

The first-order magnetoelastic transition in Eu_2In : A ^{151}Eu Mössbauer study

D. H. Ryan,^{1, a)} Durga Paudyal,² Francois Guillou,² Yaroslav Mudryk,² Arjun K. Pathak,³ and Vitalij K. Pecharsky^{2, 4}

¹⁾Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec, H3A 2T8, Canada

²⁾Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA

³⁾Department of Physics, SUNY Buffalo State, Buffalo, New York 14222, USA

⁴⁾Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA

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Our ^{151}Eu Mössbauer investigation of Eu_2In and Eu_2Sn shows that the europium in both materials is fully divalent. We confirm the distinct thermodynamic orders of the magnetic transitions and reveal a remarkable difference between the magnetic environments of the europium atoms in the two compounds. Possible structural and electronic origins for these differences are discussed using DFT calculations.

I. INTRODUCTION

First-order magnetic transitions (FOMTs) with large differences in magnetisation are important in the development of advanced functional magnetic materials, *e.g.* magnetocalorics, and isosymmetric magnetoelastic FOMTs that do not perturb the crystal symmetry are especially rare. Eu_2In exhibits a particularly sharp ferromagnetic (FM) to paramagnetic (PM) transition at $T_c=55$ K (FWHM <1 K) with a remarkable combination of large latent heat and magnetocaloric response, small volume discontinuity, and negligible hysteresis¹. By contrast the nearly isostructural Eu_2Sn exhibits a conventional second-order antiferromagnetic transition at $T_N=31$ K.

Here we study the differences in local magnetic behaviour between Eu_2In and Eu_2Sn using ^{151}Eu Mössbauer spectroscopy and band structure calculations. We confirm the different thermodynamic nature of the transitions and find that the magnetic environments of the europium in the two isostructural compounds are completely different.

II. EXPERIMENTAL METHODS

Polycrystalline Eu_2In and Eu_2Sn samples were prepared by melting stoichiometric quantities of elemental starting materials in sealed Ta crucibles under ultrapure argon as described in detail elsewhere¹. X-ray diffraction confirmed that both materials adopt the closely related Co_2Si - and Co_2P - type orthorhombic $Pnma$ (SG #62) structures, respectively, where the europium atoms occupy two crystallographically distinct $4c$ sites^{1,2}. For Eu_2Sn , Rietveld refinement leads to the following crystal structure parameters: $a = 7.8300(3)$ Å, $b = 5.4038(2)$ Å and $c = 9.8975(3)$ Å. All of the atoms occupy $4c$ sites

$(x, \frac{1}{4}, z)$: Eu(I) ($x = 0.0133(9)$, $z = 0.6996(6)$), Eu(II) ($0.1753(7)$, $0.0803(6)$) and Sn ($0.2448(9)$, $0.4001(7)$).

Magnetic measurements were carried out in a 7 T magnetic property measurement system MPMS (Quantum Design) magnetometer equipped with a reciprocating sample option (RSO).

Samples were prepared for Mössbauer spectroscopy by hand grinding under hexane in a nitrogen-filled glove-box to reduce the possibility of oxidation. However as will be seen in the spectra presented below, some oxidation occurred during mounting.

The ^{151}Eu Mössbauer spectroscopy measurements were carried out using a 4 GBq $^{151}\text{SmF}_3$ source, driven in sine mode and calibrated using a standard $^{57}\text{CoRh}/\alpha\text{-Fe}$ foil. Isomer shifts are quoted relative to EuF_3 at ambient temperature. The 21.6 keV gamma rays were recorded using a thin NaI scintillation detector. The sample was cooled in a vibration-isolated closed-cycle helium refrigerator with the sample in a helium exchange gas. The spectra were fitted to a sum of Lorentzian lines with the positions and intensities derived from a full solution to the nuclear Hamiltonian³.

III. RESULTS

The magnetisation *vs.* temperature shown in Fig.1 serves to emphasise the remarkable difference between the two materials. The FOMT in Eu_2In is marked by a large discontinuous step in the magnetisation at 55 K while Eu_2Sn exhibits a cusp at 31 K marking a conventional second-order transition.

The ^{151}Eu Mössbauer spectrum of Eu_2Sn at 5.6 K shown in Fig. 2 is relatively simple, consisting of a single magnetic pattern, despite there being two crystallographically distinct sites occupied by the europium. The isomer shift of $-9.71(3)$ mm/s is consistent with fully divalent europium, however the hyperfine field (B_{hf}) is remarkably small, being only 12.7(1) T. A linear fit to the high temperature susceptibility yields an effective paramagnetic moment of $7.94\mu_B$ ¹ and DFT calculations give

^{a)}Corresponding author: D.H. Ryan dhryan@physics.mcgill.ca

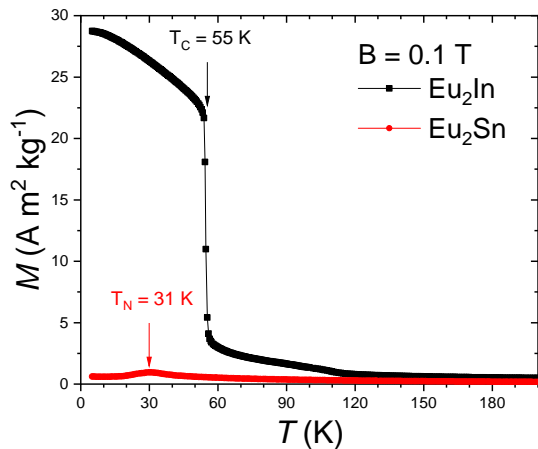


FIG. 1. Magnetisation *vs.* temperature for Eu_2In and Eu_2Sn showing the remarkable difference in behaviour. The first-order PM \rightarrow FM transition at 55 K in Eu_2In contrasts strongly with the second-order PM \rightarrow AFM transition at 31 K in Eu_2Sn .

europium moments of $7\mu_B$ at both sites¹. If the europium does indeed carry the full $7\mu_B$ expected for Eu^{2+} then the observed B_{hf} of 12.7(1) T in Eu_2Sn may be the smallest in any metallic Eu^{2+} system, and values of 20 T – 40 T are more typical⁴. The thermal evolution of the spectra is unremarkable (Fig. 3) and $B_{hf}(T)$ is well fitted using a $J=\frac{7}{2}$ Brillouin function, yielding $T_N=30.4(1)$ K, fully consistent with the cusp observed in $M(T)$.

By contrast, the ^{151}Eu Mössbauer spectra of Eu_2In shown in Fig. 4 are very different. At 5 K there are two, equal-area magnetic components present with hyperfine fields of 27.2(1) T and 16.8(2) T. Not only are the fields at the two sites remarkably different, they are also much larger than the single site field seen in Eu_2Sn . Saturation magnetisation measurements give $7.2 \mu_B/\text{Eu}$ while DFT calculations give $7\mu_B/\text{Eu}^1$. These results combined with the observed isomer shift of $-9.01(4)$ mm/s all point to fully divalent europium being present in Eu_2In . The evolution of the spectra with temperature confirms the first-order nature of the transition at 55 K. As can be seen in Fig. 3, $B_{hf}(T)$ at both sites declines slowly as the temperature is increased, and by 55 K they are down by about 25%, then they vanish at the FOMT. Fitting the temperature dependence to a $J=\frac{7}{2}$ Brillouin function suggests that the low temperature ferromagnetic phase would have an ordering temperature of ~ 80 K if the first-order structural transition did not occur. In addition, the Eu^{2+} component exhibits a small (2–3 T) broadening above the FOMT that extends to about 100 K suggesting that some weak residual order persists well above the FOMT. This is consistent with the pedestal apparent in $M(T)$ above the FOMT in Fig. 1.

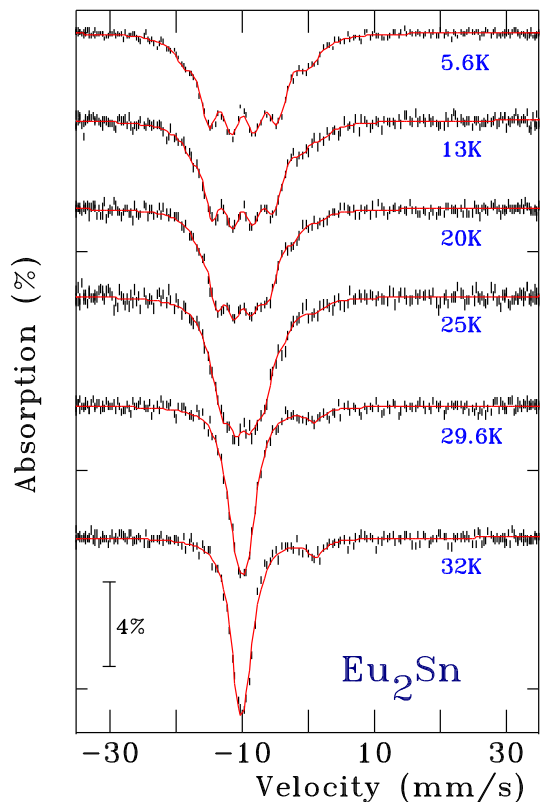


FIG. 2. ^{151}Eu Mössbauer spectra of Eu_2Sn . Solid lines are fits to a full Hamiltonian solution (see text). The feature near 0 mm/s that is clearly visible above 25 K is a small (4(1)%) Eu^{3+} impurity, likely an oxide or hydroxide introduced during sample preparation and handling.

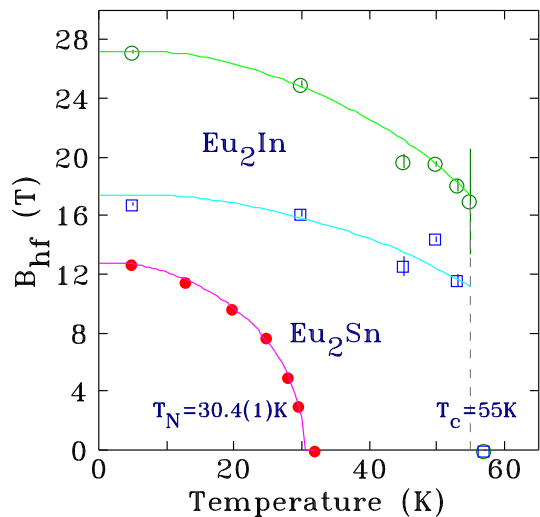


FIG. 3. Temperature dependence of B_{hf} for Eu_2In and Eu_2Sn . Eu_2In shows two distinct europium sites and the thermal evolution of B_{hf} ends abruptly at 55 K as Eu_2In undergoes a first-order magnetic transition. By contrast, $B_{hf}(T)$ for Eu_2Sn follows a conventional $J=\frac{7}{2}$ Brillouin function, yielding $T_N=30.4(1)$ K.

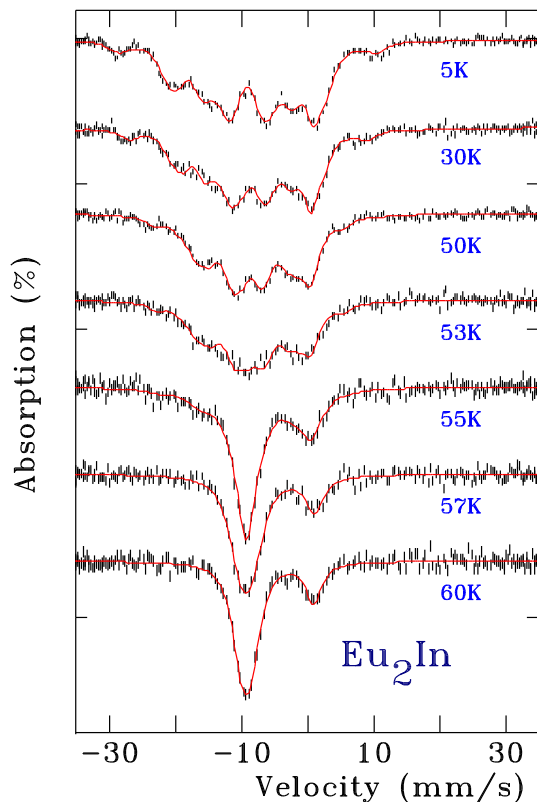


FIG. 4. ^{151}Eu Mössbauer spectra of Eu_2In . Solid lines are fits to a full Hamiltonian solution (see text). The feature near 0 mm/s that is clearly visible above 53 K is a (17(1)%) Eu^{3+} impurity, likely an oxide or hydroxide introduced during sample preparation and handling.

IV. DISCUSSION

Given that x-ray absorption spectroscopy (XAS) demonstrates purely divalent state of Eu in Eu_2In^1 , the significant (17(1)%) Eu^{3+} contribution seen in Fig. 4 near 0 mm/s, which is much larger than the detection limit of XAS, is attributed to an impurity phase, likely the sesquioxide, Eu^{3+} hydroxide, or a mixture of both, formed during grinding and mounting. The Eu^{3+} impurity is much more limited in Eu_2Sn (4(1)%), indicating its lower reactivity with moist air. The present Mössbauer data thus provide an additional experimental confirmation of Eu^{2+} state in Eu_2Sn .

The evolution of the hyperfine fields (Fig. 3) in Eu_2In and Eu_2Sn is markedly different, with the former exhibiting clear discontinuities for two distinct europium sites. These differences are in agreement with earlier density functional theory (DFT) calculations that show much reduced density of states (DOS) at the Fermi level, E_F , as well as lower induced moments on Eu 6s, 6p, and 5d states of Eu_2Sn^1 . Replacement of In with Sn in the Co_2Si -type structure shifts the total DOS further below the Fermi level leading to semi-metallic-like topology at E_F (Fig. 5). Consequently, negligible spin polarization

due to lack of electronic states at E_F does not support ferromagnetism in Eu_2Sn in either the Co_2P -type¹ or Co_2Si -type (this study) structures.

For Eu_2In the ratios of the lattice parameters $a/c \sim 0.723$ and $b/a \sim 0.749$ are typical of other rare earth intermetallics adopting the Co_2Si -type structure. On the other hand, $a/c \sim 0.690$ of Eu_2Sn is closer to that of the Co_2P -type structure⁵. Further, one of the Eu(II)–Sn bond distances extends by nearly 10% compared to its analog in Eu_2In (4.463 Å vs. 4.071 Å, respectively) and the bond is essentially broken in Eu_2Sn , which provides an additional reason to treat the Co_2Si and Co_2P structure types differently⁵. These anisotropic differences in lattice parameters and atomic arrangements lead to modified local environments around the Eu atoms, although most of the changes are minor. For example, the average Eu–Eu interatomic distance in the Eu(I) nearest neighbor environment is shorter by 0.3% in Eu_2In (3.871 Å) compared to Eu_2Sn (3.885 Å), even though the unit cell volume of the former is larger by 2.4% compared to the latter. Crystallographic differences together with the modifications of the electronic structure are, therefore, responsible for the variation of magnetic behavior of Eu_2In and Eu_2Sn .

Analysis of the differences in the interatomic bonding between Eu(I) and Eu(II) in Eu_2In reveals closer Eu(I)–Eu(I) (3.841 Å) than Eu(II)–Eu(II) distance (4.101 Å). At the same time, Eu(II)–In bonds are significantly shorter compared to the Eu(I)–In ones: the average Eu(II)–In distance is 3.535 Å, while the average Eu(I)–In distance is 3.657 Å. Considering the critical role of Eu 5d – In 4p hybridization in defining the ordered magnetic state of the Eu_2In compound¹, the stronger Eu(II)–In interactions may explain different hyperfine fields of the two europium sites. The relative strengths of the Eu–In interactions may, however, be opposite to the strengths of the corresponding hyperfine fields, considering that DFT calculations¹ predict $7.36\mu_B/\text{Eu(I)}$ and $7.25\mu_B/\text{Eu(II)}$. Ultimately, a neutron diffraction study of the magnetic structures appears to be necessary to shed the light on the behavior of hyperfine fields in both compounds.

V. CONCLUSIONS

While ^{151}Eu Mössbauer spectroscopy shows that the europium in both Eu_2In and Eu_2Sn is fully divalent and confirms the first-order (Eu_2In) and second-order (Eu_2Sn) natures of the respective magnetic transitions, It also reveals some striking differences in the ordered states of these two compounds. Eu_2In exhibits two clearly distinct Eu sites with hyperfine fields that differ by more than 50%. By contrast not only are the two sites not resolved in Eu_2Sn , but the observed hyperfine field is remarkably small. The isomer shifts for the two compounds are also distinct, $-9.01(4)$ mm/s and $-9.71(3)$ mm/s for In and Sn respectively, pointing to significant differences

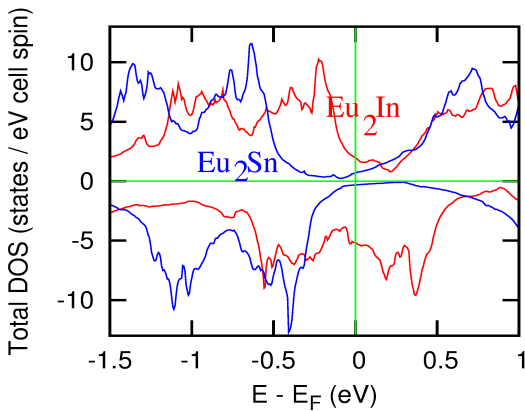


FIG. 5. Spin polarized total density of states of Eu_2In and Eu_2Sn calculated using the electronic structure method explained in Guillou *et al.*¹.

in the local density of states around the europium in these compounds.

Neutron diffraction measurements are needed both to establish the actual magnetic structures of these compounds and to determine the moments on the two eu-

ropium sites in each one.

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