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Modulated ferromagnetic ordering and the magnetocaloric response of Eu_4PdMg

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Neutron powder diffraction confirms that the primary ordering mode in Eu_4PdMg is ferromagnetic with a europium moment of 6.5(2) μ_B. ^{151}Eu Mössbauer spectroscopy shows that the unusual linear temperature dependence of the magnetisation reported for this system is an intrinsic property and not an artefact of the applied field. The form and temperature evolution of the ^{151}Eu Mössbauer spectra strongly suggest that there is an incommensurate modulation to the magnetic structure that modifies the basic ferromagnetic order. This modulated structure may be the origin of the broad magnetocaloric response previously observed in Eu_4PdMg. *© 2015 AIP Publishing LLC.*
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I. INTRODUCTION

Following the discovery of the giant magnetocaloric effect (MCE) in $Gd_5(Si,Ge)_4$,[1,2] extensive efforts have been devoted to finding other candidate materials. As there is necessarily a magnetic entropy change associated with magnetic ordering, and as that ordering is almost invariably affected by an externally applied magnetic field, the physics behind the phenomenon is relatively straightforward and all magnetic systems exhibit some degree of magnetocaloric effect. The technological interest lies in optimising this effect. Parameters of interest include the magnitude of the effect, the field needed to drive the changes, broad operating temperature range, and extensive cyclability. However, there is a fundamental tension between the first and last of these parameters. The MCE is often maximised by exploiting a coupled first-order magnetostructural transition, but the repeated passage through the first-order structural transition can lead to rapid degradation of the material.[3]

Recently, it was noticed that Eu_4PdMg exhibited an unusually flat, almost linear temperature dependence to its magnetisation,[4] and an investigation of its magnetocaloric behaviour showed a significant MCE that extended over a broad plateau, over 100 K wide.[5] As Eu_4PdMg is apparently ferromagnetic with $T_c = 150(1)$ K and a saturation moment of 7.13(1) μ_B/Eu,[4] the origins of the magnetisation behaviour and the MCE plateau are not immediately obvious, but something other than simple ferromagnetic order seems likely.

Here, we use ^{151}Eu Mössbauer spectroscopy to investigate the local ordering of the europium moments and show that the linear temperature dependence of the magnetisation is intrinsic to the material and not just an artefact of the applied field used to measure it. We further show that the environment of the europium ions evolves with temperature in a way that is not consistent with simple ferromagnetic ordering. Neutron powder diffraction is used to show that the primary magnetic ordering mode in Eu_4PdMg is indeed ferromagnetic, and so we propose that Eu_4PdMg has a modulated ferromagnetic structure. As the magnetocaloric response in Eu_4PdMg derives from a field-driven change in the magnetic structure rather than its crystal structure, there should be essentially no limits on cyclability and this may represent a new class of magnetocaloric materials.

II. EXPERIMENTAL METHODS

A polycrystalline sample of Eu_4PdMg was synthesised by induction melting of the elements in a sealed tantalum tube in a water-cooled sample chamber. The sample was annealed at 900 K for 2 h and subsequently characterized by x-ray powder diffraction (XRD) and Energy Dispersive X-Ray (EDX) analysis. Eu_4PdMg adopts the face-centred cubic, Gd_4RhIn–type crystal structure (space group $F\bar{4}3m$ #216) with $a = 14.9568(7)$ Å and the europium atoms occupying three distinct crystallographic sites (24 *g*, 24*f*, and 16 *e*). A detailed description of sample preparation and phase analysis is given elsewhere.[4]

^{151}Eu transmission Mössbauer spectra were collected on a constant acceleration spectrometer using a 4 GBq $^{151}SmF_3$ source. The 21.6 keV γs were detected using a NaI(Tl) scintillation detector and the spectrometer's velocity scale was calibrated using ^{57}Co**Rh** and α–Fe. All ^{151}Eu isomer shifts are quoted relative to the $^{151}SmF_3$ source. Low-temperature spectra were collected using a vibration-isolated closed-cycle refrigerator. Initial fitting of the spectra was carried out

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using a conventional non-linear least-squares minimisation routine to a sum of Lorentzians with the positions and intensities calculated from a simple nuclear Hamiltonian (no contribution from an electric field gradient was used). More detailed fitting to a modulated field distribution model is described later.

Powder neutron diffraction measurements were made at a wavelength of 1.3286(2) Å using a large-area flat-plate mount[6] to reduce the impact of the large absorption cross section of natural europium. The neutron diffraction patterns were collected on the 800-wire C2 powder diffractometer at the Canadian Neutron Beam Centre, Chalk River, Ontario, and were refined using the GSAS/EXPGUI package.[7,8]

III. RESULTS AND DISCUSSION

A comparison of the powder neutron diffraction patterns taken above and well below the 150 K ordering transition revealed that all of the magnetic scattering occurred at positions allowed by the $F\bar{4}3m$ space group, supporting the conclusion that this material is ferromagnetic. The magnetic scattering was fitted by adding a purely magnetic phase to the nuclear-only phase used to fit the nuclear scattering. The magnetic phase was generated with a $P1$ space group (to avoid symmetry limitations) and all 64 europium positions taken from the $F\bar{4}3m$ nuclear structure. As Eu_4PdMg is cubic, and believed from magnetisation data to be ferromagnetic,[4,5] it is not possible to determine the ordering direction from a powder pattern. Therefore, all of the moments were constrained to be equal in magnitude and to point along the *a*-axis. The results of this analysis are shown in Figure 1 where it is clear that a simple ferromagnetic model fits the data.

While the fitted europium moment is 6.5(2) μ_B, somewhat smaller than the expected 7 μ_B for the $J = \frac{7}{2}$ Eu^{2+} ion, and the saturation moment of 7.13(1) μ_B/Eu (Ref. 4) measured in an applied field of 8 T, it is clear from the residuals plotted in Figure 1 that there are no nuclear-disallowed peaks in the magnetic pattern. The conventional goodness of fit R-factors for this refinement is $wR_p = 6.3$, $R_p = 4.8$, and $R(F^2) = 8.0$, yielding a χ^2 of 5.3.

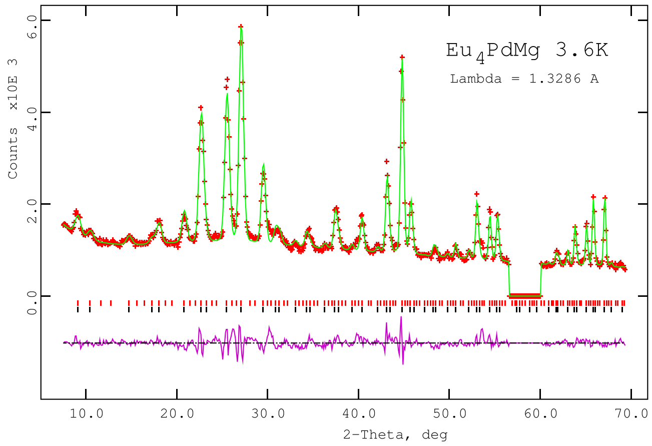

FIG. 1. Fitted neutron diffraction pattern for Eu_4PdMg at 3.6 K. A ferromagnetic structure with a europium moment of 6.5(2) μ_B was used. Bragg markers for the magnetic (top) and nuclear (bottom) are shown with a residual pattern below. A section near $2\theta = 60°$ contained scattering from the sample mount and was excluded from the fit. Note: the large number of magnetic (red) markers is the result of using a $P1$ space group for the magnetic scattering.

^{151}Eu Mössbauer spectroscopy provides a local measure of the ordered moments on the europium atoms that is carried out with no externally applied magnetic field, and does not depend significantly on the details of the actual magnetic structure. While the magnitude of the observed hyperfine field cannot be used as a direct measurement of the local moment in any given system,[9] its temperature dependence does appear to track well with the ordered moment.

At 160 K, the ^{151}Eu Mössbauer spectrum (Figure 2) appears as a single line that is broadened by an unresolved quadrupole interaction (full-width at half maximum 1.24(5) mm/s, $eQV_{zz} = 7.1(5)$mm/s) with an isomer shift of −7.57(3) mm/s, typical of Eu^{2+} and consistent with the observed magnetic ordering and large moment. On cooling below T_c, the spectra broaden and a magnetic splitting develops. The point

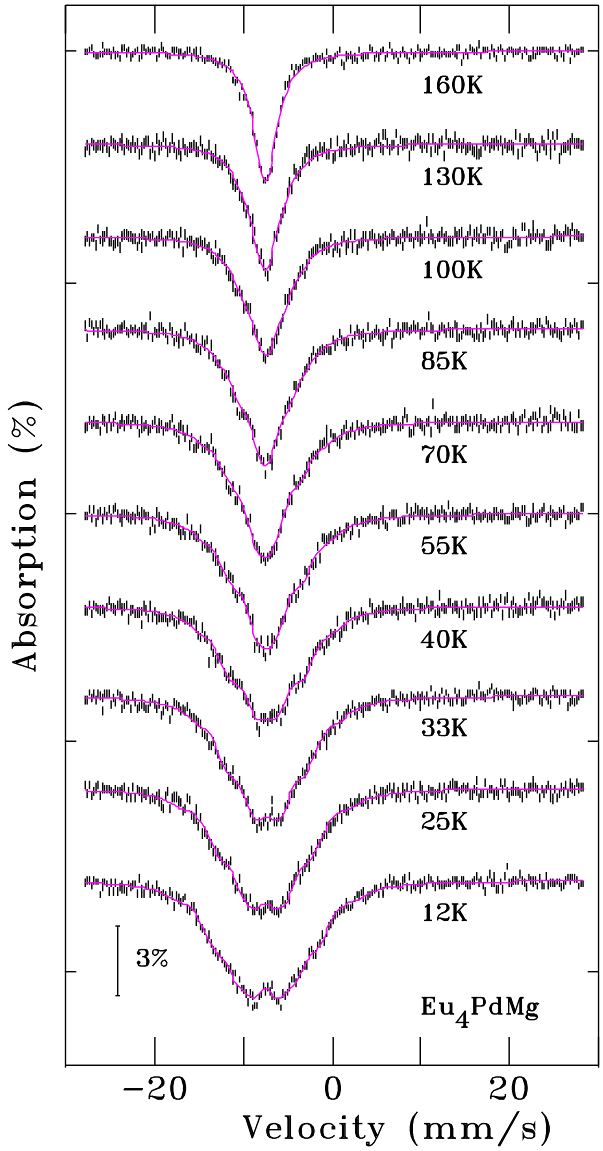

FIG. 2. ^{151}Eu Mössbauer spectra of Eu_4PdMg showing the onset of magnetic order and the rather broad patterns in the ordered state. Solid lines are fits as described in the text.

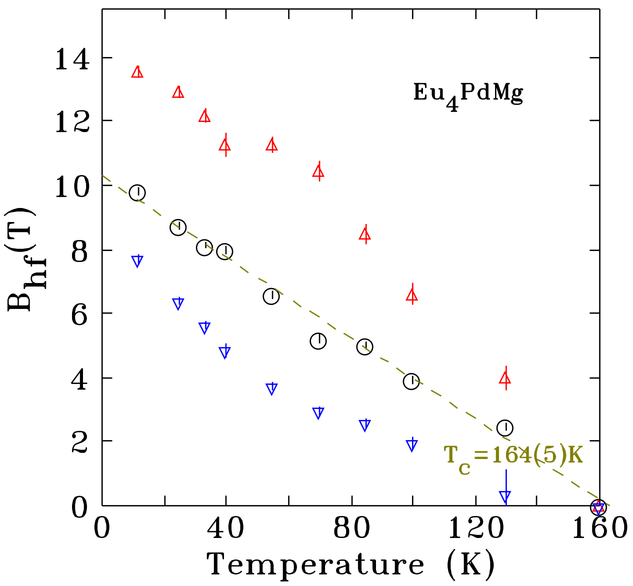

FIG. 3. Temperature dependence of the hyperfine field (B_{hf}) derived from two of the simple models used to fit the spectra in Figure 2. The field derived from a single-site fit (○) yields a linear temperature dependence and an estimated transition temperature of 164(5) K. A two-site fit with high-field (△) and low-field (▽) components gave a better fit, but the average field tracked that derived from the single-site fit.

symmetries of the three europium sites are quite low ($2\,mm$, $2\,mm$, and.$3\,m$ for the $24\,g$, $24f$, and $16\,e$ sites, respectively) so the electric field gradient cannot be assumed to be zero, consistent with the observed quadrupole interaction at 160 K, however the spectra appear symmetric about their centres so in light of this, and the severe line broadening in the ordered state, eQV_{zz} was set to zero in the analysis that follows. Furthermore, since we were able to fit the neutron diffraction pattern (Figure 1) with a common europium moment, and the magnetisation data suggest a full 7 μ_B/Eu is present, it would seem reasonable to expect the hyperfine field (B_{hf}) to be the same at each of three sites. However, the spectrum at 12 K is not formed from a single hyperfine field, but rather exhibits severe line overlap and does not appear to be well resolved.

Several simple approaches were tried in order to parameterise the spectra (without a proper model to support them, these could not be considered "fits" in a meaningful sense). These included a single site with broadened lines; two sites with linewidths, isomer shifts, and areas constrained to be equal; two sites with only the linewidths and isomer shifts constrained to be equal. Three-site fits did not yield stable behaviour. While the fit quality improved with increasing degrees of freedom, one feature remained consistent: The average hyperfine field ($\langle B_{hf}(T)\rangle$) was linear in temperature, as shown in Figure 3. As $\langle B_{hf}\rangle$ is a local measure of the ordered moment and is largely unaffected by the details of the magnetic structure, this provides clear confirmation that the linear temperature dependence of the magnetisation is an intrinsic feature of the ordering in Eu$_4$PdMg and not an artefact of the large fields used in the magnetisation measurements.

Closer examination of the spectra in Figure 2 shows that their shape evolves on warming from 12 K (the central gap is lost before the overall magnetic splitting is significantly reduced). Since a single site does not fit the observed spectra, despite the expectation of ferromagnetic ordering, and the two-site forms have no real structural basis, we turn to a more general approach. The spectral shape at 12 K is consistent with that seen in systems with incommensurately modulated (ICM) structures.[10] Since B_{hf} is proportional to the moment, if that moment is modulated along some incommensurate propagation vector **k** then the moment, and hence B_{hf}, can be described by the expression[10]

$$B(kx) \propto m(kx) = \sum_{l=0}^{n} m_{2l+1} \sin(2l+1)kx,$$

where the m_n are the odd Fourier coefficients of the modulation. The m_n can be fitted by generating $P(B_{hf})$ from $m(kx)$ to calculate the resulting spectral shape, and minimising the deviation by adjusting the m_n. In EuNiGe$_3$, for example, the modulation is sinusoidal near $T_N = 13$ K and then squares up on cooling through 10 K.[11] Since the modulation is assumed to be incommensurate with the lattice, every site in the system has a unique B_{hf}, so the site-wise correlation between B_{hf} and eQV_{zz} is lost, and the impact of the quadrupole interaction on the spectral shape will, to first order, be averaged out. This provides a possible explanation for the absence of a

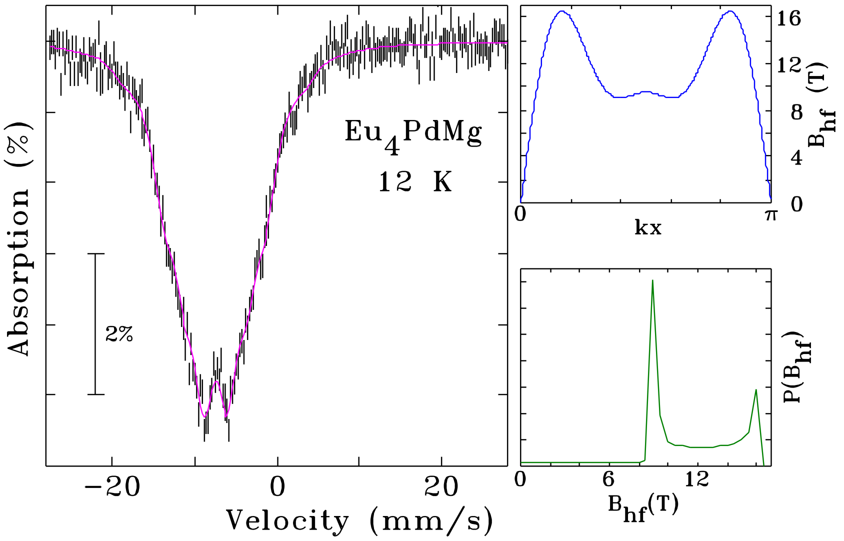

FIG. 4. ^{151}Eu Mössbauer spectrum of Eu$_4$PdMg at 12 K fitted using a modulated model (see text). The right panels show B_{hf}(kx) (top) and P(B_{hf}) (bottom) derived from this model.

quadrupole contribution to the observed spectra in the ordered state.

A fit to the 12 K spectrum using this expression is shown in Figure 4, along with the form of the modulation and the derived $P(B_{hf})$. Comparison of $P(B_{hf})$ in Figure 4 with the two fields in Figure 3 shows that the fields in the simpler model are related to the two sharp features in the distribution generated by the modulated model, however, shifts in the balance between the high and low field components now reflect changes in the form of the modulation rather than being a simple parameterisation of the spectral shape. The average hyperfine field derived from the modulated model also exhibits a linear temperature dependence and an extrapolated T_c of 173(3) K. As with the dependence seen in Figure 3, T_c is higher than the 150 K derived from magnetisation measurements, however in all our fits to the Mössbauer data, we are limited to temperatures of 130 K and below as the line overlap eventually makes the fits unstable. It is likely that the linear behaviour breaks down very close to the transition and that these extrapolations are overestimating T_c.

Direct confirmation of an incommensurately modulated magnetic structure can only come from long-wavelength neutron diffraction measurements as a long period modulation may contribute low-*q* peaks to the magnetic scattering. These measurements will be carried out in the near future.

IV. CONCLUSIONS

Initial neutron diffraction measurements confirm that the primary magnetic ordering of Eu_4PdMg is indeed ferromagnetic. ^{151}Eu Mössbauer spectroscopy shows that the unusual linear temperature dependence of the magnetisation is an intrinsic feature of the magnetic order and not an artefact of the large fields used in the magnetisation measurements. Finally, both the form of the ^{151}Eu Mössbauer spectra at low temperatures and their evolution on warming strongly suggest that there is an additional incommensurate modulation of the ferromagnetic order present in Eu_4PdMg and this modulation may be the origin of the unusually broad magnetocaloric response in this system.

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