The first-order magnetoelastic transition in Eu$_2$In: A $^{151}$Eu Mössbauer study

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ABSTRACT

Our $^{151}$Eu Mössbauer investigation of Eu$_2$In and Eu$_2$Sn 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$_2$In 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 hysteresis. $^1$ By contrast the nearly isostructural Eu$_2$Sn exhibits a conventional second-order antiferromagnetic transition at $T_N=31$ K.

Here we study the differences in local magnetic behaviour between Eu$_2$In and Eu$_2$Sn 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$_2$In and Eu$_2$Sn samples were prepared by melting stoichiometric quantities of elemental starting materials in sealed Ta crucibles under ultrapure argon as described in detail elsewhere.$^1$ X-ray diffraction confirmed that both materials adopt the closely related Co$_2$Si- and Co$_2$P-type orthorhombic Pnma (SG #62) structures, respectively, where the europium atoms occupy two crystallographically distinct 4c sites.$^1$ For Eu$_2$Sn, 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 $^{151}\text{Eu}$ 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 $\text{EuF}_3$ 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 Hamiltonian.

III. RESULTS

The magnetisation vs. temperature shown in Fig. 1 serves to emphasise the remarkable difference between the two materials. The FOMT in $\text{Eu}_2\text{In}$ is marked by a large discontinuous step in the magnetisation at 55 K while $\text{Eu}_2\text{Sn}$ exhibits a cusp at 31 K marking a conventional second-order transition.

The $^{151}\text{Eu}$ Mössbauer spectrum of $\text{Eu}_2\text{Sn}$ 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 $\mu_B$. DFT calculations give europium moments of $7\mu_B$ at both sites. 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 $\text{Eu}_2\text{Sn}$ may be the smallest in any metallic Eu$^{2+}$ system, and values of 20 T - 40 T are more typical.

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 $^{151}\text{Eu}$ Mössbauer spectra of $\text{Eu}_2\text{In}$ shown in Fig. 4 are very different. At 5 K there are two, equal-area magnetic
As can be seen in Fig. 3, in Eu$_2$In of Eu$^{2+}$ have an ordering temperature of $\sim$80 K if the first-order structural transition did not occur. In addition, the Eu$^{2+}$ impurity, likely an oxide or hydroxide introduced during sample preparation and handling, 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$_2$Sn (4(1)%), indicating its lower reactivity with moist air. The present Mössbauer data thus provide an additional experimental confirmation of Eu$^{3+}$ state in Eu$_2$Sn.

The evolution of the hyperfine fields (Fig. 3) in Eu$_2$In and Eu$_2$Sn 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$_2$Sn. Replacement of In with Sn in the Co$_2$Si-type structure shifts the total DOS further below the Fermi level leading to semimetallic-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$_2$Sn in either the Co$_2$P-type or Co$_2$Si-type (this study) structures.

For Eu$_2$In the ratios of the lattice parameters $a/c \sim$0.723 and $b/a \sim$0.749 are typical of other rare earth intermetallics adopting the Co$_2$Si-type structure. On the other hand, $a/c \sim$0.690 of Eu$_2$Sn is closer to that of the Co$_2$P-type structure. Further, one of the Eu(II)–Sn bond distances extends by nearly 10% compared to its analog in Eu$_2$In ($4.463\,\text{Å}$ vs. $4.071\,\text{Å}$, respectively) and the bond is essentially broken in Eu$_2$Sn, which provides an additional reason to treat the Co$_2$Si and Co$_2$P structure types differently. 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$_2$In ($3.871\,\text{Å}$) compared to Eu$_2$Sn ($3.885\,\text{Å}$), 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$_2$In and Eu$_2$Sn.

Analysis of the differences in the interatomic bonding between Eu(I) and Eu(II) in Eu$_2$In reveals closer Eu(I)–Eu(I) ($3.841\,\text{Å}$) than Eu(II)–Eu(II) distance ($4.101\,\text{Å}$). At the same time, Eu(II)–In bonds are significantly shorter compared to the Eu(I)–In ones: the average

IV. DISCUSSION

Given that x-ray absorption spectroscopy (XAS) demonstrates purely divalent state of Eu in Eu$_2$In, 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$_2$Sn (4(1)%), indicating its lower reactivity with moist air. The present Mössbauer data thus provide an additional experimental confirmation of Eu$^{3+}$ state in Eu$_2$Sn.

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![FIG. 4. $^{151}$Eu Mössbauer spectra of Eu$_2$In. 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.](image)
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 Eu₂In compound, 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 calculations predict 7.36 μ_B/Eu(I) and 7.25 μ_B/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 Eu₂In and Eu₂Sn is fully divalent and confirms the first-order (Eu₂In) and second-order (Eu₂Sn) natures of the respective magnetic transitions, it also reveals some striking differences in the ordered states of these two compounds. Eu₂In 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 Eu₂Sn, 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 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 europium sites in each one.

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