

Absence of charge fluctuations of europium in metallic single crystals of EuCu_2Si_2

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Abstract The ^{151}Eu Mössbauer effect study in the temperature range 2.2–299.5 K on pulverized single crystals of EuCu_2Si_2 synthesized from an indium flux is presented. In contrast to previous studies on polycrystalline samples in which valence fluctuations for Eu were reported, we find that the Eu atoms are divalent in the whole temperature range. Therefore, there are no charge fluctuations of Eu in EuCu_2Si_2 .

Key words valence fluctuation · divalent Eu

1 Introduction

The ternary alloy EuCu_2Si_2 is one of the first europium-based alloys in which intermediate valence behaviour was observed [1]. It is also one of the most well studied [2–5]. Previous ^{151}Eu Mössbauer studies of EuCu_2Si_2 [1, 4, 5] found that the effective valence of Eu changes from ~ 2.6 at room temperature to ~ 2.8 at lowest temperature.

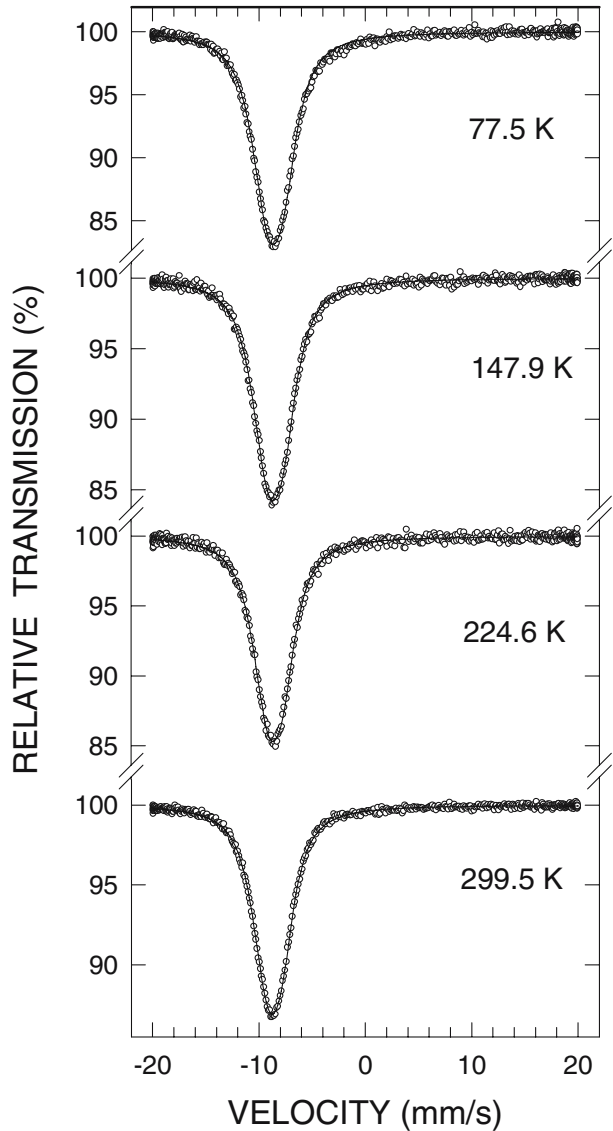
Recently, single crystals of EuCu_2Si_2 were synthesized from an In flux and studied again [6, 7]. Surprisingly, magnetic susceptibility, electron-spin-resonance, and specific heat results [6, 7] are consistent with Eu being in stable divalent state. Here, we present the preliminary ^{151}Eu Mössbauer spectroscopy results on the single crystals of EuCu_2Si_2 . We demonstrate that Eu in EuCu_2Si_2 is in the divalent state in the temperature range 2–300 K.

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Figure 1 ^{151}Eu Mössbauer spectra of EuCu_2Si_2 at various temperatures above the magnetic ordering temperature. The zero of the velocity scale is relative to the $^{151}\text{Sm}(\text{SmF}_3)$ source at room temperature. The *solid line* is a least-squares fit, as described in the text.

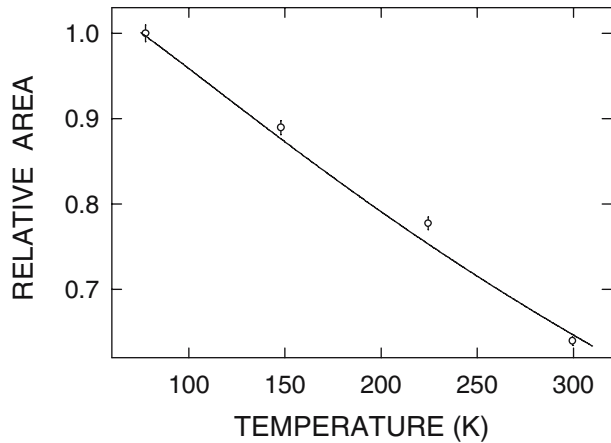


2 Experimental procedure

Single crystals of EuCu_2Si_2 were synthesized from an In flux, as described in [7]. They were found to be single phase, crystallizing in the tetragonal ThCr_2Si_2 structure with lattice constants $a=4.10 \text{ \AA}$ and $c=9.93 \text{ \AA}$ [7].

^{151}Eu Mössbauer measurements were performed in the temperature range 2.2–299.5 K with a standard Mössbauer spectrometer operating in a sine mode using a 330 mCi $^{151}\text{Sm}(\text{SmF}_3)$ source kept at room temperature. The spectrometer was calibrated with a 6.35- μm $\alpha\text{-Fe}$ foil, and the spectra were folded. The Mössbauer absorber was prepared by mixing the

Figure 2 Temperature dependence of the normalized area under the resonance curve. The solid line is a least-squares fit based to the expression for the Lamb–Mössbauer factor within the Debye model of lattice vibrations.



pulverized crystals of EuCu_2Si_2 with powdered BN to ensure a uniform thickness of the absorber and the random orientation of sample particles. This mixture was then put into a plastic sample holder. The surface density of the Mössbauer absorber was 18.0 mg Eu/cm^2 , which corresponds to the effective absorber thickness $8.1f_a$, where f_a is the absorber Lamb–Mössbauer factor.

3 Results and discussion

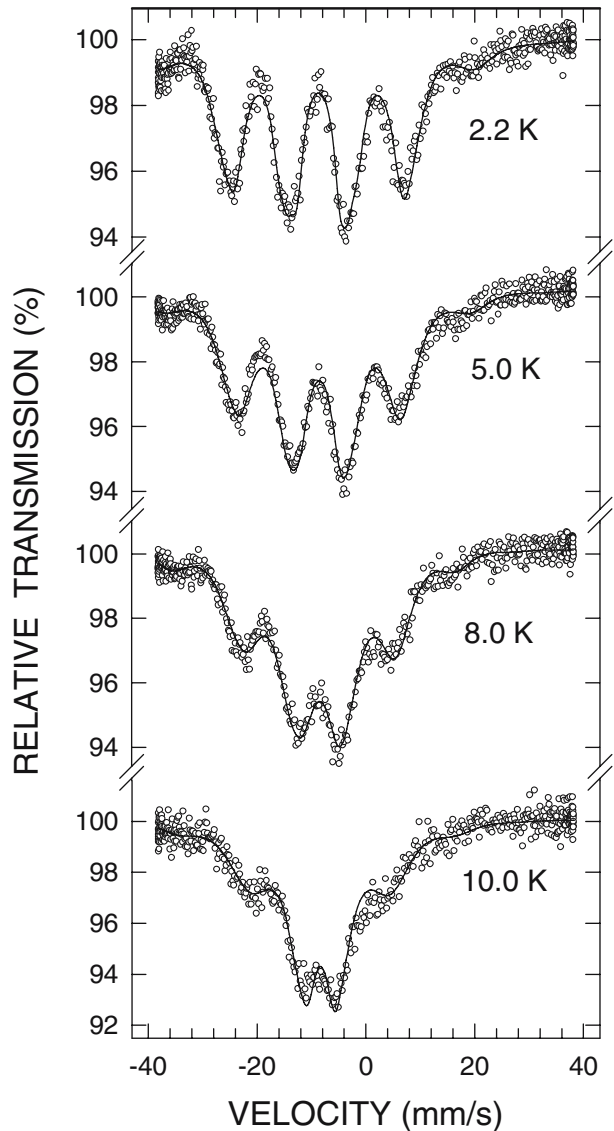
The Mössbauer spectra of EuCu_2Si_2 at selected temperatures above the antiferromagnetic ordering temperature $T_N=8.5 \text{ K}$ [8] are shown in Figure 1. In contrast to the Mössbauer spectra of a polycrystalline EuCu_2Si_2 [1, 4, 5], the spectra of the studied specimen consist of one line located at $\sim -8.65 \text{ mm/s}$. This shows that Eu is divalent and there are no signs of valence fluctuations in the temperature range $77.5\text{--}299.5 \text{ K}$.

The spectra in Figure 1 result from a pure electric quadrupole interaction. They were fitted with the transmission integral and the positions and relative intensities of absorption lines were calculated by numerical diagonalization of the hyperfine Hamiltonian [8]. The source $^{151}\text{Sm}(\text{SmF}_3)$ used is not a monochromatic source as ^{151}Sm nuclei are located in the SmF_3 matrix at the site of noncubic symmetry. By measuring the spectra of the cubic EuSe we determined [8] that the electric quadrupole coupling constant eQ_gV_{zz} in our source is $-3.98(13) \text{ mm/s}$ ($Q_g=0.903 \text{ b}$ [9]), which is very close to the value found in [10]. The precise shape of the source emission line was taken into account in the fits of the spectra in Figure 1.

The values of the electric quadrupole coupling constant eQ_gV_{zz} and the asymmetry parameter η obtained from the fits of the spectra in Figure 1 are temperature independent [8] and are, respectively, $6.11(8) \text{ mm/s}$ and $\eta=1.0(1)$. The temperature dependence of the area under the resonance curve (Figure 2) derives from the temperature dependence of f_a . The fit of the relative area to the expression for f_a within the Debye theory of lattice vibration gives the Debye temperature $\Theta_D=236(4) \text{ K}$. This value is close to the value of 210 K found from the specific heat data for the polycrystalline EuCu_2Si_2 [2].

The Mössbauer spectra of EuCu_2Si_2 at selected temperatures below and around T_N are shown in Figure 3. It is evident that these spectra are the spin relaxation spectra, even at the

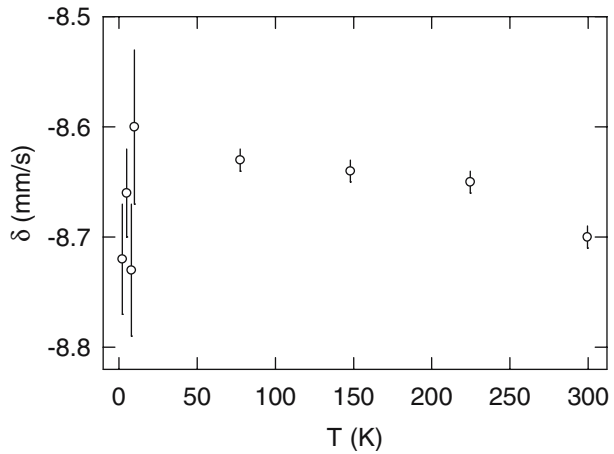
Figure 3 ^{151}Eu Mössbauer spectra of EuCu_2Si_2 at various temperatures below and around the magnetic ordering temperature. The zero of the velocity scale is relative to the ^{151}Sm (SmF_3) source at room temperature. The *solid line* is a least-squares fit, as described in the text.



lowest temperature of 2.2. K. They were fitted (Figure 3) using the line shape function given by Blume and Tjon [11]. The analysis of these relaxation spectra are discussed in detail elsewhere [8]. Here we notice that the isomer shift δ of these spectra is ~ -8.68 mm/s. This demonstrates that the Eu atoms in the studied alloy are divalent.

The temperature dependence of δ of the spectra in Figures 1 and 3 is shown in Figure 4. It is evident that δ changes very little with temperature and its value proves that Eu in EuCu_2Si_2 is divalent in the temperature range 2.2–299.5 K. Consequently, there are no charge fluctuations of Eu in EuCu_2Si_2 .

Figure 4 Temperature dependence of the ^{151}Eu isomer shift in EuCu_2Si_2 .



4 Conclusions

The ^{151}Eu Mössbauer effect study in the temperature range 2.2–299.5 K on a ternary alloy EuCu_2Si_2 synthesized from an In flux has been presented. The values of the electric quadrupole coupling constant eQ_gV_{zz} and the asymmetry parameter η are, respectively, 6.11 (8) mm/s and $\eta=1.0(1)$. The Debye temperature of the studied alloy is 236(4) K. The Eu atoms are in stable divalent state in the temperature range 2.2–299.5 K.

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