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^{151}Eu Mössbauer study of magnetic ordering in flux-grown ferromagnetic and antiferromagnetic forms of $EuCd_2As_2$

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ABSTRACT

$EuCd_2As_2$ is a remarkably complex magnetic semimetal that may behave as a topological insulator or host two pairs of Weyl points, depending on the growth conditions and the final magnetic state. Both antiferromagnetic (AFM) and ferromagnetic (FM) forms have been grown, and we show here, using ^{151}Eu Mössbauer spectroscopy, that the differences between the AFM and FM forms extend well beyond their ground state magnetic structures. Whereas the AFM form undergoes a conventional AFM → paramagnetic transition on warming, the FM form passes through a complex incommensurate modulated state before becoming paramagnetic.

I. INTRODUCTION

The prediction that $EuCd_2As_2$ might host a pair of protected Dirac points[1] has led to extensive investigations of this remarkable system. Of particular interest is the competition between antiferromagnetic (AFM) and ferromagnetic (FM) ordering. Originally reported to be simply AFM below T_N ~9.5 K,[2] resonant x-ray scattering has found evidence for FM correlations well above T_N.[3,4] Furthermore, high pressure μSR measurements revealed a transition to FM order above ~2 GPa,[5] with T_c increasing with further application of pressure. The pressure regime has been exteneded to over 40 GPa using synchrotron Mössbauer spectroscopy (SMS), finding that T_c continues to increase, reaching a remarkable ~80 K by 43 GPa.[6]

Investigation of the AFM/FM interplay in $EuCd_2As_2$ has been greatly simplified, or at least brought to ambient pressure, by the discovery that subtle adjustments in the growth conditions[7] or sub-percent doping with either sodium or silver[8] can be used to tune $EuCd_2As_2$ between AFM and FM ground states. Here we investigate both AFM and FM forms of $EuCd_2As_2$ using ^{151}Eu Mössbauer spectroscopy, and show that there are very significant differences in the ordering behaviour of the two forms.

II. EXPERIMENTAL METHODS

The three samples of $EuCd_2As_2$ used here were taken from the same batches of material studied extensively by Jo *et al.*[7] and the full preparation details are given there. The two salt-flux grown single crystals of $EuCd_2As_2$ were grown following a qualitatively similar procedure to that described by Schellenberg *et al.*,[2] but with significant differences in the ratios of starting elements and salts.[7] Eu (Ames Laboratory, 99.99+%), Cd (Alfa Aesar, 99.9997%) and As (Alfa Aesar, 99.9999 %) were weighed in the molar ratio of 1:2:2 for FM(salt)-$EuCd_2As_2$ and 1.75:2:2 for AFM(salt)-$EuCd_2As_2$, and mixed with fourfold mass ratio of an equimass mixture of NaCl and KCl (Alfa Aesar, ultra dry, 99.99% and 99.95 % respectively). All work was done under argon in a glove box. The materials were sealed in fused silica ampoules and growth proceeded through slow heating to 847 °C followed by slow cooling to 630 °C and air-quenching. The AFM(Sn)-EuCd$_2$*As*$_2$ single crystals were grown from a tin flux using an initial stoichiometry of Eu:Cd:As:Sn = 1:2:2:10 loaded into a fritted alumina crucible (CCS)[9,10] and sealed in fused silica tube under a partial pressure of argon. The ampoule was heated up to 900 °C over 24 hours, and held for 20 hours, cooled to 500 °C over 200 hours, and decanted.[11] Structural and magnetic characterisation was presented in detail by Jo *et al.*[7]

The ^{151}Eu Mössbauer spectroscopy measurements were carried out using a 3 GBq ^{151}SmF$_3$ source, driven in sine mode and calibrated using a standard ^{57}CoRh/α-Fe foil. Isomer shifts are quoted relative to EuF$_3$ at ambient temperature. The sample was cooled in a vibration-isolated closed-cycle helium refrigerator with the sample in a helium exchange gas. For the AFM samples where the lines remained sharp at all temperatures, the spectra were fitted to a sum of Lorentzian lines with the positions and intensities derived from a full solution to the nuclear Hamiltonian.[12]

The spectra of the FM sample taken at 5K and well above the magnetic transition were fitted with the same model used for the AFM samples. However at all intermediate temperatures, the spectra exhibited significant line broadening and the spectral shape evolved in a complex manner. The shape and evolution of the spectra with temperature were inconsistent with dynamic effects, such as slow paramagnetic relaxation. We therefore turned to a model in which the moments are assumed to be affected by an incommensurate modulation of their magnitudes.[13,14] Model details are given below, where it is used.

III. RESULTS

The behaviours of the two AFM samples of EuCd$_2$*As*$_2$ were indistinguishable. Isomer shifts (δ) and hyperfine fields (B$_{hf}$) at 5 K given in Table I were typical of divalent europium in an intermetallic compound. A small (~5% in the salt-grown sample and ~1% in the sample grown from tin) trivalent impurity was detected in both samples, likely due to oxide introduced during preparation or handling. This impurity is well isolated from the primary divalent component so it had no impact on the analysis. The spectra shown in Figure 1 exhibit sharp Mössbauer lines at all temperatures and the evolution of the hyperfine field (B$_{hf}$) shown for both samples in Figure 2, followed the expected J=$\frac{7}{2}$ mean-field function yielding a Néel temperature (T$_N$) of 9.45(3) K, fully consistent with previous reported values of ~9.5 K[2] and ~9.2 K.[7] We emphasise that both AFM samples were used here and they are fully equivalent, with essentially identical values for B$_{hf}$ at any given temperature (Figure 2). The flux used (salt mixture or Sn) has no impact on the magnetic behaviour of the two AFM samples as seen by ^{151}Eu Mössbauer spectroscopy.

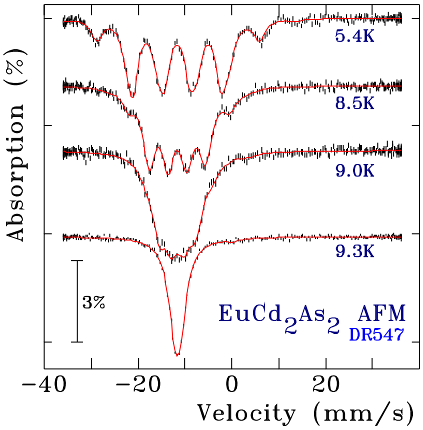

FIG. 1. ^{151}Eu Mössbauer spectra of the AFM form of EuCd$_2$*As*$_2$ showing the evolution of the spectra with temperature. The lines remain sharp at all temperatures and the solid red lines are fits derived from a full Hamiltonian solution as described in the text. Spectra shown are for the Sn-flux grown DR547 sample, however those for the salt-flux grown DR437 sample were essentially identical as Figure 2 shows.

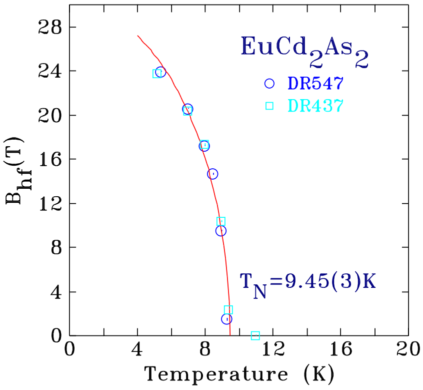

FIG. 2. Temperature dependence of the fitted hyperfine field (B$_{hf}$) in the AFM form of EuCd$_2$*As*$_2$ derived from fits using full Hamiltonian solution as described in the text. Data for both samples are shown. The solid line is a fit to J=$\frac{7}{2}$ mean-field function (expected for Eu^{2+}) that yields a Néel temperature (T$_N$) of 9.45(3) K.

TABLE I. Samples, flux used, magnetic ordering and ^{151}Eu Mössabauer parameters for the three EuCd$_2$*As*$_2$ samples studied here. Both the isomer shift (δ) and hyperfine fields (B$_{hf}$), derived from the 5 K spectra, are typical of divalent europium intermetallics. The quadrupole contribution (Δ) is taken from a paramagnetic pattern measured above T$_{C/N}$.

Sample	Flux	Order	δ (mm/s)	Δ (mm/s)	B$_{hf}$ (T)	T$_{C/N}$ (K)
DR437	Salt	**AFM**	−11.43(2)	+4.5(6)	23.7(1)	9.45(3)
DR547	Sn	**AFM**	−11.59(2)	+4.4(6)	23.9(1)	
DR251	Salt	**FM**	−11.39(2)	+4.5(5)	27.2(1)	30.3(2)

The quadrupole contribution (Δ) at 50 K (Table I) is relatively small, using the full Hamiltonian[12] allows us to fit for the angle, θ, between V$_{ZZ}$ (the principal axis of Δ) and B$_{hf}$. The $\bar{3}m$ point symmetry of the Eu1*a* site constrains V$_{ZZ}$ to be parallel to the crystallographic c-axis, so θ is also the angle between B$_{hf}$, and by extension the Eu moments, and the c-axis. Our fits give $\theta = 60(3)°$ for both AFM forms. This is inconsistent with the $\theta = 90°$ that would be expected for the planar AFM structure reported by Rahn *et al.*[3] based on resonant x-ray scattering. The origin of this discrepancy is unknown at this time, however, given the extreme doping sensitivity of this system, and the complex ordering of the FM form described below, it is possible that the ordering of the AFM is not as simple as initially thought.

The FM sample of $\mathrm{EuCd_2}As_2$ shows some remarkable differences from the (apparently) simple behaviour of the AFM samples. At 5 K, the spectrum of the FM sample (top of Figure 3) is almost the same as that of the AFM samples at the same temperature (top of Figure 1). As Table I shows, the isomer shift for the FM sample is barely different from that of the AFM samples, while B_{hf} at 5 K is a little over 10% larger. However, on warming substantial differences become apparent. Tracking the average hyperfine field (Figure 4) yields a Curie temperature of T_c=30.3(2) K, more than three times the T_N=9.45(3) K seen in the two AFM samples. It is certainly remarkable, and possibly unprecedented that such a small (sub-percent) change in sample composition could change the ordering temperature by a factor of three.

However, the more immediate difference is that the *shape* of the spectra changes on warming. The spectral lines broaden and the spectra develop excess weight towards the centre of the patterns. As noted in the methods section, this evolution of the spectral shape for the FM sample is characteristic of a system in which the magnetic order includes an incommensurate modulation of the moment magnitudes. Such behaviour occurs quite frequently in AFM Eu-based intermetallics, but so far as we know, it has never been reported in a FM system. Its development here likely results from a FM/AFM instability associated with remarkably close proximity of the FM and AFM forms of $\mathrm{EuCd_2}As_2$.

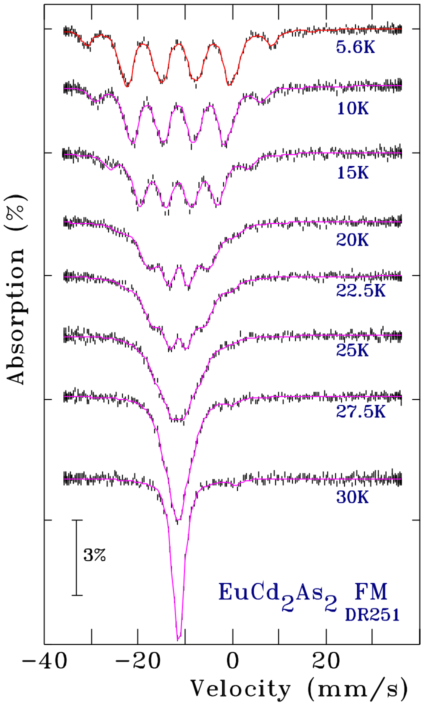

FIG. 3. ^{151}Eu Mössbauer spectra of the FM form of $\mathrm{EuCd_2}As_2$ showing the evolution of the spectra with temperature. The lines clearly broaden on warming and the spectra develop a characteristic "droop" towards the centre. The solid red line through the 5.6 K spectrum is a fit derived from the full Hamiltonian solution, while the magenta lines through the remaining spectra are fits derived from the incommensurate modulation model (see text for details of both models).

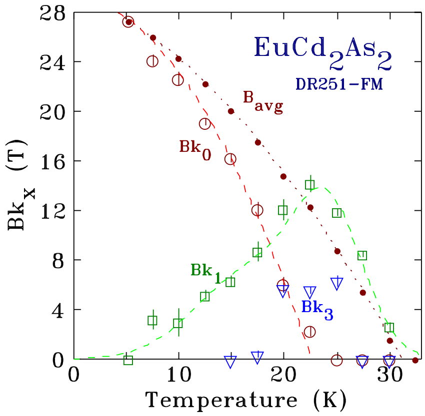

FIG. 4. Temperature dependence of the average hyperfine field (B_{avg}) and three Fourier components (Bk_0, Bk_1 and Bk_3) for the FM form of $\mathrm{EuCd_2}As_2$ derived from the incommensurate modulated model. Fitting a power-law through B_{avg}(T) yields a transition temperature of 30.3(2) K. A similar fit to Bk_0(T) shows that the uniform component is lost at 22.6(2) K, at essentially the same temperature that Bk_1(T) passes through its maximum at 22.8(4) K.

To fit the spectra, we assume that the moment modulation along the direction of the propagation vector **k** can be written in terms of its Fourier components, and further assume that the observed hyperfine field is a linear function of the magnitude of the Eu moment at any given site. The variation of B_{hf} with distance x along the propagation vector **k** can then be written as a sum of the odd Fourier coefficients (Bk_n) of the field (moment) modulation.[13] A square-wave modulated structure can be modeled either as a sum over a very large number of Fourier coefficients, or by simply using the Bk_0 term with all of the other Bk_n set to zero. A purely sinusoidal modulation requires only the first harmonic, Bk_1, to fit the spectrum. However, if the modulation becomes more square, additional harmonics (Bk_3, Bk_5...) are needed. Variations of this model have been used to fit spectra of EuPdSb[13] and $\mathrm{Eu_4PdMg}$.[15]

The results of these fits are shown as magenta lines through the spectra in Figure 3. The temperature dependence of the average B_{hf} (plotted as B_{avg} in Figure 4) allows us to determine the transition temperature, where the field (and by assumption, the time-averaged moment) goes to zero. This yields T_c=30.3(2) K. Just below T_c, the ordering is dominated by a sinusoidal modulation of the moments, and only the Bk_1 term is present. However, this modulation cannot persist to 0 K as the fluctuations that support the modulated order must die away on cooling to permit the Eu^{2+} ions to take on their full 7 μ_B moments throughout the material. This process is seen in the ^{151}Eu Mössbauer spectra by the appearance of higher harmonics as the modulation squares up – Bk_3 appears near 25 K.

In an incommensurate antiferromagnet at 0 K a moment reversal occurs along some direction with a periodicity that does not match that of the underlying crystallographic lattice in that direction. Introducing a magnitude modulation on warming simply softens the edges of the reversal without changing the basic AF nature of the order. By contrast, modulating the moment of a *ferromagnetic* system introduces a new periodicity into the order but it cannot include a moment reversal as this would make the system antiferromagnetic. Thus, in Figure 4 we observe the development of a weak modulation term (Bk_1) on warming but the constant (Bk_0) term dominates. The loss of the Bk_0 term at 22.6(2) K implies a fundamental change in nature of the order: with no constant term present, the order would appear to be incommensurate antiferromagnetic.

IV. DISCUSSION

As Mössbauer spectroscopy is fundamentally a short-ranged probe of magnetic order, it provides very little direct information about the detailed nature of the long-ranged magnetic order in this system. However some key statements can be made.

The AFM form of $EuCd_2As_2$ appears to be a fairly conventional antiferromagnetic system. The temperature dependence of B_{hf} (and by assumption, the europium sublattice magnetisation) follows the expected $J=\frac{7}{2}$ mean-field function with T_N=9.45(3) K, reasonably consistent with previous reports[2] and earlier work on these samples.[7] This behaviour appears independent of the growth method (NaCl/KCl or Sn-flux) as long as the AFM form is obtained.

By contrast, the FM form of $EuCd_2As_2$ is far from conventional. Fitting the average hyperfine field (B_{avg}(T)) with a power-law (a mean-field function does not give anything close to a satisfactory fit) yields an ordering temperature of 30.3(2) K, well above the 26.4 K derived from C_p(T) data for the same FM sample by Jo *et al.*[7] However the departure from conventional behaviour is much more significant than just exhibiting an unusual B_{avg}(T). The ^{151}Eu Mössbauer spectra shown in Figure 3 provide clear evidence for some form of incommensurate moment modulation developing on warming from 5 K. This modulated component grows and by ~23 K it is the *only* component present. Our analysis leads to the conclusion that the ordering in the FM form of $EuCd_2As_2$ is actually AFM for 23 K <T <30 K.

The presence of an incommensurate moment modulation overlaying FM order points to a rather complex magnetic structure for the "FM" form of $EuCd_2As_2$. Unfortunately, Mössbauer spectroscopy cannot provide any information on either the direction or periodicity of the modulation, and further investigation will require the use of neutron diffraction.

V. CONCLUSIONS

^{151}Eu Mössbauer spectroscopy shows that the temperature dependence of the magnetic ordering in the AFM form of $EuCd_2As_2$ is fully conventional, but that of the FM form involves the development of an incommensurate moment modulation that grows on warming and ultimately dominates. The ordering of the FM form of $EuCd_2As_2$ appears to pass through the unusual sequence: FM → incommensurate+FM → incommensurate–AFM → paramagnet on warming. Neutron diffraction measurements will be required to fully elucidate the detailed nature of this ordering behaviour.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

D. H. Ryan: Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Na Hyun Jo**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Brinda Kuthanazhi**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Sergey L. Bud'ko**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Paul C. Canfield**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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