Thermal neutron diffraction determination of the magnetic structure of $EuCu_2Ge_2$

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The magnetic structure of $EuCu_2Ge_2$ has been determined by flat-plate neutron powder diffraction. Two magnetic phases are present in the neutron diffraction pattern at 3.5 K. They have the same moment, within error, and a common transition temperature. Both ^{151}Eu and ^{153}Eu Mössbauer spectroscopy show that the two magnetic phases belong to the same crystallographic phase. Both phases can be modelled by planar helimagnetic structures: one with a propagation vector of [0.654(1), 0, 0], the other with a propagation vector of [0.410(1), 0.225(1), 0]. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4853095]

I. INTRODUCTION

Following the behaviour of an isostructural series of rare earth (RE) compounds such as $RECu_2Ge_2$ can provide insight into magnetism as electrons are added or subtracted while other parameters are held fixed.

All of the $RECu_2Ge_2$ compounds adopt the tetragonal $ThCr_2Si_2$ structure (space group $I4/mmm$, #139). As we work our way across the rare earth series we find that $CeCu_2Ge_2$ adopts an incommensurate planar helimagnetic structure, with a propagation vector of [0.28, 0.28, 0.54],[1] while the Pr compound orders as a simple AF-I type c-axis antiferromagnet with a propagation vector of [0, 0, $\frac{1}{2}$].[2] There then follows a large gap: The neodymium compound does not appear to have been studied except for some single crystal magnetisation work that suggests antiferromagnetic ordering parallel to the c-axis below $T_N = 4.7$ K,[3] $PmCu_2Ge_2$ cannot be made and the Sm–Eu–Gd block is conventionally omitted due to perceived difficulties associated with the large neutron absorption cross sections of these elements. For Dy,[4] Tb, and Ho,[5] the systems adopt a commensurate antiferromagnetic structure with a propagation vector k of [$\frac{1}{2}$, 0, $\frac{1}{2}$]. The erbium compound continues this trend, ordering at $T_N = 3.0$ K[6] but only adopting the commensurate $k_1 = [\frac{1}{2}, 0, \frac{1}{2}]$ structure below 2.5 K. Between 2.5 K and 3.0 K there is evidence for the coexistence of two magnetic structures as an additional incommensurate modulated magnetic structure having a propagation vector $k_2 = [0.5514(7), 0, 0.5375(37)]$ appears.[6] By thulium, the trend breaks down completely and $TmCu_2Ge_2$ orders at $T_N = 2.5$ K with an incommensurate sine-modulated magnetic structure described by the propagation vector $k = [0.117(3), 0.117(3), 0]$ at 0.47 K.[7]

This leaves the magnetic structure of $EuCu_2Ge_2$, the subject of the current work. Europium lies in the middle of the block of neglected compounds and determination of the magnetic structure of $EuCu_2Ge_2$ would show whether the europium compound adopts one of the simpler commensurate antiferromagnetic structures like Pr or Dy–Ho, or one of the more complex incommensurate structures seen for Ce and Tm. A single europium site is found by ^{151}Eu Mössbauer spectroscopy, with $T_N = 13$ K,[8] consistent with the typical values for this series, ranging from 6.4 K for Ho[9] to 16 K for Pr.[2] However, single crystals of the europium compound grown by an indium-flux method exhibit dynamic effects.[10,11] Here, we apply a large-area flat-plate technique[12] to reduce the impact of the large neutron absorption cross section of natural europium (4530 b) and determine the magnetic stucture of $EuCu_2Ge_2$.

II. EXPERIMENTAL METHODS

$EuCu_2Ge_2$ was prepared by arc melting europium (Alfa Aesar 99.9%), copper (Johnson Matthey Electronics 99.9%), and germanium (Alfa Aesar 99.999%) under Ti-gettered argon. The elements were arc melted in stoichiometric ratios, except for the europium which had a 15% excess by weight. Rietveld refinement of the Cu K_α x-ray diffraction pattern using the GSAS/EXPGUI package[13,14] confirmed the expected tetragonal $ThCr_2Si_2$ structure (space group $I4/mmm$, #139). The lattice constants at room temperature were a = 4.2210(5) Å and c = 10.151(1) Å, consistent with previous work.[8,15] The peaks in the diffraction pattern are sharp and well resolved, showing that $EuCu_2Ge_2$ forms as a single phase. No impurity phases were detected.

^{151}Eu Mössbauer spectroscopy was carried out using a 4 GBq $^{151}SmF_3$ source driven in sine-mode. The velocity was calibrated with an α-Fe foil. The 21.6 keV transition was measured by a thin NaI scintillation detector. A closed-cycle He compressor was used to regulate the temperature of the sample between 5 K and 295 K.

^{153}Eu Mössbauer spectroscopy was carried out using a 2.5 GBq $^{153}Sm_2O_3$ source prepared by neutron activation at

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the McMaster University Research Reactor, Hamilton, Ontario. Both source and sample were cooled to 5 K by mounting them vertically in a helium-flow cryostat. The source was driven in sine-mode with the velocity calibrated with a laser interferometer. A high purity germanium detector was used to detect the 103 keV γ–rays.

Powder neutron diffraction measurements were made using a large-area flat-plate mount[12] to reduce the impact of the large absorption cross section of natural europium. The neutron diffraction patterns were collected at a wavelength of 2.3731(1) Å, on the 800-wire C2 powder diffractometer at the Canadian Neutron Beam Centre, Chalk River, Ontario, and were refined using FullProf.[16]

III. ^{151}Eu and ^{153}Eu MÖSSBAUER SPECTROSCOPY

The ^{151}Eu Mössbauer spectrum measured at 5 K (Figure 1) shows four inner lines of roughly equal intensity and two outer lines of lower intensity, characteristic of a magnetically split ^{151}Eu spectrum with one europium site. The isomer shift, δ, of −9.9(1) mm/s and hyperfine field, B_{hf}, 33.0(2) T at 5 K are consistent with the Felner and Nowik[8] results of $\delta = -9.9$ mm/s and $B_{hf} = 32.5(3)$ T, and are typical of a magnetically ordered divalent europium compound.

The ^{153}Eu Mössbauer spectrum taken at 5 K (also shown in Figure 1), is less well resolved. It was fitted with the hyperfine field constrained to 33.0 T from the ^{151}Eu Mössbauer spectrum. The partially constrained fit describes the ^{153}Eu spectrum well, confirming the ^{151}Eu Mössbauer results. The isomer shift is +12.6(1) mm/s, typical of divalent europium as seen by ^{153}Eu Mössbauer spectroscopy.

The ^{151}Eu hyperfine field plotted in the lower panel of Figure 2 was fitted with a $J = \frac{7}{2}$ Brillouin function, appropriate for the Eu^{2+} ion, and yields an ordering temperature of 12.9(1) K. This is consistent with T_N of 13 K reported in a previous ^{151}Eu Mössbauer study.[8]

IV. NEUTRON DIFFRACTION

Neutron diffraction measurements were made over an angular range (2θ) of 3°–83° at temperatures from 20 K down to 3.5 K. The neutron diffraction pattern at 20 K exhibits only nuclear scattering and the first three Bragg peaks are apparent in the restricted range shown in Figure 3. Cooling

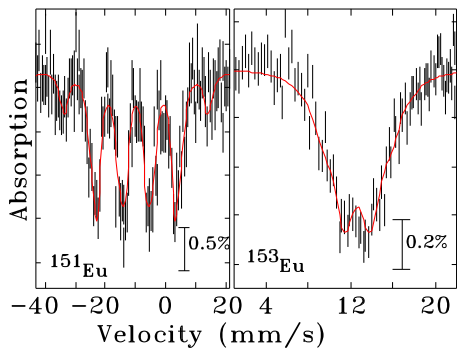

FIG. 1. ^{151}Eu (left) and ^{153}Eu (right) Mössbauer spectra at 5 K. Both spectra have been fitted with a hyperfine field (B_{hf}) of 33.0(2) T.

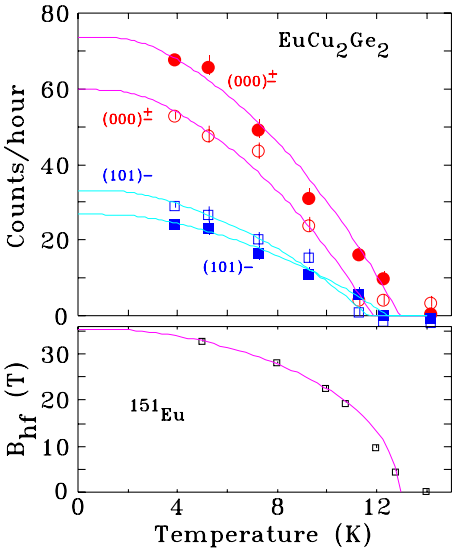

FIG. 2. Top panel: neutron diffraction intensity of several magnetic reflections for $EuCu_2Ge_2$ with fits to a squared $J = \frac{7}{2}$ Brillouin function. Peaks from the k_1 phase are shown as open symbols, while those from the k_2 phase are shown as solid symbols. Bottom panel: ^{151}Eu hyperfine field for the same sample fitted to a $J = \frac{7}{2}$ Brillouin function.

to 3.5 K leads to magnetic ordering and the appearance of many new diffraction peaks. These peaks are emphasised in Figure 3 by subtracting the 20 K pattern from the 3.5 K data.

The flat-plate mounting necessitates a two-step fitting process. First, a LeBail refinement over the full 2θ range is used to determine the instrument zero, peak profiles and lattice parameters. A Rietveld refinement is then carried out over a more restricted 2θ range to reduce the impact of absorption effects which become progressively more severe as the scattered beam becomes more parallel to the sample surface. As the magnetic scattering is invariably concentrated at lower angles, and there are sufficient nuclear peaks to set the nuclear to magnetic scaling, this angular restriction does not affect the analysis.

An EuO impurity of less than 1% by weight is present in the diffraction pattern. EuO orders ferromagnetically ($T_c = 77(1)$ K[17]) and was refined assuming a 7 μ_B Eu^{2+} moment. Its presence does not affect our analysis as the first

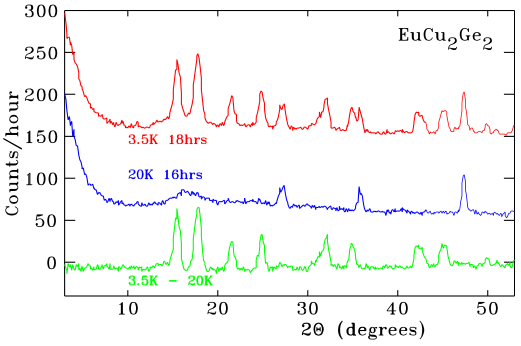

FIG. 3. Neutron diffraction patterns of $EuCu_2Ge_2$ at: (top, red) 3.5 K, showing both the magnetic and the nuclear scattering; (centre, blue) 20 K, showing only the nuclear scattering above the magnetic ordering transition; (bottom, green) the difference between the 3.5 K and 20 K patterns showing only the magnetic scattering. A wavelength of 2.3731(1) Å was used for these measurements.

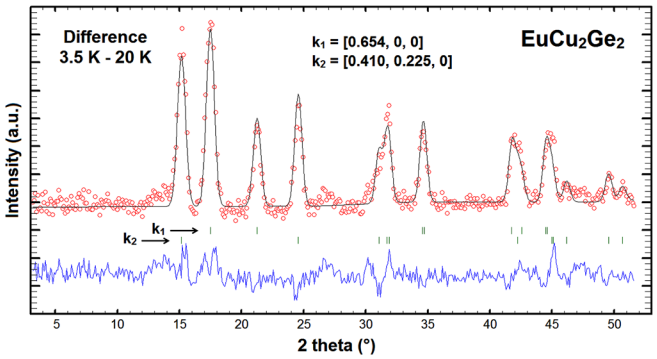

FIG. 4. A planar helimagnetic structure fit, (solid black line), to the difference pattern between 20 K and 3.5 K, shown as (red) dots. The residuals are shown below. The peaks from the magnetic phases are indicated by the Bragg markers, the top set is from the first phase (k_1) and the bottom set is from the second phase (k_2).

reflection occurs near $2\theta = 47^\circ$ and does not overlap with any of those from $EuCu_2Ge_2$.

The 3.5 K–20 K difference pattern in Figure 4 shows several magnetic diffraction peaks which cannot be fitted using a single propagation vector. These peaks can however be indexed using *two* propagation vectors, $k_1 = [0.654(1), 0, 0]$ and $k_2 = [0.410(1), 0.225(1), 0]$, indicating the presence of two magnetic phases. Given the single site refinement of both ^{151}Eu and ^{153}Eu Mössbauer spectra, we can exclude modulated magnetic structures, such as those reported for $ErCu_2Ge_2$[6] and $TmCu_2Ge_2$.[7] The 3.5 K diffraction pattern for $EuCu_2Ge_2$ was therefore refined using a planar helimagnetic structure similar to that reported for $CeCu_2Ge_2$.[1] The best refinement was obtained with the two magnetic phases constrained to have equal weights, and their moments oriented in the *bc*–plane (Figure 4). Magnetic moments of 6.4(1) μ_B and 6.5(1) μ_B were found for the first and second magnetic phases, respectively.

All of our measurements indicate that the two magnetic phases coexist within the same crystallographic phase. The moments are the same, within error, consistent with the single europium site found in both the ^{151}Eu and ^{153}Eu Mössbauer spectra (Figure 1). Both the x-ray and the neutron diffraction patterns have sharp well defined peaks, consistent with a single crystallographic phase, and no significant impurity contributions were detected. Furthermore, the temperature dependence of the intensity of the first four magnetic peaks (two from each of the magnetic phases), plotted in Figure 2, show similar behaviour and can be fitted with squared $J = \frac{7}{2}$ Brillouin functions. The transition temperatures derived from these fits are consistent with each other, and with the value derived from ^{151}Eu Mössbauer spectroscopy. We therefore conclude that the two magnetic phases coexist and are associated with the same crystallographic phase.

Given the largely unexplored gap from Nd to Gd, it is not clear whether the complex ordering of $EuCu_2Ge_2$ is part of a trend in the middle of the rare earth series, or is the result of europium being divalent in this compound. Further work on the remaining members of the series (Nd–Gd) will be needed to shed light on this.

V. CONCLUSIONS

The 3.5 K neutron powder diffraction pattern of $EuCu_2Ge_2$ has been fitted using a planar helimagnetic structure. The fit used two equal-weight magnetic phases with propagation vectors $k_1 = [0.654(1), 0, 0]$ and $k_2 = [0.410(1), 0.225(1), 0]$. The first phase has a moment of 6.4(1) μ_B and the second phase has a moment of 6.5(1) μ_B. ^{151}Eu and ^{153}Eu Mössbauer spectroscopy only show one site with well resolved absorption lines. The ^{151}Eu Mössbauer spectrum at 5 K had a hyperfine field of 33.0(2) T, and the temperature dependence of B_{hf} gave $T_N = 12.9(1)$ K. A squared Brillouin fit to the magnetic peak intensities showed a common transition temperature of 12.2(1) K. No difference in transition temperature was observed between the two magnetic phases.

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[1]G. Knopp, A. Loidl, K. Knorr, L. Pawlak, M. Duczmal, R. Caspary, U. Gottwick, H. Spille, F. Steglich, and A. P. Murani, Z. Phys. B **77**, 95 (1989).
[2]A. Szytuła, W. Bażela, and J. Leciejewicz, Solid State Commun. **48**, 1053 (1983).
[3]T. Shigeoka, K. Hirata, H. Mitamura, Y. Uwatoko, and T. Goto, Physica B **346**, 117 (2004).
[4]P. A. Kotsanidis, J. K. Yakinthos, and E. Roudaut, Solid State Commun. **50**, 413 (1984).
[5]P. Schobinger-Papamantellos, A. Niggli, P. A. Kotsanidis, and J. K. Yakinthos, J. Phys. Chem. Solids **45**, 695 (1984).
[6]B. Penc, S. Baran, D. Kaczorowski, A. Hoser, and A. Szytuła, J. Alloys Compd. **503**, L18 (2010).
[7]B. Penc, S. Gerischer, A. Hoser, and A. Szytuła, J. Magn. Magn. Mater. **324**, 657 (2012).
[8]I. Felner and I. Nowik, J. Phys. Chem. Solids **39**, 767 (1978).
[9]P. A. Kotsanidis and J. K. Yakinthos, Solid State Commun. **40**, 1041 (1981).
[10]P. Wang, Z. M. Stadnik, J. Żukrowski, B. K. Cho, and J. Y. Kim, Solid Sate Commun. **150**, 2168 (2010).
[11]P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, M. F. Hundley, M. S. Sercheli, R. R. Urbano, C. Rettori, Z. Fisk, and S. B. Oseroff, Phys. Rev. B **63**, 092406 (2001).
[12]D. H. Ryan and L. M. D. Cranswick, J. Appl. Crystallogr. **41**, 198 (2008).
[13]A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748, 2000.
[14]B. H. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[15]W. Rieger and E. Parthé, Monatsch. Chem. **100**, 444 (1969).
[16]J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).
[17]N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **127**, 2101 (1962).