu M4,5-edge XMCD and Eu L2,3-edge XMCD spectroscopies. The M4,5-edge XMCD is associated...
with the excitation of electrons from the 3d shell to 4f states of Eu; therefore it directly probes the magnetization of Eu in the 4f shell. The L_{2,3}-edge x-ray absorption spectra (XAS) corresponds to the 2p to 5d transition in Eu, and hence XMCD at the L_{2,3} absorption edges of Eu probes its 5d magnetization. An XMCD effect is expected at the L_{2,3} edges of Eu if there is an ordered 5d moment due to the on-site 4f-5d exchange,\textsuperscript{26} intrasite 5d-3d exchange between Eu and Fe, or both. For Eu, the 4f-5d exchange integral is calculated to be 8 mRy; therefore a strong interaction between 4f local moments and 5d band electrons is thus expected.\textsuperscript{27} Because Fe is magnetically ordered in Eu_{0.95}Fe_{4}Sb_{12}, as in AFe_{3}Sb_{12} (A = Na or K), it would be desirable to know if the 5d band of Eu is magnetically polarized through an interaction with Fe 3d band electrons, similar to the case of RFe_{2} compounds.\textsuperscript{26}

By comparing the L_{2,3}-edge XMCD measurement in Eu_{0.95}Fe_{4}Sb_{12} with a suitable reference Eu compound, in which only the rare-earth ion is the magnetic ion and whose 4f magnetic moment is known from other measurements such as magnetization or neutron diffraction, the L_{2,3}-edge XAS and XMCD can give a good comparison of the 5d magnetic moments in the two compounds. Such a comparison can also help us understand the possible interaction between Eu 5d electrons and Fe 3d band electrons in Eu_{0.95}Fe_{4}Sb_{12}. For this purpose, we have measured the Eu L_{2,3}-edge XMCD in Eu_{0.95}Ga_{16}Ge_{30}, which works as a reference compound with a pure Eu^{2+} valence state and without a magnetic transition-metal ion. Eu_{0.95}Ga_{16}Ge_{30} orders in the clathrate structure, which is described by the stacking combinations of EuX_{20} and EuX_{24} (X = Ga or Ge) polyhedra and is shown in Fig. 1(b). Eu_{0.95}Ga_{16}Ge_{30} orders ferromagnetically below 34 ± 2 K, and the saturation magnetic moment of Eu is known to be \sim 7 \mu_{B}.\textsuperscript{28–32}

\section{II. EXPERIMENTAL SECTION}

Polycrystalline samples of EuFe_{2}Sb_{12} (y is less than or equal to 1) and Eu_{0.95}Ga_{16}Ge_{30} were prepared from the purest available elements as described in detail previously in Refs. 19 and 20. Briefly, EuFe_{2}Sb_{12} was prepared directly from the elements in a carbon-coated, evacuated, and sealed silica tube. The tube was heated to 1030 °C for 40h, quenched into water bath, and then heated at 700 °C for 1 week to form the correct skutterudite phase. The clathrate compound Eu_{0.95}Ga_{16}Ge_{30} could be prepared by several methods; the simplest of which was the direct arc melting of the constituent elements on a water-cooled copper hearth in an Ar atmosphere. Powder x-ray diffraction patterns measured at room temperature confirmed the formation of the desired compounds with no other phases present. The Eu site filling fraction y was estimated to be close to 0.95 from the intensity analysis of the x-ray diffraction patterns. The samples were further characterized by dc magnetization, which confirmed the ferromagnetic transition (see Fig. 2) in both samples. The magnetization, M(T), was scaled by its lowest-temperature value, which is approximated as M(0), and the reduced magnetization \frac{M(T)}{M(0)} is displayed in Fig. 2 for both the skutterudite and the clathrate. The reduced magnetization could be fitted by the power law

\[ M(T)/M(0) = (1 - T/T_{C})^b, \]  \hspace{1cm} (1)

where \( T_{C} \) is the transition temperature and \( b \) is an exponent. For the clathrate, we find a very good fit using the above equation for the entire temperature range. For the skutterudite, the best fit by the power law could be obtained for the \( T \geq 50 \) K region. The magnetization at low temperatures is likely to have more complex temperature dependence because there are two magnetic sublattices, one of Eu and the other of Fe, in this compound. The value of the \( T_{C} \) obtained from the fits agrees with the literature values for the respective compounds.\textsuperscript{13,14,30,32} The exponent \( b \) values are given in Fig. 2.

The powder samples were ground, filtered through a 20 \( \mu \)m mesh, and coated onto tapes for Eu L-edge measurements. A multilayered tape, optimized for the L_{3} absorption edge jump of Eu, was used in the XMCD measurements performed in the transmission geometry. XMCD at the Eu L_{2,3} edges was measured at the hard x-ray beamline 4-ID-D at the Advanced Photon Source (APS) at Argonne National Laboratory. The helicity of the photons was modulated between left-circular polarization and right-circular polarization using a diamond (111) phase retarder operated near a Bragg angle in transmission geometry within the energy region of 6.9–7.7 keV. The XMCD spectra were measured in the lock-in detection mode\textsuperscript{33} in the temperature range of 4.8–155 K in a 0.5 T horizontal field superconducting magnet. XMCD is defined as \( \Delta \mu(E) = (\mu^+ - \mu^-) \) and the x-ray absorption coefficient is defined as \( \mu(E) = (\alpha + \alpha\mu'), \) where \( \mu^+ \) and \( \mu^- \) are the x-ray absorption measured with positive and negative photon helicities, respectively. At each temperature, the XMCD spectrum was measured for parallel and antiparallel directions of the magnetic field relative to the photon wave vector and the resulting spectra were averaged. The value of the magnetic field used in the L_{2,3}-edge XMCD measurements varied in the range of 0.29–0.5 T. The XAS and XMCD at Eu M_{4,5} and Fe L_{2,3} edges in the skutterudite Eu_{0.95}Fe_{4}Sb_{12} were measured at the soft x-ray beamline 4-ID-C at the APS. The measurements were performed by detecting the total electron yield on a hot pressed and highly polished pellet of polycrystalline sample at 2.3 K in an applied field of 2 T.

\section{III. RESULTS AND DISCUSSION}

A. XAS in Eu_{0.95}Fe_{4}Sb_{12} and Eu_{0.95}Ga_{16}Ge_{30}

Figure 3 shows the XAS measured at Eu L_{2,3} edges in Eu_{0.95}Fe_{4}Sb_{12} and in the reference compound Eu_{0.95}Ga_{16}Ge_{30}. These spectra are normalized such that their L_{3}-edge jump is unity. The Eu L_{2,3} XAS in Eu_{0.95}Ga_{16}Ge_{30} has a single peak, and the edge energy determined from the derivative maximum comes out to be 6971 ± 0.5 eV, suggesting a pure Eu^{2+} valence state. In contrast, a strong peak and a satellite are observed in the Eu L_{2,3} XAS spectra of Eu_{0.95}Fe_{4}Sb_{12}. The main peak is located exactly at the same energy as in Eu_{0.95}Ga_{16}Ge_{30}, confirming a dominant contribution from Eu^{2+} valence state. There is a satellite peak in the absorption spectra about 8 eV above the main position of the peak. Based on the position of this satellite with respect to the position of the
main peak, we identify the satellite with the Eu$^{3+}$ valence state, which is in agreement with the L$_{2,3}$ absorption spectra reported for other mixed-valence Eu compounds, such as EuNi$_2$S$_2$. To further establish the origin of this satellite peak, we have calculated the near-edge XAS at the L$_3$ edge of Eu in EuFe$_4$Sb$_{12}$ using FEFF8, an automated program for full multiple-scattering calculation with self-consistent potentials for the cluster of atoms. The result, which is shown together with the experimental XAS in Fig. 3(b), shows that the satellite peak is not associated with the near-edge structure of Eu$^{2+}$ ions in support of our interpretation. We have used arctangent as an ad hoc step function for representing the transition to the continuum states. The relative intensities of Eu$^{2+}$ and Eu$^{3+}$ ionic contributions are determined by fitting the XAS to a two-component model consisting of an arctangent step function and a Lorentzian peak for each valence state. Such a fit is often used for the analysis of mixed valence in rare-earth intermetallic compounds. The fit was constrained such that the threshold energy for both the XAS (Lorentzian) peak and the step function for a given valence state is the same, i.e., same as in the model used by Godart et al. for the analysis of S. valence in Sm$_{1-x}$Gd$_x$S.

Fig. 4 shows the XAS and XMCD at Eu M$_{4,5}$ edges in Eu$_{0.95}$Fe$_4$Sb$_{12}$ measured at 4.9 K in an applied field of 2 T. The XAS at the M$_4$ and M$_5$ edges show at least four peaks that can be associated with the multiplet splittings of Eu$^{2+}$ and Eu$^{3+}$ ions. The positions of these multiplet peaks are found to be nearly the same as the theoretical positions of Eu$^{2+}$ and Eu$^{3+}$ ions reported in the literature. Then, the Eu M$_4$-edge XAS spectrum was fitted to linear combination of the theoretical XAS from Eu$^{2+}$ and Eu$^{3+}$ ions. From the best fit, we find that the Eu$^{2+}$ valence state has a 48% ± 2% contribution and the Eu$^{3+}$ valence state has a 52% ± 2% contribution. We would like to note that the Eu$^{3+}$ contribution estimated from the soft x-ray absorption measurement at the M$_4$ edge is much larger than the 12% found in the hard x-ray absorption spectroscopy measurement at the L$_3$ edge. We attribute the discrepancy to the higher fraction of the Eu$^{3+}$ states, most likely from an impurity in the sample surface, which are preferentially probed in the soft x-ray absorption measurements (50 Å in total electron yield mode). The XMCD displayed in Fig. 4(b) has a negative sign for the M$_5$ edge and positive sign for the M$_4$ edge. Because the XMCD measured at the Eu M$_{4,5}$ edges is associated with a 3d initial state and a 4f final state, it directly gives a measure of the magnetic polarization in the 4f shell of Eu ions. The sum-rule analysis enables the estimation of spin and orbital magnetic moments of Eu from the measured intensities of XAS and XMCD spectra. For the M$_{4,5}$ edges of Eu, the sum rules for the expectation values of the orbital angular momentum $\langle L_z \rangle$ and the spin angular momentum $\langle S_z \rangle$ can be written as

![Fig. 3. (Color online) (a) Normalized x-ray absorption spectra at Eu L$_3$ and L$_2$ edges in Eu$_{0.95}$Fe$_4$Sb$_{12}$ and Eu$_6$Ga$_{10}$Ge$_{30}$ at 4.8 K in an applied field of 0.5 T. Inset shows the XAS with a fit to two-component model consisting of an arctangent step function with Lorentzian. (b) Experimental (filled circles) and FEFF calculation (solid line) of Eu L$_3$-edge x-ray absorption spectrum in Eu$_{0.95}$Fe$_4$Sb$_{12}$.](image1)

![Fig. 4. (Color online) Eu M$_{4,5}$-edge (a) XAS and (b) XMCD in Eu$_{0.95}$Fe$_4$Sb$_{12}$ measured at 4.9 K in an applied field of 2 T. The XAS at the M$_4$ and M$_5$ edges show at least four peaks that can be associated with the multiplet splittings of Eu$^{2+}$ and Eu$^{3+}$ ions.](image2)
\[
\langle L_2 \rangle = -\frac{(A_{M4} + A_{M5})N_{4f}}{\mu_0(M)} \tag{2}
\]
and
\[
\langle S_2 \rangle + (7/2)\langle T_2 \rangle = -\frac{(2A_{M5} - 3A_{M4})N_{4f}}{2\mu_0(M)}, \tag{3}
\]
where \( A_{M5} = \int M_5 \Delta \mu(E)dE \) is the integrated XMCD intensity at the Eu \( M_5 \) edge, \( A_{M4} = \int M_4 \Delta \mu(E)dE \) is the integrated XMCD intensity at the Eu \( M_4 \) edge, \( N_{4f} \) is the number of holes in the 4f shell of Eu, \( \mu_0(M) \) is the sum of the integrated XAS intensity at Eu \( M_5 \) and Eu \( M_4 \) edges, \( \int M_5 + M_4 \mu(E)dE \), and \( \langle T_2 \rangle \) is the magnetic-dipole operator of Eu. \( \mu_{orb} = -(L_2) \) and \( \mu_{tot} = -(L_2) + 2\langle S_2 \rangle \) are the orbital magnetic moment and the total magnetic moments of Eu, respectively. We assumed that \( \langle T_2 \rangle = 0 \), as Eu site has a cubic symmetry in this compound. With the XAS and XMCD spectra, shown in Fig. 4, the Eu\(^{2+} \) valence population of \( 48 \% \pm 2 \% \) with the assumption of \( N_{4f} = 7 \) yielded \( \mu_{orb} = (0.13 \pm 0.1) \mu_B \) and \( \mu_{tot} = (7.07 \pm 0.3) \mu_B \) per Eu\(^{2+} \) ion. The total moment per Eu\(^{2+} \) ion is therefore \( (7.2 \pm 0.3) \mu_B \). The Eu\(^{4f} \) magnetic moment and the Fe 3d total magnetic moment, \( \sim 0.21 \mu_B \) per Fe, are almost antiferromagnetically coupled in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\).\(^{20}\)

Figure 5(a) shows the Eu \( M_5 \)-edge XMCD at various temperatures both below and above the ferrimagnetic transition temperature of \( \sim 85 \) K. Figure 5(b) shows the temperature dependence of the integrated XMCD intensity of the individual peaks from Eu\(^{2+} \) and Eu\(^{3+} \) valence sites, extracted by fitting the data [shown in Fig. 5(a)] to three Lorentzian peaks. Note that the XMCD signal from Eu\(^{2+} \) state is strongly temperature dependent and clearly indicates the ferrimagnetic transition in the vicinity of 85 K. The XMCD signal from Eu\(^{3+} \) impurities shows a weak temperature dependence and does not indicate any magnetic transition.

C. Comparison of Eu \( L_{2,3} \)-edge XMCD in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\) and Eu\(_{0.95}\)Ga\(_2\)Ge\(_3\)

XMCD spectra at the Eu \( L_{2,3} \) edges in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\) and Eu\(_{0.95}\)Ga\(_2\)Ge\(_3\) measured on multilayered tape of samples at 4.8 K in an applied field of 0.5 T are presented in Figs. 6 and 7, respectively. Hysteresis measurements confirmed that the magnetization of Eu or the XMCD signal heights are saturated in a field of 0.5 T. The XMCD peak or minimum positions occur at the same edge energies in the two compounds and confirm that the magnetism originates from the Eu\(^{2+} \) ions in the two compounds. A comparison of the XMCD signal heights at the \( L_3 \) and \( L_2 \) edges in the two compounds indicates that the dichroism in the skutterudite is about a factor of 2 larger than the dichroism in the clathrate. The degree of polarization in the 5d shell or the 5d magnetic moment of Eu determines the intensity of the Eu \( L_{2,3} \)-edge XMCD signal in these compounds. Because the XMCD intensity is proportional to the magnetization or magnetic moment, the larger \( L \)-edge XMCD in the skutterudite implies that its Eu 5d moment is larger than the Eu 5d moment in the clathrate. Therefore, the Eu 5d moment in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\) has

FIG. 5. (Color online) (a) Eu \( M_5 \)-edge XMCD in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\) measured in a field of 2 T in the temperature range of 5–130 K. (b) Temperature dependence of the integrated intensity from the 1128 eV (Eu\(^{2+} \)), 1130 eV (Eu\(^{3+} \)), and 1125.6 eV (Eu\(^{4+} \)) peaks in the Eu \( M_5 \)-edge XMCD spectra in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\).

FIG. 6. (Color online) (a) XAS and (b) XMCD at the Eu \( L_{2,3} \) edges in Eu\(_{0.95}\)Fe\(_4\)Sb\(_{12}\) measured at 4.8 K in an applied field of 0.5 T.
The intensity $I(T)$, plotted in Fig. 8(a), is nearly zero for $T \gg 100$ K. It starts to increase as the sample is cooled below 100 K toward the ferromagnetic ordering temperature of Eu$_{0.95}$Fe$_4$Sb$_{12}$. A similar behavior of the Eu $L_3$-edge XMCD intensity is also observed below 37 K in Eu$_8$Ga$_{16}$Ge$_{30}$, indicating a ferromagnetic ordering of the Eu moments. The temperature dependence of XMCD intensity $I(T)$ in the ferromagnetic state of the two compounds could be fit by the power law,

$$I(T) = I(0)(1 - T/T_C)^\beta,$$

where $I(0)$ is the intensity at $T=0$ K, $T_C$ is the Curie temperature, and $\beta$ is the magnetization exponent. The best fits are displayed as the solid lines over the data in Figs. 8(a) and 8(b). The fit presented in Fig. 8(a) yielded $I(0)=9.0 \pm 2$, $T_C=88 \pm 1.5$ K, and $\beta=0.52 \pm 0.05$ for Eu$_{0.95}$Fe$_4$Sb$_{12}$. The fitted value of $T_C$ agrees with the values reported in the literature. The value of $\beta$ is in agreement with the mean-field theoretical prediction of the magnetization critical exponent 0.5. The fit to the $I(T)$ in Eu$_8$Ga$_{16}$Ge$_{30}$ in Fig. 8(b) yielded $I(0)=4.6 \pm 0.09$, $T_C=33.4 \pm 0.3$ K, and $\beta=0.356 \pm 0.03$. The value of $T_C$ returned by the fit is within the range of values, 32–36 K, reported in the literature.

The $T_C$ and exponent $\beta$ values found here for both the compounds also agree with the $T_C$ and exponent $\beta$ values found from the dc magnetization for the respective compounds in Sec. II. The value of the exponent $\beta$ for Eu$_8$Ga$_{16}$Ge$_{30}$ agrees with the theoretical values of the magnetization critical exponents of three-dimensional (3D) models, $\beta=0.367 \pm 0.002$ of the 3D Heisenberg model and $\beta=0.3485 \pm 0.0002$ of the 3D XY model. The error bar on the theoretical exponent value accounts for the results from different theoretical approaches reported in the literature.

The applied field plays the role of aligning magnetic domains in the ferromagnetic or ferrimagnetic state, and it does not induce any additional moment. Therefore the measured XMCD signal gives a good measure of the order parameter in the magnetically ordered state. Above $T_C$, the large applied field can induce magnetization in the critical paramagnetic region and hence result in an XMCD signal, and the magnetic transition appears broadened. The bulk magnetization, shown in Fig. 2, also shows broadening of the transition in a field of 7 T. Therefore, the applied field induces additional error in the exponent values. The error bars reported above already include this contribution.

The ferrimagnetic ordering of Eu, as proven by the observation of the phase transition at $T_C=88 \pm 1.5$ K in the temperature dependence of Eu $L_3$-edge XMCD, suggests that Eu plays a dominant role in the onset of metallic ferrimagnetism. The evidence of bandlike 5d states of Eu and the metallic behavior in the resistivity are consistent with the ferrimagnetic ordering mediated by the coupling of Eu 4f moment with the nearly ferromagnetic conduction-electron band of the [Fe$_3$Sb$_2$]$_{12-2}$-host lattice through Eu 5d states. A similar coupling between Gd and Fe has been recently reported to account for the ferromagnetic ordering in GdFe$_2$Zn$_{20}$. While Eu plays a key role in the magnetic
ordering in Eu$_{0.95}$Fe$_2$Sb$_{12}$. Yb has no detectable magnetic moment in the Zintl phase compound Yb$_{14}$MnSb$_{43}$ in which only Mn orders ferromagnetically below 53 K. It would be interesting to compare and contrast the magnetic and thermoelectric properties of such compounds to know the role played by intra-atomic and inter-atomic exchange interactions in electrical conductivity and thermal transport properties. We suggest first-principles electronic structure calculations of magnetic properties, including the XMCD spectra at Eu $M$ edges and Eu $L$ edges in these compounds, for more insights into the relation between the magnetism and thermopower and electrical conductivity in this class of materials.

IV. SUMMARY

The valence of Eu and temperature dependence of the element-specific and shell-specific magnetic behavior of Eu in the filled skutterudite ferrimagnet Eu$_{0.95}$Fe$_2$Sb$_{12}$ have been investigated using x-ray absorption and x-ray magnetic circular dichroism spectroscopies at the Eu $M_{4,5}$ edges and at the Eu $L_{2,3}$ edges. Bulk sensitive Eu $L_3$ XAS indicates that Eu ions are in the divalent state in the pure skutterudite phase. The total magnetic moment of Eu is shown to be $(7.2 \pm 0.3)\mu_B$ per Eu$^{2+}$ ion which is mostly antiparallel to magnetic moment on the Fe sites. Strong temperature dependence of the XMCD from Eu$^{2+}$ ions has been observed in the measurements at the Eu $M_{4,5}$ edges. The Eu $L_{2,3}$ XAS/XMCD are compared with the divalent Eu ferromagnetic ($T_C = 34 \pm 2$ K) clathrate reference compound Eu$_9$Ga$_{13}$Ge$_{30}$. The Eu $L_3$-edge XMCD signal in the skutterudite is found to be nearly twice that of the clathrate, indicating a substantial enhancement of the $5d$ polarization arising from the $5d$-$3d$ interatomic exchange interaction. The temperature dependence of the Eu $L_3$-edge XMCD gives a measure of the order parameter in the magnetically ordered state below $T_C$ and confirms that there exists a strong on-site exchange coupling between localized 4$f$ moment and the $5d$ conduction electrons of Eu in both Eu$_{0.95}$Fe$_2$Sb$_{12}$ and Eu$_9$Ga$_{13}$Ge$_{30}$.

ACKNOWLEDGMENTS

The authors would like to gratefully acknowledge very helpful discussion with D. J. Singh. This research is sponsored by Materials Science and Engineering Division, Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC. The work at the APS, Argonne National Laboratory is sponsored by the Office of Sciences, U.S. Department of Energy under Contract No. DE-AC02-06CH11357.


35 FEFF8 is an automated program for the multiple-scattering calculations of x-ray absorption fine structure and x-ray absorption near-edge structure for clusters of atoms. For further details, see http://leonardo.phys.washington.edu/feff/


