Magnetic and structural transitions in $EuAg_4As_2$ studied using ^{151}Eu Mössbauer spectroscopy

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ABSTRACT

^{151}Eu Mössbauer spectroscopy confirms that the europium in $EuAg_4As_2$ is fully divalent and that the spectrum at 5 K consists of a single, sharp magnetic pattern with a hyperfine field (B_{hf}) of 27.1(1) T and an isomer shift of −11.04(3) mm/s (relative to EuF_3). The temperature dependence of the spectra shows that the ordering of the Eu moments proceeds via an incommensurate sine modulated structure starting at 15 K. The structure squares up below 9 K. A search for charge density or phonon softening signatures at the 120 K structural transition was not successful.

I. INTRODUCTION

The recently described trigonal $CaCu_4P_2$−type ($R\bar{3}m$ #166) $EuAg_4As_2$ is part of a wide family of 1-4-2 pnictides.[1] Preliminary magnetic characterisation suggested antiferromagnetic (AF) ordering occurred below T_N=15 K[2] and that the Eu was divalent. The isostructural $SrAg_4As_2$ compound hosts non-magnetic, formally divalent Sr in place of the Eu and serves as a well-defined reference. It is a diamagnetic metal with a structural transition around 110 K.[3] A transport and neutron diffraction study of flux-grown single crystal $EuAg_4As_2$ revealed a structural transition at 120 K and two magnetic transitions at 15 K and 9 K.[4] Neutron diffraction suggested short-range AF correlations develop at 15 K followed by incommensurate long-range AF order at 9 K.[4]

Here we present the results of an extensive ^{151}Eu Mössbauer study of $EuAg_4As_2$ using flux-grown crystals.[4] Spectra were taken from 5 K to 200 K to investigate the magnetic behaviour below 20 K, the transport-detected event near 90 K and the structural transition at 120 K.

II. EXPERIMENTAL METHODS

The single-crystal samples of $EuAg_4As_2$ used here were grown using Ag_2As as a self-flux as described by Shen *et al.*[4] The crystals were hand ground under hexane, to reduce oxidation, and mixed with boron nitride powder to make a uniform random absorber.

The ^{151}Eu Mössbauer spectroscopy measurements were carried out using a 4 GBq $^{151}SmF_3$ source, driven in sine mode and calibrated using a standard $^{57}CoRh/\alpha$-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. Most of the spectra were fitted to a sum of Lorentzian lines with the positions and intensities derived from a full solution to the nuclear Hamiltonian.[5] However, those spectra taken in the incommensurate modulated phase between 15 K and 9 K were fitted using a model that derives a distribution of hyperfine fields from an (assumed) incommensurate sinusoidally modulated magnetic structure.[6,7]

If 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 Eu moment at any given site, then the variation of B_{hf} with distance x along the propagation vector **k** can be written as:[6]

$$B_{hf}(kx) = Bk_0 + \sum_{l=0}^{n} Bk_{2l+1} \sin(2l+1)kx \quad (1)$$

where the Bk_n are the odd Fourier coefficients of the field modulation. As $+B_{hf}$ and $-B_{hf}$ are indistinguishable, kx only needs to run over half the modulation period, and in this case, a square-wave modulated structure can be modelled 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. We found the fits to be far more stable with the Bk_0 term included rather than using a large set of Bk_n, however the two approaches are effectively equivalent. Variations of this model have also been used to fit spectra of EuPdSb[6] and Eu_4PdMg.[8]

In-plane ac (f = 16 Hz) resistivity measurements were performed in a standard, linear, four-probe configuration using an ACT option of a Quantum Design Physical Property Measurement System (PPMS). Electrical contacts to the sample were made using Epotek H20 silver epoxy.

III. RESULTS

The ^{151}Eu Mössbauer spectrum of $EuAg_4As_2$ shown in Fig. 1 confirms that the europium is fully divalent (isomer shift of −11.04(3) mm/s at 5 K) and the sharp lines (HWHM=1.10(4) mm/s) show that Eu^{2+} moments are in a single magnetic environment with a hyperfine field (B_{hf}) of 27.1(1) T and zero (within uncertainty) quadrupole contribution. Similar linewidths with zero quadrupole contribution were observed in the paramagnetic state (*e.g.* 1.16(5) mm/s at 200 K) so we conclude that while not required by the $\bar{3}$m point symmetry of the 3*a* site occupied by the europium, the electric field gradient is unfortunately zero. This means that ^{151}Eu Mössbauer spectroscopy is effectively blind to rotations of the moment directions within the crystallographic cell and we are not able to observe any effects that could reflect the incommensurate non-collinear magnetic structure reported by Shen *et al.*[4] Our measured hyperfine field of 27.1(1) T is consistent with the europium carrying a fully ordered 7 μ_B moment and therefore in agreement with the 6.3 μ_B derived from neutron diffraction.[4]

The temperature dependence of B_{hf} shown in Fig. 2 was determined in two ways. Using a single magnetic site and allowing the linewidth to increase in order to reproduce the clear broadening apparent above 10 K in Fig. 1 yields increasingly unsatisfactory fits and linewidths that reach 3.4(3) mm/s by 13 K, however the behaviour of the derived fields shown as open circles in Fig. 2 appears quite reasonable. Far better fits were obtained using a model that described the spectral broadening by using an incommensurate sinusoidal modulation of B_{hf} and did not rely on artificially broadening the lines[6–8] and the average B_{hf} derived from these fits is also shown on Fig. 2 as open squares.

Fitting B_{hf}(T) to a J=$\frac{7}{2}$ Brillouin function (appropriate for Eu^{2+}) yields T_N=14.4(1) K, consistent with the onset of short-range order

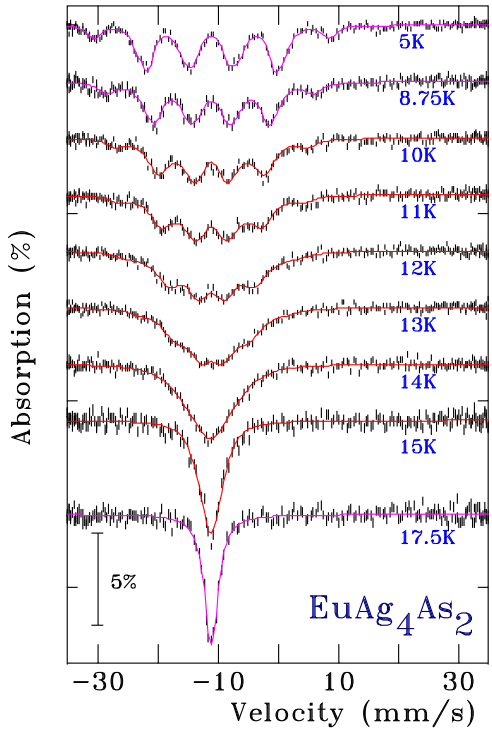

FIG. 1. ^{151}Eu Mössbauer spectra of $EuAg_4As_2$ showing the evolution of the spectral with temperature. Below 10 K the spectra could be fitted with a single, sharp magnetic pattern but the marked changes in the shape of the spectra at higher temperature led us to use a model based on an incommensurate modulated structure to fit the data (see text for details). The solid lines are fits derived from either a full Hamiltonian solution (magenta lines: T < 10 K; T=17.5 K) of from the modulated model (red lines: 10 K ≤ T < 17.5 K).

at T_2=15 K reported from neutron diffraction.[4] There is no break in behaviour at 9 K (marked as "T_N" on Fig. 2) the reported onset of long-range magnetic order derived from the intensity of the (1 0 1)+Q magnetic diffraction peak.[4]

The temperature dependence of the Fourier components used to fit the distribution of B_{hf} shown in Fig. 3 reveals the sequence of magnetic ordering in $EuAg_4As_2$ seen by ^{151}Eu Mössbauer spectroscopy. On cooling through 16 K the single paramagnetic line seen at higher temperatures starts to broaden. Fitting the spectra shows that a small amplitude sinusoidal modulation has developed – Bk_1 is now non-zero. The initial ordering that sets in at about 15 K appears to be to an incommensurate sinusoidally modulated state. Further cooling leads first to a growth in Bk_1 and then to the appearance of the third harmonic (Bk_3) as the modulated order starts to square up for T ≤ 13 K. While it would be natural to follow the squaring process further by adding higher harmonics, the fifth harmonic, even for a perfect square wave is a factor of five weaker than the fundamental, and is even weaker here as the modulation starts to square up. Including Bk_5 gave small values with large uncertainties and tended to destabilise the fits. More consistent behaviour was achieved by modelling the final stages of the squaring process by allowing Bk_0, the constant term, to be present. As we cool below 12 K, Bk_1 and Bk_3

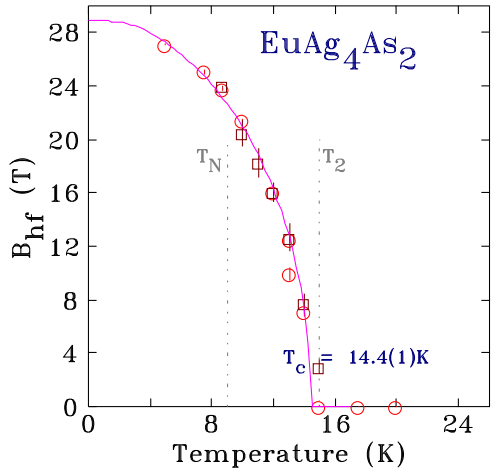

FIG. 2. Temperature dependence of the hyperfine field (B_{hf}) in $EuAg_4As_2$. Fitted values are taken from (open circles): single-site full Hamiltonian fits with the linewidth free to increase; (open squares): average field derived from the incommensurate modulated model. (see text for details) The solid line through the data is a fit to $J=\frac{7}{2}$ Brillouin function that yields an ordering temperature of 14.4(1) K. Also shown as vertical dotted lines are T_N and T_2 identified by Shen *et al.*[4] using neutron diffraction.

decline rapidly and by 9 K only Bk_0 remains. As noted above, we are unable to say anything about the *direction(s)* of the moments below 9 K, but it is clear that the moments all have the same magnitude and that the modulation is gone. Thus the ordering on cooling proceeds to the noncollinear state seen by Shen *et al.*[4] via an initial modulated state.

Transport measurements in the ab-plane (Fig. 4) show two additional features above the magnetic ordering transitions, at ~90 K and ~120 K (the latter feature was labelled T_1 by Shen *et al.*[4] and shown to be associated with a structural distortion). As structural transitions are frequently associated with the development of a soft phonon mode, it was of interest to see whether any evidence for such a mode could be found in the Mössbauer spectra: Softening of a phonon mode that includes the europium site would lead to an increased vibration amplitude near the transition and a corresponding reduction in the recoil-free fraction (spectral area).[9] As the data in Fig. 5 show, no departure from simple Debye behavior was detected. Fitting the temperature dependence of the normalised

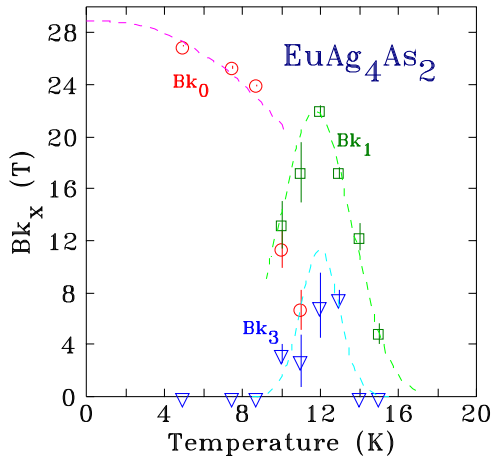

FIG. 3. Temperature dependence of the three lowest-order Fourier components of B_{hf} used to fit the spectra for 10 K ≥T ≥17.5 K using the modulated model. Bk_0 is a uniform dc offset and reflects a constant (non-modulated) ordering of the Eu^{2+} moments. Bk_1 and Bk_3 are the fundamental and third harmonic components in the Fourier series describing the field distribution that arises from the incommensurate order.

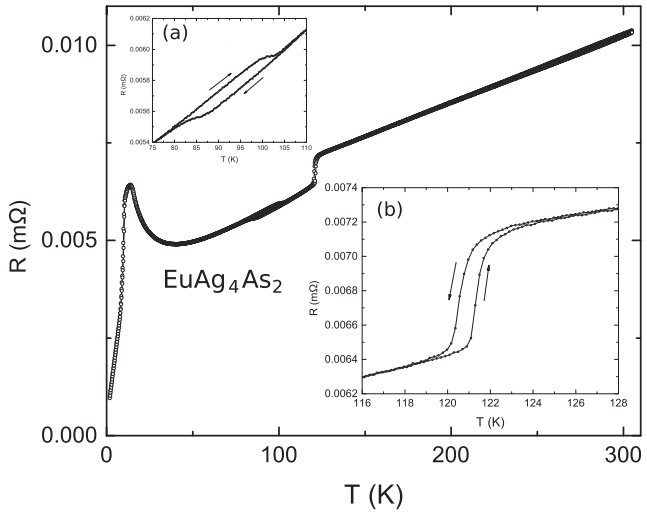

FIG. 4. In-plane ac (f = 16 Hz) resistance data for $EuAg_4As_2$ showing the magnetic transition near 10 K and two further features near 90 K (inset (a)) and 120 K (inset (b)).

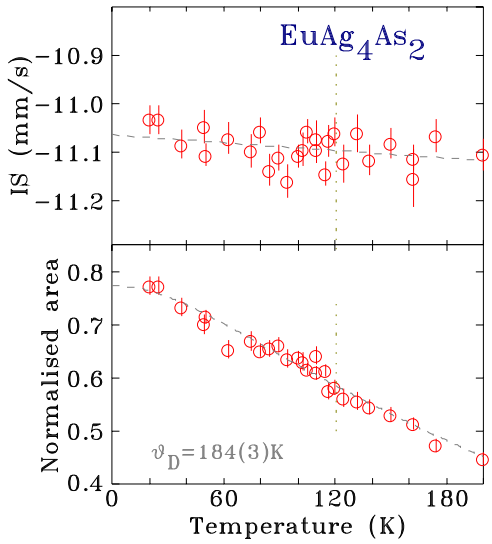

FIG. 5. Temperature dependence of the isomer shift (top), and normalised area (bottom) for $EuAg_4As_2$. Dashed line in the top figure is a guide to the eye. The dashed line in the lower panel is a fit to the Debye model yielding θ_D =184(3) K.

area gave a Debye temperature of 184(3) K, somewhat higher than the 140 K determined by heat capacity for $SrAg_4As_2$,[3] but it should be noted that the Mössbauer value is locally weighted to the Eu site rather than representing a global average as heat capacity is. If either transport feature were associated with a significant change in the electron density of states around the europium site we might expect this to affect the isomer shift. However as the temperature dependence of the isomer shift shown in Fig. 5 makes clear, no such changes are observed. ^{151}Eu Mössbauer spectroscopy is unfortunately insensitive to the two features detected in the transport data, and no new insights are provided.

IV. DISCUSSION

Recent single-crystal neutron diffraction measurements on $EuAg_4As_2$ concluded that short-range order appears at ~15 K, followed by long-range incommensurate magnetic order below ~9 K.[4] The ^{151}Eu Mössbauer data presented here confirms both events but provides an alternative view of the magnetic ordering.

B_{hf} *cannot* be used as a direct measurement of the europium moment as values ranging from ~20 T to over 40 T have been observed in materials where the europium moment has been confirmed by neutron diffraction to take its full value of $7\mu_B$.[10] However, the value of B_{hf}=27.1(1) T seen here for $EuAg_4As_2$ at 5 K (the fit in Fig. 2 extrapolates to 29.0(2) T at T=0 K) is solidly in the middle of the range expected for europium carrying its full $7\mu_B$. This is fully consistent with the moment derived from neutron diffraction.[4]

We turn now to the nature of the magnetic order between 9 K and 15 K. While Mössbauer spectroscopy is fundamentally a *local* probe and therefore cannot be used to unequivocally establish the presence (or indeed absence) of long-range magnetic order, the evolution of both the spectral shape (as seen through the fitted Fourier components) and the average hyperfine field strongly suggests that long-range order develops immediately, at 15 K, and not at 9 K. The spectral shape for 9 K ≤ T ≤ 15 K is not consistent with the presence of slow relaxation dynamics, but it is well fitted using a model that invokes an incommensurate, sinusoidally modulated magnetic structure. This model *assumes* that the order is long-range. Furthermore, on cooling from 15 K, the spectral shape evolves precisely as one would expect – the amplitude modulation grows, squares up, and finally becomes uniform as the europium moments all take their expected value. There is no break in B_{hf}(T) as the modulation ends, suggesting a smooth progression from incommensurate-modulated to incommensurate-noncollinear ordering.

Thus ^{151}Eu Mössbauer spectroscopy confirms the two magnetic events reported by Shen *et al.*,[4] we differ on the nature of the events. The Mössbauer data suggest that a rather complex, incommensurate modulated, but long range, order is established at 15 K and that on cooling, the modulation squares up, and by 9 K the incommensurate structure seen in single-crystal neutron diffraction is established. This sequence may be more consistent with the observed behavior of C_p(T),[4] where the bulk of the magnetic entropy change occurs close to 15 K, and it is easy to imagine missing the incommensurate peak(s) that might be associated with the initial modulated order.

V. CONCLUSIONS

^{151}Eu Mössbauer spectroscopy shows that magnetic ordering in $EuAg_4As_2$ proceeds through an incommensurate sinusoidally modulated state that later squares up to form the incommensurate noncollinear state seen by neutron scattering. Our data suggests that the initial state for 9 K ≤ T ≤ 15 K exhibits long-range order, and further suggests that the europium carries its full $7\mu_B$ moment by 5 K.

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