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The mixed-valence magnetic ground state of Eu ions in the high-pressure synthesised compound EuNi with the Laves phase structure (C15)

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Abstract. High pressures and temperatures were used to synthesise the previously unknown compound EuNi. Magnetic measurements, and Mössbauer effect measurements for ^{151}Eu and ^{119}Sn impurity atoms are reported. Ferromagnetic ordering below 139 K and a mean valence value of 2.3 ± 0.1 for Eu ions were found.

1. Introduction

As a rule the elements of the rare-earth series in the solid state have three conduction electrons. Exceptions to this rule are Eu and Yb, which have the approximate electronic configurations $4f^7 5d^0 6s^2$ and $4f^{14} 5d^0 6s^2$, respectively (Coqblin 1977). Europium has a magnetic moment of $7.12 \mu_B$, close to the magnetic moment of the divalent Eu^{2+} ion. As it has two conduction electrons, Eu really belongs to the Ca, Sr and Ba group. However, from the literature (Buschow 1968) it is known that at atmospheric pressure in the Eu–T (T = Fe, Co, Ni) systems, one EuNi_5 compound is formed, and in this compound the Eu ions are trivalent (Oliver *et al* 1978). For the Eu^{3+} ion, the spin S and the orbital angular momentum L are coupled to give the total angular momentum J : $J = L - S = 0$ ($S = 3$, $L = 3$).

From Mössbauer effect measurements it is known that the average valence of Eu metal increases with increasing pressure up to 12 GPa and antiferromagnetic ordering persists over the pressure range 0 to 14 GPa for temperatures below the Néel temperature of about 90 K (Farrell and Taylor 1987).

For ytterbium, which is an analogue of europium, it was shown in our earlier work (Tsvyashchenko 1986) that high pressure stabilises Yb-rich compounds in the Yb–T (including Mn) systems. This fact is connected with the increasing of the valence of Yb ions that occurs as the pressure is increased from 4.0 GPa.

We went on to investigate the Eu–Ni system. In this communication we report high-pressure crystallisation of a Eu-rich compound in the Eu–Ni system and discuss the ground state of Eu ions in the high-pressure compound EuNi. In order to establish the mean valence of Eu ions we have used the Mössbauer effect of the 21.6 keV γ -rays of

^{151}Eu . The magnetic state of the Eu ions was established by measuring the magnetisation of EuNi and the Mössbauer spectrum of 23.9 keV ^{119}Sn γ -rays.

2. Experimental details

The sample of the EuNi compound for the x-ray and magnetic investigations was prepared at a constant pressure of 7.7 GPa by melting the starting materials. The chamber constructed by Khvostantsev *et al* (1977) was used to generate the high pressure. The new compound was detected by x-ray powder photographs using Cu K α radiation. The density of the EuNi compound was determined using a pycnometric method. Its composition was verified by x-ray microanalysis to an accuracy of ± 3 at.% Eu.

The magnetic investigations of a polycrystalline sample having a spherical shape were performed using a Princeton Applied Research vibrating sample magnetometer at various temperatures from 4.2 to 300 K in magnetic fields up to 0.9 T.

The sample of EuNi used for the investigation of the Mössbauer effect was prepared by direct melting of a mixture of Eu metal, Ni metal and a small quantity of ^{119}Sn metal in a rocksalt tube at a constant pressure of 7.7 GPa. The tin impurity concentration in the compound was varied in the range from 0.3 to 0.5 at.%. The absorber was made from a fine powder which had a particle size ranging from 1 to 5 μm .

$^{151}\text{SmF}_3$ and $\text{Ca}^{119}\text{SnO}_3$ sources were employed for the ^{151}Eu and ^{119}Sn measurements, respectively. The sources were kept at room temperature. To register the Mössbauer radiation, constant-acceleration spectrometers with SmF_3 and CaSnO_3 detectors were used (Reiman *et al* 1984). The spectrum for the ^{119}Sn impurity atoms in the EuNi host was measured at 5 K. The spectra for the ^{151}Eu were measured at 80 K and 300 K. To determine the hyperfine structure parameters the usual procedure of approximating the spectra by a sum of Lorentzian lines was used.

Table 1. X-ray data for $\text{Yb}_{0.56}\text{Ni}_{0.44}$ (C15 structure type), with $a = 7.334(5)$ Å.

Intensity†	d_{obs} (Å)	hkl	d_{cal} (Å)
vw	4.220	111	4.234
s	2.585	220	2.592
vs	2.209	311	2.211
M	2.115	222	2.117
vw	1.679	331	1.682
s	1.494	422	1.497
s	1.408	511	1.411
		333	
MS	1.294	440	1.296
vw	1.158	620	1.160
vw	1.116	533	1.118
w	0.979	642	0.980
w	0.955	553	0.955
w	0.864	660	0.864
w	0.847	555	0.847

† vs: very strong; s: strong; MS: medium strength; M: medium; w: weak; vw: very weak.

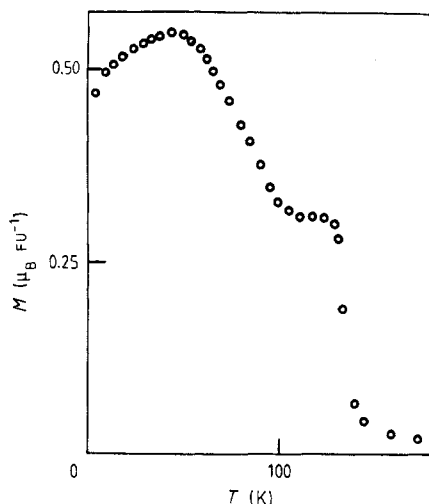


Figure 1. The magnetisation of EuNi versus temperature in an external magnetic field of 0.05 T.

3. Results and discussion

The x-ray powder data for the new phase with composition $\text{Eu}_{0.56}\text{Ni}_{0.44}$ were indexed on the basis of the cubic unit cell of MgCu_2 -type (C15) structure and space group $\text{Fd}\bar{3}m$, as for R-Fe where R is a light rare earth element (Tsvyashchenko *et al* 1985). The x-ray data for the new phase $\text{Eu}_{0.56}\text{Ni}_{0.44}$ are listed in table 1. The $\text{Eu}_{0.56}\text{Ni}_{0.44}$ compound has the unit cell parameter $a = 7.334(5) \text{ \AA}$ and the observed pycnometric density ρ is $6.9(1) \text{ g cm}^{-3}$ (the x-ray density is 7.1 g cm^{-3}).

The magnetic measurements showed that the EuNi is probably ferromagnetically ordered with a Curie temperature of 139 K. Figure 1 shows the magnetisation curve as a function of temperature in an external magnetic field of 0.05 T. The magnetisation values rise rapidly at temperatures below 100 K and then pass through a maximum at 45 K. From this magnetisation versus temperature curve it may be assumed that the magnetic structure of EuNi changes below 100 K. However, on the magnetisation versus the applied magnetic field (M - H) curves the 'knee' observed on transformation from an antiferromagnetic to a ferromagnetic structure is not seen (figure 2). The saturation magnetisation value defined at 4.2 K is equal to $4.8 \mu_{\text{B}} \text{FU}^{-1}$.

The ^{151}Eu Mössbauer effect in the EuNi_5 compound and EuNi_5H_x has been used by Oliver *et al* (1978) to define the valence of the Eu ions. EuNi_5 has an isomer shift of $+2.29 \text{ mm s}^{-1}$ at 2.6 K and EuNi_5H_x has an isomer shift of -10.54 mm s^{-1} at 2.6 K. The isomer shift value for the EuH_2 hydride is equal to -11.4 mm s^{-1} (Mustochi 1974). The values for the EuPd_3 and EuRh_2 intermetallic compounds with trivalent Eu ions are equal to $+3.6 \text{ mm s}^{-1}$ and $+2.0 \text{ mm s}^{-1}$ respectively (Wickman *et al* 1968). In order to obtain an estimate of nominal valence, \bar{V} , of the Eu ions from the isomer shift of the EuNi compound, where $\bar{V} = 2 + \nu$ and the fractional occupation of the $\text{Eu}^{3+} 4f^6$ state, $\nu = (\delta - \delta_2)/(\delta_3 - \delta_2)$ (Bauminger *et al* 1973), we will use $\delta_2 = -11.0 \text{ mm s}^{-1}$ and $\delta_3 = +2.6 \text{ mm s}^{-1}$, where δ_2 (δ_3) are the isomer shifts of integral valent Eu^{2+} (Eu^{3+}), respectively.

Typical ^{151}Eu Mössbauer absorption spectra of EuNi at ambient pressure and two selected temperatures are shown in figure 3. The top of the figure shows the spectrum obtained at room temperature which consists of a main component, with $\delta =$

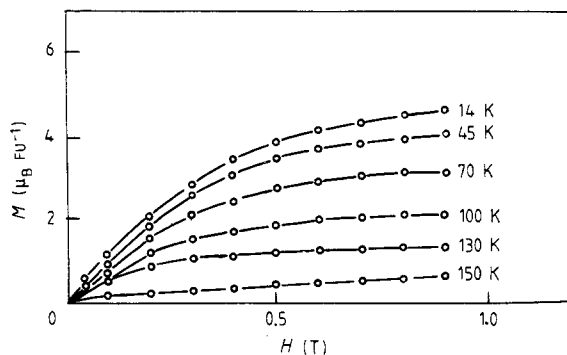


Figure 2. The magnetisation versus the applied magnetic field for EuNi.

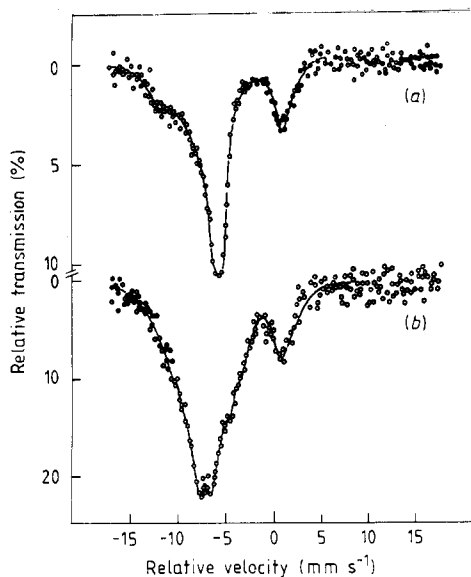


Figure 3. (a) ^{151}Eu Mössbauer spectra of EuNi at room temperature; (b) at 80 K.

$-5.86(5) \text{ mm s}^{-1}$ and a relatively weak satellite, plus a contribution from Eu_2O_3 . The Eu_2O_3 impurity on the sample surface arose from the interaction between oxygen and europium as the EuNi powder absorber was prepared in the air. The formation of Eu_2O_3 has been observed on hydriding EuNi_5 also (Oliver *et al* 1978). Satellite lines have also been observed in all Mössbauer studies of EuPd_2Si_2 (Croft *et al* 1981) and EuCu_2Si_2 (Bauminger *et al* 1973). The Mössbauer spectrum obtained at 80 K shows a magnetic hyperfine splitting characteristic of a magnetically ordered Eu compound (figure 3(b)). The magnitudes of the hyperfine magnetic field B_{hf} and isomer shift δ are $1.6(2) \text{ T}$ and $-7.14(5) \text{ mm s}^{-1}$, respectively. We find a mean valence value of $\bar{V} = 2.38(5)$

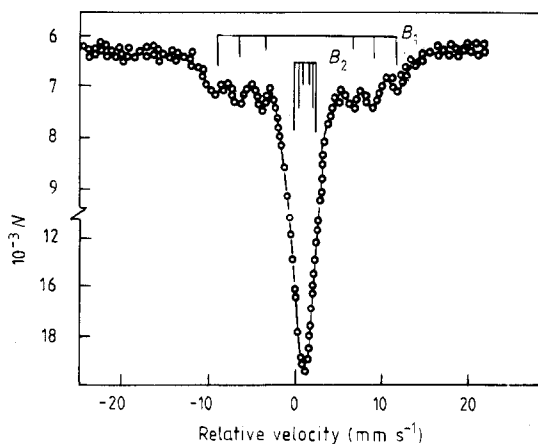


Figure 4. The Mössbauer spectrum for ^{119}Sn impurity atoms in the EuNi host, measured at 5 K.

at room temperature and of $\bar{V} = 2.28(5)$ at 80 K. The mean valence value defined from the saturation magnetisation M_s at 4.2 K is

$$\bar{V}_M = 2 + (M(\text{Eu}^{2+}) - M_s)/M(\text{Eu}^{2+}) = 2.33(5) \quad (M(\text{Eu}^{2+}) = 7.12 \mu_B).$$

Thus it is seen that the intermediate valence is preserved with decreasing temperature and the onset of ferromagnetic ordering, and the valence value is almost unchanged. On the basis of the analysis of the isomer shift data and of the saturation magnetisation we estimate the ground-state valence of the Eu in EuNi to be 2.3(1).

It should be noted that this ground state of Eu in the EuNi compound corresponds to a low value of the magnetic hyperfine field in comparison with that of Eu metal. In fact, from Mössbauer effect measurements made by Farrell and Taylor (1987) it is known that for Eu metal the increase of the valence up to 2.4 with an increase of pressure up to 14 GPa leads to a decrease in the magnetic hyperfine field to almost 7 T.

The Mössbauer spectrum for ^{119}Sn in the EuNi host obtained at 5 K is shown in figure 4. The magnetic hyperfine structure corresponding to $B_1 = 14.6$ T is well resolved but that corresponding to $B_2 = 1.8$ T is poorly resolved. The isomer shift is equal to $+2.0(1)$ mm s^{-1} . Absence of published data on the magnetic hyperfine fields for ^{119}Sn impurity atoms in the RNi_2 intermetallic compounds, prevents us from discussing in detail the results obtained. However, we hope that these results will be discussed in our future work.

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