$Eu_2Ni_3Si_5$: A new valence-fluctuation system

Sujata Patil
Indian Institute of Technology, Bombay 400 076, India

R. Nagarajan and L. C. Gupta
Tata Institute of Fundamental Research, Bombay 400 005, India

C. Godart
Laboratoire Chimie Metallurgique des Terres, F-92190 Meudon, France

R. Vijayaraghavan
Tata Institute of Fundamental Research, Bombay 400 005, India

B. D. Padalia
Indian Institute of Technology, Bombay 400 076, India
(Received 21 September 1987)

In our search for new valence-fluctuating systems, we have synthesized for the first time the compound $Eu_2Ni_3Si_5$. The powder x-ray-diffraction pattern shows that the compound forms in the orthorhombic $U_2Co_3Si_5$-type structure. The value of the isomer shift of the ^{151}Eu Mössbauer resonance (−2.8 mm/sec at 300 K) and its strong temperature dependence (−1.1 mm/sec at 4.8 K) clearly establish that the Eu ion in this system is in a valence-fluctuating state. The average valence varies from 2.6 at 300 K to 2.8 at 4.8 K. The valence-fluctuating nature is further confirmed by magnetic-susceptibility studies.

Even though the phenomenon of valence fluctuation (VF), often referred to as mixed valence, has been known for more than a decade, it continues to hold the attention of research workers in the physics and chemistry of rare-earth-based systems, as there are still many questions left unanswered. For instance, though there are reasonably well-established theories, one is not in a position to predict whether a particular compound in a rare-earth series would be a VF compound. This is particularly true in the case of Eu-based compounds as only a few VF systems are known for Eu. Only very recently, as a result of extensive studies in the series EuM_2Si_2 (M are transition elements) has a systematics of the valency of Eu begun to emerge.[1,2] Thus, the need for identification of more Eu-based VF systems and a systematic study of the related compounds is imperative.

VF behavior of Eu compounds is of particular interest, as one can study this phenomenon microscopically using ^{151}Eu Mössbauer-effect spectroscopy (MES). This is because the isomer shift (IS) of the resonance is quite different for the Eu^{2+} and the Eu^{3+} states. In this paper we present our successful identification of the VF behavior of Eu in the new ternary system $Eu_2Ni_3Si_5$ through the measurements of MES and dc magnetic susceptibility.

The samples of $Eu_2Ni_3Si_5$ were prepared by standard induction or arc melting in a titanium-gettered argon atmosphere. Any loss in weight due to evaporation of Eu was compensated by adding the requisite amount of Eu and remelting. One batch of the material was wrapped in tantalum foil and was annealed at 900 K in a vacuum-sealed quartz tube for nearly one month.

X-ray powder diffraction measurements were carried out in a Siemens diffractometer with Cu $K\alpha$ radiation. An internal KCl standard ($a = 6.2931$ Å) was included. Lattice parameters were determined by the method of least-squares fitting using reflections in the 2θ range ($20 \leq 2\theta \leq 70$). ^{151}Eu Mössbauer studies were performed against a 500-mCi- $^{151}SmF_3$ source using a conventional constant-accelerator spectrometer in conjunction with a multiscaler analyzer. Spectra were taken over the temperature range 4.8–300 K using a gas-flow-type cryostat. dc magnetic susceptibility studies were carried out over the temperature range 4.2–300 K using a Faraday microbalance.

X-ray diffraction patterns of $Eu_2Ni_3Si_5$ show that it forms in the orthorhombic $U_2Co_3Si_5$-type structure. All reflections follow the conditions (i) $h+k+l=2n$, (ii) if $h=0$, then $k=2n$ and $l=2n$, (iii) if $k=0$, then $h=2n$ and $l=2n$ as required by the space group Ibam and the $U_2Co_3Si_5$-type crystal structure.[3] In this structure, all the Eu ions occupy crystallographically equivalent sites. A minority phase ($\sim 10\%$) which could not be identified was also seen. The lattice parameters of the system, determined by the method of least-squares fitting, are $a = 9.479$ Å, $b = 12.021$ Å, and $c = 5.667$ Å.

The Mössbauer spectrum of the as-cast sample of $Eu_2Ni_3Si_5$ at 300 K exhibits a major line with IS ~ -2.8 mm/sec and two minor lines, one with IS $\sim +0.4$ mm/sec and another with IS ~ -8.2 mm/sec as shown in Fig. 1(a). These lines were taken as an indication of the

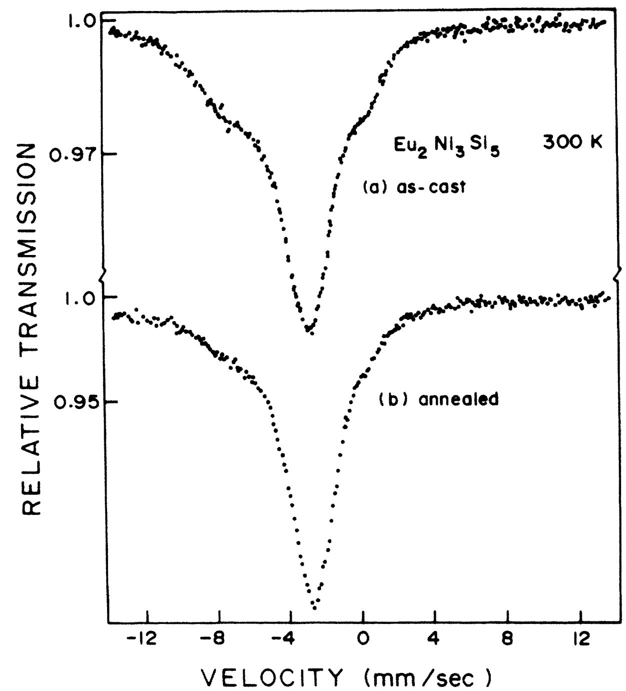

FIG. 1. ^{151}Eu Mössbauer spectra of $Eu_2Ni_3Si_5$ at 300 K for (a) as-cast and (b) annealed samples.

presence of some amount of minority phases with Eu in divalent and trivalent states. On annealing the sample though, no perceptible difference was seen in the x-ray diffraction pattern, there was marked reduction in the minor lines of the Mössbauer spectrum [Fig. 1(b)].

The Mössbauer spectra of the annealed samples, taken at a few selected temperatures, are shown in Fig. 2. The IS of the line at 300 K is -2.8 mm/sec. This IS is close to neither that usually observed for trivalent Eu (~ 0 to 4.5 mm/sec) nor that for divalent Eu (~ -8 to -12 mm/sec).[4] This leads us to conclude that Eu in $Eu_2Ni_3Si_5$ is in an intermediate valence state or valence fluctuating state. The VF state of Eu is further confirmed from the fact that IS exhibits a strong temperature dependence (-2.8 mm/sec at 300 K to -1.1 mm/sec at 4.8 K) (Fig. 3). The width of the observed resonance does not exhibit any significant change with temperature.

dc magnetic-susceptibility measurements also give important information about the phenomenon of mixed valency as Eu^{3+} is a nonmagnetic ion with temperature-independent Pauli paramagnetism, whereas Eu^{2+} is a magnetic ion with a free-ion moment of $7.9\mu_B$. The Ni ion in our system is not expected to contribute to the magnetic properties, as the transition-metal ion in similar materials such as $R_2Fe_3Si_5$ ($R =$Y, Sc, Lu) has been found to carry no magnetic moment.[5] Our results of dc magnetic susceptibility studies are shown in Fig. 4. The inverse susceptibility varies linearly in the temperature range 100–300 K and therefore was fitted to a Curie-Weiss behavior in this temperature range. The effective magnetic moment μ_{eff}, estimated from the Curie-Weiss behavior is $\sim 6\mu_B$ with a Curie-Weiss temperature Θ_P of

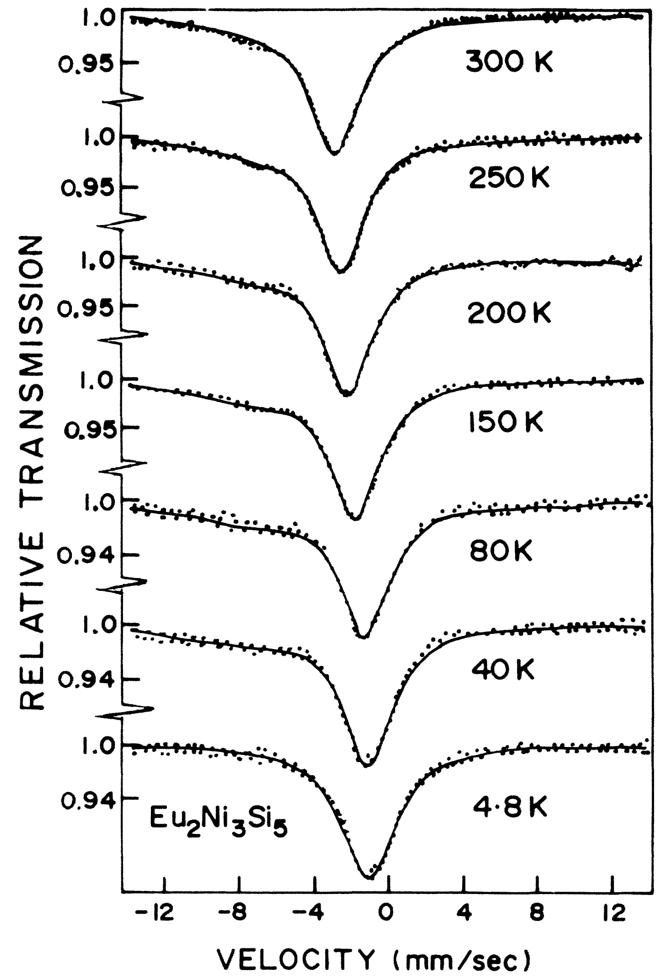

FIG. 2. ^{151}Eu Mössbauer spectra of annealed $Eu_2Ni_3Si_5$ samples at various temperatures.

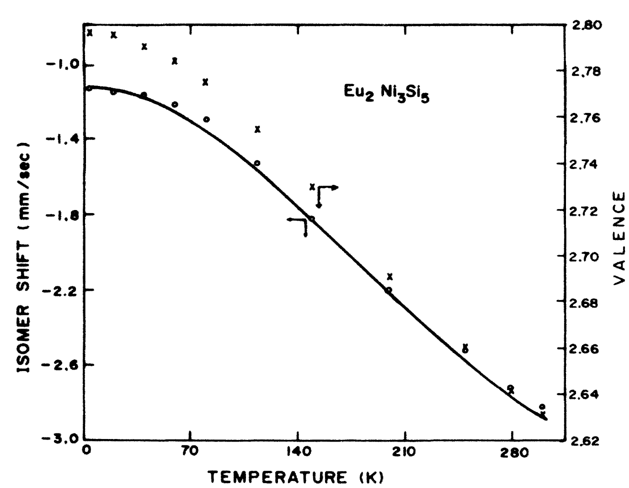

FIG. 3. ^{151}Eu Mössbauer isomer shift and average valence of $Eu_2Ni_3Si_5$ as a function of temperature. The solid line is the simulated curve for the variation of IS with temperature for $E_{ex} = 730$ K and $T_{sf} = 235$ K.

~ -160 K. This effective magnetic moment is smaller than that for the free Eu^{2+} ion ($7.9\mu_B$) which is consistent with the mixed valence behavior of the Eu ion in this system.

The magnetic susceptibility at low temperature ($T<50$ K) shows a divergence indicating a contribution coming from stable divalent Eu ions, also seen in the Mössbauer spectra. In view of the evidence for the presence of stable Eu^{2+} ions, the Mössbauer spectra were fitted to two Lorentzians taking into account a divalent line near -8.2 mm/sec. The solid lines in Fig. 2 at each temperature are the result of such a fitting. This analysis indicated the amount of divalent Eu to be between 15 and 20%. The effective magnetic moment obtained from the dc susceptibility corrected for 15% divalent Eu is $5.6\mu_B$. Thus, these results clearly establish that Eu is in a VF state in this system.

The energetics of VF systems can be described in terms of the two-level model[6] wherein Eu^{3+} is taken as the ground state and Eu^{2+} is taken as the excited state separated by an energy E_{ex}. The fluctuation of the ion between the two states broadens the $4f$ level; the broadening is represented by a spin-fluctuation temperature T_{sf}, which is also a measure of the fluctuation frequency. The occupation probabilities P_2 (E_{ex}, T^*) and P_3 (E_{ex}, T^*) of the divalent and trivalent configurations are given by

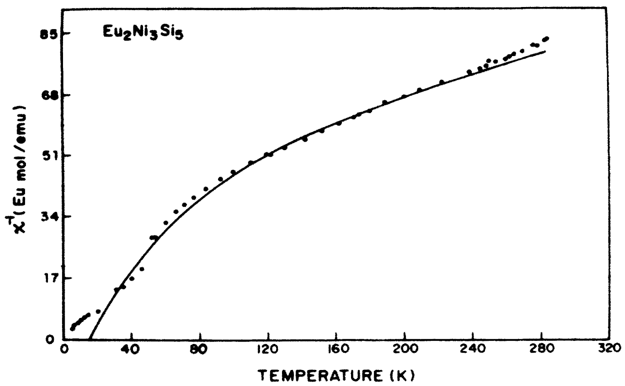

FIG. 4. Inverse dc magnetic susceptibility of $Eu_2Ni_3Si_5$ as a function of temperature. The solid line is the simulated curve for inverse susceptibility for $E_{ex}=730$ K and $T_{sf}=235$ K.

$$\frac{P_2}{P_3}=\frac{8\exp(-E_{ex}/T^*)}{1+3\exp(-480/T^*)+5\exp(-1330/T^*)+7\exp(-2600/T^*)} ,$$

where T^* is the effective temperature which takes into account the spin-fluctuation energy[7] and is given by,

$$T^*=(T^2+T_{sf}^2)^{1/2} .$$

In the fast-fluctuation limit, which is applicable in this case as one observes only one time-averaged Mössbauer line, the IS of the system is given by the population-weighted average,

$$S=S_2P_2+S_3P_3 ,$$

where S is the IS for valence fluctuating Eu, S_2 and S_3 are IS expected for stable Eu^{2+} and Eu^{3+} ions. The observed IS values of $Eu_2Ni_3Si_5$ were analyzed with the above considerations using S_2 and S_3 as -9.5 mm/sec and $+1.0$ mm/sec, respectively. The value of S_2 was taken from the IS observed for isostructural $Eu_2Pd_3Si_5$ and $Eu_2Cu_3Si_5$ (Ref. 8) and that for S_3 was taken from the IS observed for $EuNi_2Si_2$ (Ref. 9) as no isostructural trivalent Eu compound has been found so far. This analysis yields the values $E_{ex}=730$ K and $T_{sf}=235$ K. Simulation of IS using the above values of E_{ex} and T_{sf} (solid line in Fig. 3) shows a good agreement with the observed IS.

The above values of E_{ex} and T_{sf} were in turn used in the expression for magnetic susceptibility of the VF system, viz.,

$$\chi=P_2\chi_2+P_3\chi_3 ,$$

where χ_2 is the Curie susceptibility of Eu^{2+} ions and χ_3 is the Van Vleck susceptibility of Eu^{3+} ions at temperature T^*. The results were compared with the observed susceptibility (Fig. 4). In these calculations also, a 15% divalent Eu impurity with $T_c=15$ K was assumed to be present as evidenced by the Mössbauer data. Once again we see fairly reasonable agreement between the calculated and experimental dc susceptibility values, justifying the temperature-independent E_{ex} and T_{sf}.

The constancy of E_{ex} and T_{sf} over the observed temperature range (4.8–300 K) calls for a special mention. The VF behavior of systems such as $EuCu_2Si_2$ (Ref. 10), $EuPd_2Si_2$ (Ref. 11), $EuIr_2Si_2$ (Refs. 1 and 2) etc., has been interpreted in terms of temperature-dependent E_{ex} and T_{sf}. It appears that among the Eu-based VF systems known so far, only the Eu-Ni systems—the others being $EuNi_2P_2$ (Ref. 12) and $EuNiSi_2$ (Ref. 9)—seem to have temperature-independent E_{ex} and T_{sf}. Raman studies[13] have been very informative regarding the temperature dependence of E_{ex} and T_{sf} in the well-known mixed valence system $EuPd_2Si_2$. Such studies on $Eu_2Ni_3Si_5$ also should lead to useful information on this aspect of the material under consideration. From these investigations, it should also be possible to check the consistency of various techniques with respect to the temperature dependence of the two parameters E_{ex} and T_{sf}.

The average valence $\bar{V}$ of Eu was computed from the relation

$$\bar{V}=2P_2+3P_3$$

using the above-mentioned values of E_{ex} and T_{sf}. The variation of $\bar{V}$ with temperature is shown in Fig. 3. It may be noted that the magnitude and range of variation of $\bar{V}$ of Eu is similar to that observed in $EuNiSi_2$ (Ref. 9).

In conclusion, we have synthesized a new ternary system $Eu_2Ni_3Si_5$ and established through ^{151}Eu Mössbauer spectroscopy and magnetic-susceptibility studies that Eu ion is in a valence-fluctuation state in this material. The identification of a new VF material is of significance as not many Eu-based VF systems are yet known.

The Laboratoire Chimie Metallurgique des Terres is Equipe de Recherche du Centre Nationale Recherche Scientifique No. 209.

[1]B. Chevalier, J. M. D. Coey, B. Lloret, and J. Etourneau, J. Phys. C **19**, 5421 (1986).

[2]Sujata Patil, R. Nagarajan, L. C. Gupta, B. D. Padalia, and R. Vijayaraghavan, Solid State Commun. **63**, 955 (1987).

[3]B. Chabot and E. Parthe, J. Less Common Met. **97**, 285 (1984).

[4]E. R. Bauminger, G. M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), Chap. 10.

[5]A. M. Umarji, S. K. Malik, and G. K. Shenoy, J. Appl. Phys. **57**, 3118 (1985).

[6]E. R. Bauminger, I. Felner, D. Froindlich, D. Levron, I. Nowik, S. Ofer, and R. Yanovsky, J. Phys. (Paris) Colloq. **35**, C6-61 (1974).

[7]W. Franz, F. Steglich, W. Zell, D. Wohlleben, and F. Pobell, Phys. Rev. Lett. **45**, 64 (1980).

[8]Sujata Patil, R. Nagarajan, C. Godart, L. C. Gupta, R. Vijayaraghavan, and B. D. Padalia (unpublished).

[9]R. Nagarajan, Sujata Patil, L. C. Gupta, and R. Vijayaraghavan, J. Magn. Magn. Mater. **54–57**, 349 (1986).

[10]J. Röhler, D. Wohlleben, G. Kaindl, and H. Balster, Phys. Rev. Lett. **49**, 65 (1982).

[11]E. V. Sampathkumaran, L. C. Gupta, R. Vijayaraghavan, K. V. Gopalakrishnan, R. G. Pillay, and H. G. Devare, J. Phys. C **14**, L237 (1981).

[12]R. Nagarajan, G. K. Shenoy, L. C. Gupta, and E. V. Sampathkumaran Phys. Rev. B **32**, 2846 (1985).

[13]E. Zirngiebl, S. Blumenröder, G. Güntherodt, A. Jayaraman, B. Batlogg, and M. Croft, Phys. Rev. Lett. **54**, 213 (1985).