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Incommensurate modulated magnetic structure in orthorhombic EuPdSb

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Abstract. Orthorhombic EuPdSb is known to undergo two magnetic transitions, at 12 K and at $T_{\mathrm{N}} \simeq 18$ K, and in phase III ($T < 12$ K), single crystal magnetisation data have shown that the spin structure is collinear antiferromagnetic, with magnetic moments along the crystal **a** axis. From a ^{151}Eu Mössbauer absorption study, we show that, at any temperature within phase III, all the moments have equal sizes, and that in phase II (12 K< T <18 K) the magnetic structure is modulated and incommensurate with the lattice spacings. The modulation is close to a pure sine-wave just below $T_{\mathrm{N}} = 18$ K, and it squares up as temperature is lowered. We measured the thermal variations of the first and third harmonics of the moment modulation, and we could determine the first and third harmonics of the exchange coupling. We furthermore show that the antiferromagnetic-incommensurate transition at 12 K is strongly first order, with a hysteresis of 0.05 K, and that the incommensurate-paramagnetic transition at 18 K is weakly first order. Finally, we present an explanation of the spin-flop transition observed in the single crystal magnetisation data in phase III when $\mathbf{H} \parallel \mathbf{a}$ in terms of an anisotropic molecular field tensor.

PACS. 75.30.Fv Spin-density waves – 76.80.+y Mössbauer effect, other gamma-ray spectroscopy – 75.30.Et Exchange and superexchange interactions

1 Introduction

It is well known that rare earth intermetallic compounds, where the interionic exchange interaction is the oscillatory Ruderman-Kittel-Kasuya-Yoshida (RKKY) coupling, can exhibit moment modulated or helical magnetic structures at finite temperature [1,2]. A collinear modulated structure is favoured by a strong axial anisotropy, an early studied example being metallic Er, whereas a helical structure can occur in the case of planar anisotropy. For most rare earths, there is a large magnetocrystalline anisotropy at low temperature due to the crystal electric field interaction. For Gd^{3+}- or Eu^{2+}-based alloys, the magnetocrystalline anisotropy is very weak due to the vanishing orbital moment of these ions. However, a collinear modulated magnetic structure has been observed in some Gd-based alloys [3,4] and in one Eu-based compound, EuAs$_3$ [5]. In these cases, the driving anisotropy must very probably be that of the bilinear exchange interaction.

The orthorhombic intermetallic compound EuPdSb, which contains divalent Eu ions with spin $S = 7/2$ and $g \simeq 2$, shows two phase transitions, at 12 K and at $T_{\mathrm{N}} \simeq 18$ K [6]. The low temperature phase (phase III) seems to be well characterised, by the single crystal magnetisation data, as an antiferromagnetic magnetic structure with moments aligned along the crystal **a** axis. The structure of the intermediate phase (phase II: 12 K< $T \leq 18$ K) is not known. In this work, we present evidence, using Mössbauer absorption spectroscopy on the isotope ^{151}Eu, that this phase has a modulated magnetic structure whose period is incommensurate with the lattice unit cell. We could measure the first and third harmonics of the moment modulation, and the analysis of their thermal variations using the Periodic Field Model developed in reference [7] enables us to derive the first and third Fourier components of the exchange coupling. The transition at $T_i = 12$ K is a transition from an incommensurate modulated to a simpler low temperature equal moment magnetic structure. By following the coexistence of the two ^{151}Eu Mössbauer spectral shapes in a small temperature interval around 12 K, we evidence the presence of hysteresis, thus showing that the transition at 12 K is first order. This is expected for such transitions, where the modulated structure abruptly becomes unstable below a critical temperature [7]. We also analysed the previously measured single crystal magnetisation data [6] at 4.2 K in phase III, and we attribute the spin-flop transition observed around 6.7 T when $\mathbf{H} \parallel \mathbf{a}$ to a sizeable anisotropy of the exchange coupling. This is in line with the existence of the modulated structure in phase II, where some kind of magnetic anisotropy is needed to stabilize the (probably collinear) magnetic structure. Finally, we compare the experimental magnetic specific heat in the incommensurate magnetic

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phase with that calculated in terms of the Periodic Field Model [4,7].

2 Sample preparation and crystal structure

The polycrystalline EuPdSb sample was synthetised by melting appropriate amounts of the constituents in a tri-arc furnace. X-ray diffraction revealed that the alloy has an orthorhombic ε-TiNiSi structure, with space group Pnma, and that it is single phase. The room temperature lattice parameters are: $a = 7.621$ Å, $b = 4.695$ Å, and $c = 7.927$ Å. In the ε-TiNiSi structure, all the atoms lie in the mirror planes $y = 1/4$ and $3/4$, parallel to ($\mathbf{a}$,$\mathbf{c}$). There are 4 formula units in the orthorhombic cell, and a unique crystallographic site for Eu.

3 ^{151}Eu Mössbauer spectroscopy measurements

The Mössbauer absorption spectra with the isotope ^{151}Eu ($I_g = 5/2$, $I_e = 7/2$, $E_0 = 21.55$ keV) were recorded in the temperature range 1.7 K–50 K, using a ^{151}Sm*F$_3$ γ-ray source. The spectra in the paramagnetic phase I ($T > 18$ K) present a dominant single line with an isomer shift $\delta \simeq -10$ mm/s, characteristic of Eu^{2+}, and a 5% relative intensity line with an isomer shift $\simeq$1 mm/s, characteristic of Eu^{3+}, probably pertaining to an europium oxide impurity phase. The rather large linewidth of the main Eu^{2+} line is due to unresolved quadrupolar effects. A magnetic hyperfine spectrum appears in EuPdSb below 18 K, with quite different features in phase III and in phase II. In phase III (T <12 K), the hyperfine pattern can be accounted for by a single hyperfine field spectrum, whose chief features are four dominant lines with approximately equal intensities and smaller intensity lines in the wings (see spectrum at 11.5 K in Fig. 1). At saturation ($T = 1.7$ K), the hyperfine field is 29.5 T, and it decreases smoothly as temperature increases, reaching 26.7 T at 11.5 K. The Eu^{2+} $4f$ shell magnetic moment is proportional to the hyperfine magnetic field, the proportionality constant varying according to the material. In a given compound, it can be determined by using the fact that the saturated hyperfine field corresponds to a saturated Eu^{2+} moment of $7\mu_B$. In EuPdSb, we find that this constant is 4.21 T/μ_B. We will use this value in the following to derive the magnetic moment from the measured hyperfine field at the different temperatures. The analysis of the thermal decrease of the spontaneous moment in phase III is postponed until Section 5.

On increasing temperature to enter phase II ($T >$ 12 K), an abrupt change occurs in the spectral shape, as can be seen in Figure 1, corresponding to a first order transition (see Sect. 4). The spectrum at 12.8 K still presents four dominant lines, but their intensities are not equal, the two inner lines being about twice as intense as the outer lines. In a previous publication [6], we tentatively attributed this spectral shape to the presence of two magnetically inequivalent Eu sites in phase II.

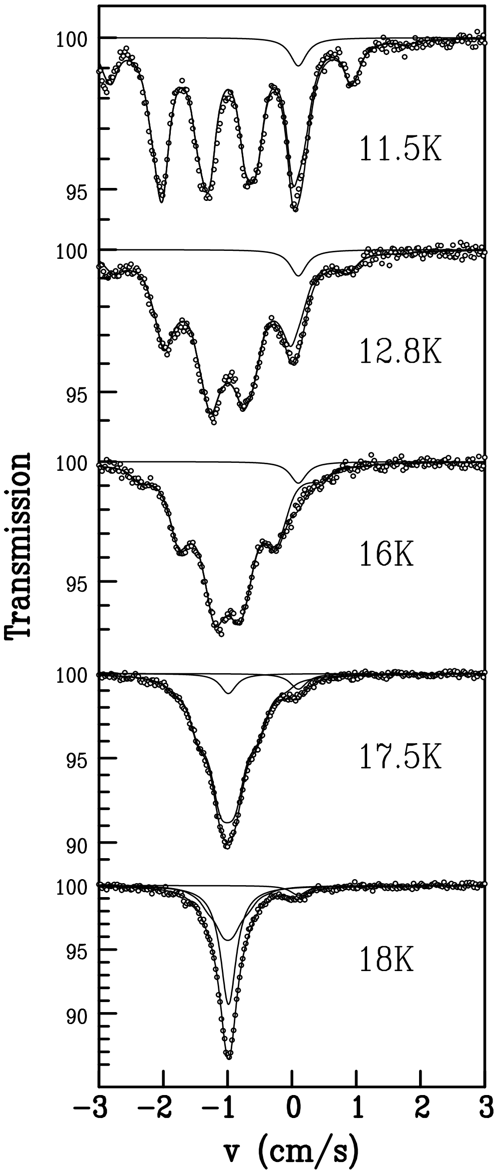

Fig. 1. ^{151}Eu Mössbauer absorption spectra in EuPdSb at selected temperatures. The small intensity line near zero velocity corresponds to Eu^{3+} in an impurity phase. The solid line at 11.5 K is a fit to a single hyperfine field spectrum, and the solid lines between 12.8 K and 18 K are fits assuming an incommensurate magnetic moment modulation. At 17.5 K and 18 K, an extra paramagnetic component (single line) is needed to correctly reproduce the spectra.

Although the obtained fits were quite good, there is no clear physical explanation for the existence of the two sites, and the thermal variation of their relative intensities [6] cannot be easily understood. The spectral shape in phase II actually reveals the presence of a distribution of hyperfine fields. Our simulations have shown that a simple symmetric gaussian distribution, due for instance to random inhomogeneities, cannot reproduce the observed shape. A situation which also leads to a continuous hyperfine field distribution is the presence of a modulated magnetic structure incommensurate with the lattice spacings. This distribution, arising from the continuum of Eu^{2+} ordered moment values due to the incommensurability between the magnetic and the lattice unit cells, has a peculiar very asymmetrical shape: it is truncated at a maximum field value corresponding to the maximum moment of the modulation, and shows a large non-zero weight at small hyperfine field values [8]. This latter feature can explain the growth of the intensities of the two inner lines of the EuPdSb spectra in phase II with respect to the single hyperfine field spectrum in phase III. We will show in the following that the spectra in phase II are very well accounted for assuming the simplest incommensurate modulated magnetic structure, *i.e.* one which is collinear. Such a structure is favoured by the presence of anisotropy which, as evidenced by the single crystal magnetisation data (see Sect. 5), is present in EuPdSb. Furthermore, an incommensurate magnetic structure has been evidenced in a number of rare earth based alloys with the same ε-TiNiSi structure [9], and therefore this interpretation rests on firmer physical grounds than does the two-site model assumed earlier [6].

In order to describe the modulation of the $4f$ shell moment underlying the distribution of hyperfine fields, we use an expansion of the moment modulation in terms of odd harmonics of a fundamental wave-vector [1]:

$$m(x) = m_1 \sin(kx) + m_3 \sin(3kx) + \ldots, \qquad (1)$$

where x is the distance along the direction of the (unknown) propagation vector $\mathbf{k}$ of the incommensurate modulation, and $m_1, m_3, \ldots$ are the Fourier coefficients of the modulation. From equation (1), the corresponding Mössbauer hyperfine spectrum can easily be computed, and the Fourier coefficients can be fitted against experimental data. The solid lines in Figure 1 for the spectra at $12.8\,\mathrm{K} \le T \le 18\,\mathrm{K}$ were obtained by fitting the two coefficients m_1 and m_3. The agreement with the experimental data is very good, and we find that (except close to T_N) the moment modulation is not a pure sine-wave, but that a sizeable third harmonics is needed to account for the lineshape. Both m_1 and m_3 coefficients increase as temperature decreases: from 18 K to 12.8 K, m_1 increases from 2.0 to 6.9 μ_B, and m_3 from 0 to 0.74 μ_B. The thermal variation of the moment modulation is shown in Figure 2: it is practically sine-wave just below 18 K, and it squares up as temperature decreases towards $T_i \simeq 12.5\,\mathrm{K}$. The measured thermal variations of the first and third harmonics are shown in Figure 3. They can be calculated in the molecular field approximation, starting from the fact that the moment modulation originates from the frustration between antagonistic, long range exchange couplings $\mathcal{J}_{ij}$ between rare earth ions.

We write the exchange interaction in terms of the Eu^{2+} spins as:

$$\mathcal{H}_{ex} = -\frac{1}{2} \sum_{i,j \neq i} \mathcal{J}_{ij} \mathbf{S}_i \mathbf{S}_j, \qquad (2)$$

and we introduce the Fourier transform $\mathcal{J}(\mathbf{q})$ of the exchange integral $\mathcal{J}_{ij}$. It can be shown [1] that, in zero external field, the moment modulation arises solely from the odd Fourier components $\mathcal{J}(n\mathbf{k})$ of the exchange integral, where $\mathbf{k}$ is the propagation vector of the modulated structure. Then, close to T_N, the nth harmonics $m_n(T)$ of the moment modulation behaves as [1]:

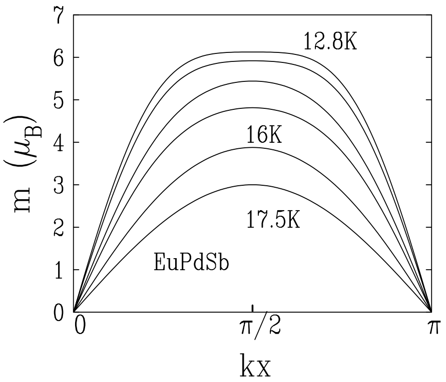

Fig. 2. Modulation of the magnetic moment on a half-period in the incommensurate magnetic phase II of EuPdSb (12 K < T <18 K), obtained from the analysis of the ^{151}Eu Mössbauer spectra.

$$m_n(T) \propto (1 - \frac{T}{T_\mathrm{N}})^{n/2}. \qquad (3)$$

The measured thermal variations of m_1 and m_3 in EuPdSb obey this general trend, as can be seen in Figure 3. A more realistic description over a wider temperature range can be achieved using the Periodic Field Model in the molecular field approximation, which has been previously applied to gadolinium compounds [7] (Eu^{2+} has the same $S = 7/2$ electronic configuration as Gd^{3+}). We performed a self-consistent calculation, where the incommensurate magnetic period is sampled at a finite number of sites (10), taking into account the two first Fourier coefficients $\mathcal{J}(\mathbf{k})$ and $\mathcal{J}(3\mathbf{k})$. It turns out that a satisfactory agreement is obtained in the whole modulated phase with the values: $\mathcal{J}(\mathbf{k}) \simeq 3.52\,\mathrm{K}$ and $\mathcal{J}(3\mathbf{k}) \simeq 0\,\mathrm{K}$ (solid lines in Fig. 3), although the main harmonics m_1 falls slightly below the experimental values. The curves calculated with the same $\mathcal{J}(\mathbf{k})$ value, but with $\mathcal{J}(3\mathbf{k}) = 1.9\,\mathrm{K}$, are also shown as dashed lines in Figure 3. The thermal dependence of m_1 is not significantly modified, whereas that of m_3 is clearly overestimated with respect to experiment. Increasing the number of sites in the magnetic period does not significantly alter these results.

A possible explanation for the discrepancy between the measured and calculated thermal variations of m_1 (and for other deviations from the mean field model discussed below in Sects. 5 and 6) could be that the transition at 18 K is weakly first order. Experimental support for this is provided by the ^{151}Eu Mössbauer data where, just below the transition, at 17.5 K and 18 K, a paramagnetic contribution (single line), which amounts to 50% at 18 K, is needed to correctly reproduce the spectra (see Fig. 1). This coexistence, near the transition temperature, of spectral shapes pertaining to the magnetically ordered and paramagnetic phases, is the hallmark of a first order transition. A first order transition is also clearly evidenced between phase II

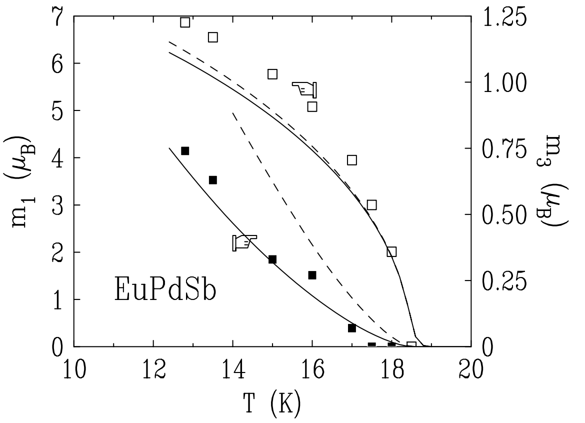

Fig. 3. Thermal variation of the first and third harmonics of the moment modulation in phase II of EuPdSb, as derived from the Mössbauer spectra. The solid lines represent fits to the model of reference [7], with Fourier components of the exchange coupling $\mathcal{J}(\mathbf{k}) = 3.52\,\mathrm{K}$ and $\mathcal{J}(3\mathbf{k}) = 0$; the dashed lines are the calculation using the same $\mathcal{J}(\mathbf{k})$ value, but $\mathcal{J}(3\mathbf{k}) = 1.9\,\mathrm{K}$.

and phase III near $T_i \simeq 12.5\,\mathrm{K}$, as is described in the next section.

4 The first order transition at $T_i = 12.5\,\mathrm{K}$

Below 12.5 K, the modulated magnetic structure becomes unstable and a transition occurs to an equal moment antiferromagnetic structure. From the sharpness of the specific heat peak, it was suggested that this transition is first order [6], and from a detailed analysis of the Mössbauer spectra in a small temperature interval around T_i, we show that it is indeed the case.

A first order phase transition is characterised by an abrupt change in the order parameter at the critical temperature. This critical temperature can be very sensitive to details of the microscopic structure of the material (presence of defects, impurities...) and, in a polycrystalline sample, it can be slightly different in different parts of the sample.

This property is generally well revealed by Mössbauer spectroscopy which is capable of showing that the two phases coexist in a narrow temperature range on both sides of the mean critical temperature [10]. The more pronounced the local inhomogeneity of the sample, the larger is the extension of this coexistence domain. Furthermore, a first order transition is often accompanied by hysteresis.

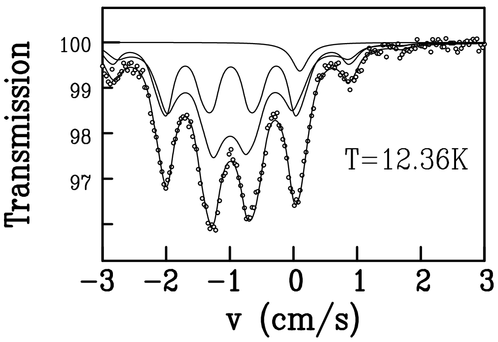

Fig. 4. ^{151}Eu Mössbauer spectrum in EuPdSb at 12.36 K (on cooling) in the middle of the first order transition between the incommensurate and antiferromagnetic phases. Two magnetic subspectra are seen, with roughly equal intensities, one corresponding to the equal moment antiferromagnetic phase, the other to the incommensurate phase.

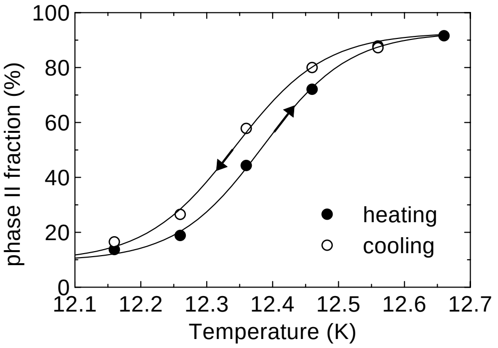

Fig. 5. Thermal variation of the relative fraction of the spectral component pertaining to the incommensurate modulated structure (phase II) in EuPdSb around the transition temperature $T_i \simeq 12.4\,\mathrm{K}$. The black circles correspond to the spectra obtained with increasing the temperature, the open circles to spectra obtained with decreasing the temperature. The lines are guides for the eye.

We therefore performed careful measurements in the temperature range $12.5 \pm 0.5\,\mathrm{K}$; we observe that the spectra in this range do evidence the phase coexistence, for they are a superposition of spectra characteristic of phase III and of phase II. The spectrum at 12.36 K obtained on cooling is shown in Figure 4. At this temperature, the two subspectra have practically equal populations, and their relative intensities can be measured with good precision. The thermal variation of the relative fraction of the spectral component characteristic of phase II is shown in Figure 5. A clear hysteresis of 0.05 K is seen when comparing the curves corresponding to heating and cooling, thus confirming the first order type of the transition. The main temperature range over which the system presents a coexistence of the two phases is $12.4\pm0.4\,\mathrm{K}$. We also observe that, on the low temperature side of the transition, the fraction of phase II goes to zero rather slowly on cooling: it is still present at 10 K at a level of a few percent. This first order transition very probably corresponds to the "lock-in" transition, where the propagation vector of the incommensurate modulation reaches a commensurate value. Below T_i, the commensurate antiferromagnetic phase remains the most stable down to 0 K.

5 The exchange tensor in phase III of EuPdSb

The single crystal magnetisation data at 4.2 K (phase III) presented in reference [6] and partially reproduced in Figure 6 show that the magnetisation is linear with the field when **H** $\parallel$ **b** or **c**, with practically identical slopes; in contrast, when **H** $\parallel$ **a**, the magnetisation is weak up to a field around 7 T where a metamagnetic transition occurs. Above 7 T the magnetisations along the three axes are identical until another transition occurs around 20 T when **H** $\parallel$ **a**. From these data, it can be concluded that, in phase III, the magnetic moments are arranged in a simple collinear antiferromagnetic structure, the moment direction being along the crystal **a** axis. The metamagnetic transition occuring near 7 T when **H** $\parallel$ **a** can then be identified with a spin-flop transition, where the two antiferromagnetic sublattice magnetisations reorient perpendicular to **H**. In the standard molecular field theory, the spin-flop transition arises due to the presence of crystalline anisotropy, and occurs at the critical spin-flop field $H_{\mathrm{sf}} \simeq \sqrt{2H_{\mathrm{A}}H_{\mathrm{E}}}$, where H_{A} is the anisotropy field and H_{E} the first neighbor exchange field. For the S-state ion Eu^{2+}, the crystal field anisotropy is very weak and is usually described *via* an axial crystal field term DS_z^2, with typically $D \sim 0.01\,\mathrm{K}$ [11]. This is equivalent to an anisotropy field $H_{\mathrm{A}} = \frac{DS}{g\mu_{\mathrm{B}}}$ of the order of 0.02-0.03 T. An estimation of the exchange field H_{E} in phase III of EuPdSb can be obtained from the common slope $\chi_\perp$ of the magnetisation curves with **H** along **a**, **b** or **c** for $H > 7\,\mathrm{T}$ through the relation: $\chi_\perp = m_0/H_{\mathrm{E}}$. One obtains: $H_{\mathrm{E}} \simeq 17.5\,\mathrm{T}$. Then the spin-flop transition, if driven by the crystalline anisotropy, would occur at a field H_{sf} around 1 T, whereas the experimental value is close to 7 T. This means that crystalline anisotropy by itself cannot drive the spin-flop transition in EuPdSb. We propose here another mechanism to account for the spin-flop transition, *i.e.* the presence of an anisotropy of the bilinear exchange interaction. An experimental hint for the presence of an exchange anisotropy is the measured anisotropy of the paramagnetic Curie temperature θ_{p} [12] when the field is along the three orthorhombic directions: $\theta_{\mathrm{p}}^a = -34.3\,\mathrm{K}$, $\theta_{\mathrm{p}}^b = -30.1\,\mathrm{K}$, $\theta_{\mathrm{p}}^c = -40.9\,\mathrm{K}$.

We describe the anisotropy of the exchange interaction through an axially symmetric molecular field tensor $\tilde{\lambda}$, with a value λ_a along **a** and λ_z along **b** or **c**. Taking **b** and **c** to be equivalent is justified as the magnetisation curves at 4.2 K with **H** $\parallel$ **b** or **c** are almost identical up to the maximum field of 30 T. In the antiferromagnetic phase at $T = 0$ in the presence of a magnetic field **H**, the total energy for a pair of magnetic moments $\mathbf{m}_1$ and $\mathbf{m}_2$ belonging to the two AF sublattices writes:

$$E = -\mathbf{m_1}\tilde{\lambda}\mathbf{m_2} - (\mathbf{m_1} + \mathbf{m_2}) \cdot \mathbf{H}. \tag{4}$$

The only relevant constants λ_z and λ_a are those linked with the exchange integrals between the two sublattices, *i.e.* the first neighbour $\mathcal{J}_1$, third neighbour $\mathcal{J}_3$,... couplings. Restricting the calculation to a (xOz) plane, where $Ox \parallel \mathbf{a}$, defining the orientations of $\mathbf{m}_1$ and $\mathbf{m}_2$ by the angle θ of their external bisectrix with Oz and the angle ε of $\mathbf{m}_1$ and $\mathbf{m}_2$ with this bisectrix, one obtains, for a given orientation ϕ of the external field with respect to Oz:

$$\begin{aligned} E = m_0^2[\lambda_z + (\lambda_a - \lambda_z)\sin^2\theta - (\lambda_a + \lambda_z)\sin^2\varepsilon] \\ - 2m_0 H \sin\varepsilon \sin(\phi + \theta), \end{aligned} \tag{5}$$

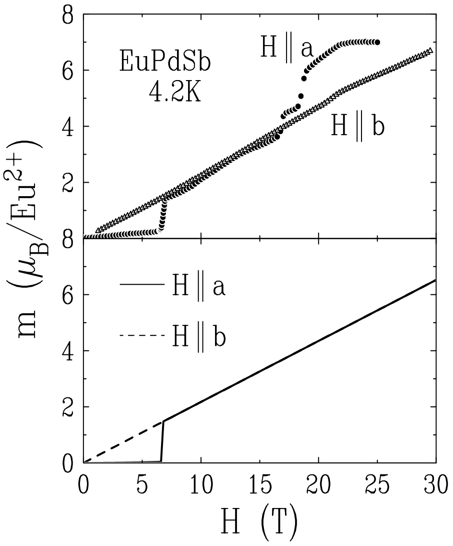

Fig. 6. Upper part: single crystal magnetisation curves at 4.2 K in phase III of EuPdSb, extracted from reference [6], when the magnetic field is along **a** and **b**; lower part: theoretical magnetisation curves at $T = 0$ obtained using the antiferromagnetic anisotropic exchange model discussed in the text, with nearest neighbor molecular field constants $\lambda_a = -2.4\,\mathrm{T}/\mu_{\mathrm{B}}$ and $\lambda_z = -2.2\,\mathrm{T}/\mu_{\mathrm{B}}$.

where $m_0 = g\mu_{\mathrm{B}}S = 7\mu_{\mathrm{B}}$ is the saturated moment of a Eu^{2+} ion. Then, assuming antiferromagnetic negative λ_a and λ_z values, and $|\lambda_a| > |\lambda_z|$ in order that the easy antiferromagnetic axis be along **a**, the determination of the ground configuration as the field is increased yields the following results:

i) when **H** $\parallel$ **a**, the magnetisation is zero up to a spin-flop field:

$$H_{\mathrm{sf}} = m_0\sqrt{\lambda_a^2 - \lambda_z^2}. \tag{6}$$

After the spin-flop, characterised by an abrupt jump, the magnetisation increases linearly with a slope:

$$\chi_\perp = \frac{1}{|\lambda_a + \lambda_z|}. \tag{7}$$

Finally, saturation is obtained at the field:

$$H_{\mathrm{s}} = m_0(|\lambda_a + \lambda_z|), \tag{8}$$

where an induced ferromagnetic magnetic structure is achieved.

ii) when **H** $\parallel$ Oz (*i.e.* **b** or **c**), the magnetisation is linear from zero field, with the same slope $\chi_\perp$ as defined above, and saturation is obtained at the same field H_{s} as above.

From expression (6), it is clear that the smaller the difference between the two components of the molecular field tensor, the smaller is the spin-flop field arising from exchange anisotropy, which of course vanishes for isotropic exchange. In the lower part of Figure 6 are represented simulated magnetisation curves for **H** $\parallel$ **a** and **H** $\parallel$ **b** for a Eu^{2+} ion in the presence of an axially symmetric molecular field tensor. The main features of the experimental

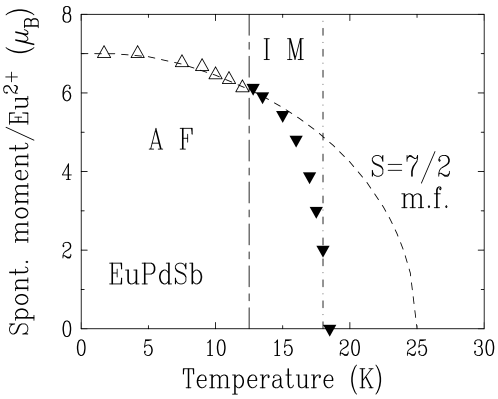

Fig. 7. Thermal variation of the Mössbauer derived spontaneous Eu^{2+} moment in the collinear antiferromagnetic phase III (AF) and of the maximum of the moment modulation in the incommensurate modulated phase II (IM) in EuPdSb. The dashed line is the mean field law for $S = 7/2$ and $T_N = 25$ K.

magnetisation data (upper part of Fig. 6) are reproduced with $\lambda_a = -2.4\,\mathrm{T}/\mu_B$ and $\lambda_z = -2.2\,\mathrm{T}/\mu_B$. With these values, one gets a spin-flop field: $H_{sf} \simeq 6.7$ T and a saturation field $H_s \simeq 32$ T, *i.e.* this model accounts for the observed spin-flop transition when $\mathbf{H} \parallel \mathbf{a}$ and for the incipient saturation transition when $\mathbf{H} \parallel \mathbf{b}$ or $\mathbf{c}$. It does not reproduce the observed abrupt transition(s) around 20 T when $\mathbf{H} \parallel \mathbf{a}$, which could be due to a change in the propagation vector of the magnetic structure (possibly a field induced re-entrant incommensurate modulated structure with the same propagation vector as that of the high temperature phase [3]).

One can try to check the coherence between the measured molecular field constants in phase III and the observed transition temperatures and θ_p values. In the molecular field approach, if $\mathbf{k}'$ is the commensurate propagation vector of the antiferromagnetic phase III, the following relationships hold [1]:

$$\mathcal{J}(\mathbf{k}') = \frac{3k_B}{S(S+1)} T_N \text{ and } \mathcal{J}(0) = \frac{3k_B}{S(S+1)} \theta_p. \qquad (9)$$

If we consider only the first ($\mathcal{J}_1$) and second ($\mathcal{J}_2$) neighbour exchange integrals, then the molecular field constants λ_i along the direction i depend only on $\mathcal{J}_1$ along this direction:

$$\lambda_i = \frac{2}{(g\mu_B)^2}\, \mathcal{J}_1^i. \qquad (10)$$

Finally, the Fourier components $\mathcal{J}(0)$ and $\mathcal{J}(\mathbf{k}')$ can be expressed as:

$$\mathcal{J}(0) = 2\mathcal{J}_1 + 2\mathcal{J}_2 \text{ and } \mathcal{J}(\mathbf{k}') = -2\mathcal{J}_1 + 2\mathcal{J}_2. \qquad (11)$$

From the derived molecular field constant along $\mathbf{a}$ $|\lambda_a| = 2.4\,\mathrm{T}/\mu_B$ and the paramagnetic Curie-Weiss temperature $\theta_p^a = -34.3$ K, one obtains, using the above relations: $\mathcal{J}_1^a = -3.2$ K and $\mathcal{J}_2^a = -0.1$ K, which yields $\mathcal{J}^a(\mathbf{k}') = 6.2$ K and $T_N = 32.5$ K. This latter value is slightly smaller than $|\theta_p^a|$ (in principle, in the molecular field approach: $T_N \geq |\theta_p|$), but it is larger than the effective transition temperature from the paramagnetic phase to the incommensurate modulated phase II ($\simeq$18 K). It is also larger than the transition temperature extrapolated from the thermal variation of the spontaneous moment in phase III, which is around 25 K (see Fig. 7). So it appears that the molecular field approximation yields satisfactory results for the thermal variation of the Fourier components of the moment modulation in the IM phase, and for the magnetisation *vs.* field curves in the presence of anisotropic exchange in the AF phase. However, it cannot account for the values of the transition temperatures in a way which would be coherent with the measured values of the other parameters. In particular, we have no explanation for the fact that both extrapolated and calculated transition temperatures for AF phase III are larger than that of the incommensurate modulated phase. This probably means that other interactions, or higher order exchange couplings, are present in EuPdSb, and these are not taken into account in the model.

6 The magnetic specific heat in EuPdSb

The Periodic Field Model can be applied to the calculation of the temperature variation of the magnetic contribution to the specific heat in the incommensurate modulated phase [4,7]. In order to extract this variation from the raw experimental data presented in reference [6], the knowledge of the lattice contribution is needed. In the absence of specific heat data in an iso-structural non-magnetic compound, we considered the following usual expression for the electronic and phonon contributions:

$$C_{latt} = \gamma T + \beta T^3, \qquad (12)$$

with the reasonable values $\gamma = 0.1\,\mathrm{J\,K^{-1}mol^{-1}}$ and $\beta = 6 \times 10^{-4}\,\mathrm{J\,K^{-3}mol^{-1}}$. The validity of the correction is corroborated by the fact that the deduced magnetic entropy approaches the theoretical value of $R \ln 8$ around $2T_N$ (35 K), as is expected [4].

After subtraction of this lattice contribution, the magnetic part of the specific heat is obtained and it is represented in Figure 8. The thermal variation calculated using the Periodic Field Model with the same exchange coefficients as above in the IM phase (*i.e.* $\mathcal{J}(\mathbf{k}) = 3.52$ K and $\mathcal{J}(3\mathbf{k}) = 0$) is reported in Figure 8 as a solid line. Surprisingly, the experimental variation in the IM phase is not well reproduced; in particular, the observed jump at T_N ($22\,\mathrm{J\,K^{-1}mol^{-1}}$) is larger than expected for a modulated structure ($13.4\,\mathrm{J\,K^{-1}mol^{-1}}$). This may be related to the result (Sect. 3) that the transition at 18 K is in fact weakly first order, as this would make the specific heat peak sharper than expected from molecular field theory. As stated in Section 3, this could also explain the small shift between the calculated and experimental thermal variations of the m_1 Fourier coefficient of the moment modulation. Above 18 K, the experimental specific heat does not vanish as predicted by the mean field model, and

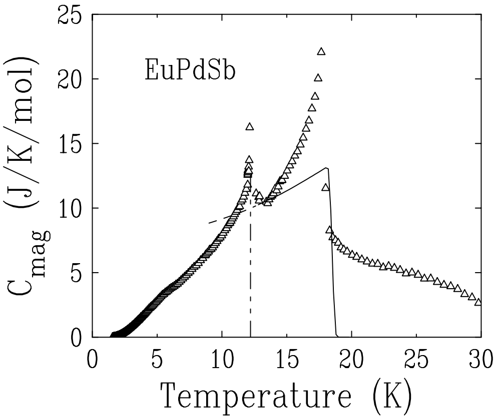

Fig. 8. Magnetic specific heat in EuPdSb, together with the curve calculated according to the Periodic Field Model [7] in the incommensurate modulated phase, with $\mathcal{J}(\mathbf{k}) = 3.52$ K and $\mathcal{J}(3\mathbf{k}) = 0$ (solid line). The peak at the first order 12.5 K transition (marked with the dash-dotted line) is truncated; it actually reaches 180 J K^{-1}mol^{-1}.

this behaviour is probably due to the persistence of short range order above the transition, in line with the fact that the full magnetic entropy is recovered only at a temperature around $2T_N$.

7 Conclusion

We have evidenced an incommensurate modulated magnetic phase in the orthorhombic alloy EuPdSb, in the temperature range 12.5 K–18 K, using ^{151}Eu Mössbauer absorption spectroscopy. In polycrystalline Eu samples, neutron diffraction experiments are difficult due to the strong absorption cross section of Eu, and ^{151}Eu Mössbauer spectroscopy appears to be a valuable tool, in conjunction with other techniques, for the investigation of magnetic structures in Eu compounds. Only one neutron diffraction experiment has been devoted to the study of a modulated structure in a Eu-based compound: in a single crystal $EuAs_3$ sample, an incommensurate magnetic structure has been observed in a narrow temperature range of 1 K just below $T_N = 11.3$ K [5].

In EuPdSb, we measured the thermal variations of the first and third harmonics of the moment modulation in the incommensurate magnetic phase. High order harmonics can in general be observed in neutron diffraction experiments, and Mössbauer spectroscopy appears to be another well adapted technique for detecting them, especially in polycrystalline Eu alloys, because they strongly influence the spectral lineshape [8]. We also showed that the transition at 12.5 K towards the antiferromagnetic phase of EuPdSb is strongly first order. The Periodic Field Model developed in references [4, 7] has been applied to describe the characteristics of the modulated phase. Whereas this model satisfactorily reproduces the thermal variations of the Fourier components of the moment modulation, with exchange Fourier coefficients $\mathcal{J}(\mathbf{k}) \simeq 3.52$ K and $\mathcal{J}(3\mathbf{k}) = 0$, it fails to account for the magnetic specific heat. This latter discrepancy is probably due to the fact that the transition at 18 K is weakly first order, as also suggested by the ^{151}Eu Mössbauer analysis.

In the antiferromagnetic phase ($T < 12$ K), the magnetic moments lie along the crystal **a** axis, and a spin-flop transition has been observed around 7 T in the single crystal magnetisation curve when the field is applied parallel to **a**. As the Eu^{2+} ion possesses a vanishing magnetocrystalline anisotropy, we propose that the driving mechanism for this transition is the anisotropy of the bilinear exchange. We could reproduce the magnetisation curves within a molecular field model with an anisotropic (first neighbour) exchange tensor. This anisotropy certainly favours the onset of the high temperature modulated phase, which is probably a collinear structure.

However, important issues about the precise magnetic structure of EuPdSb could not be resolved by the Mössbauer spectroscopy experiments. These are: the value of the propagation vectors in phase II and phase III, and the thermal variation of the propagation vector in the incommensurate phase, which should vary from an incommensurate value at T_N (18 K) to a commensurate value at T_i (12.5 K), in a manner analogous to that occurring in $EuAs_3$ [5]. This would explain the first order transition at T_i. Neutron or magnetic X-ray diffraction experiments on single crystal EuPdSb would provide answers to these questions.

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