PHYSICAL REVIEW B VOLUME 32, NUMBER 5 1 SEPTEMBER 1985

Anomalous behavior of the Mössbauer resonance width in mixed-valence $EuNi_2P_2$

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(Received 1 June 1984)

We present here the results of our detailed Mössbauer measurements on the mixed-valence system $EuNi_2P_2$. The linewidth of the resonance exhibits a broad peak at ~ 40 K. We argue that this feature is anomalous in that it cannot be understood in terms of the known mechanisms that can give rise to line broadening. The system exhibits strong mixed valence—the average valence being ~ 2.5—even at $T=1.4$ K. This is the first Eu-based material having truly mixed valence behavior as $T \rightarrow 0$; all others tend to approach the trivalent configuration as $T \rightarrow 0$.

I. INTRODUCTION

Interconfiguration fluctuation of europium has been reported in a number of Eu-based materials, such as $EuCu_2Si_2$ (Ref. 1) and $EuPd_2Si_2$ (Ref. 2). Mössbauer isomer-shift (IS) measurements have proved to be of crucial importance in all of these investigations. One observes[3] a single, motionally averaged, line in such systems as the valence fluctuation is fast enough to satisfy the condition $\tau_{sf}(S_2-S_3)<1$. Here $1/\tau_{sf}$ is the frequency of fluctuation and S_2 and S_3 are the isomer shifts of europium in the divalent ($4f^7$) and the trivalent ($4f^6$) configurations. The isomer shift of the averaged line lies between S_2 and S_3. The spectrum does not exhibit, in many cases, any significant variation of the resonance linewidth with temperature. $EuPd_6B_4$, however, behaves rather differently in that the variation of the resonance linewidth as a function of temperature is rather striking.[4] Felner and Nowik[4] pointed out that this behavior is a consequence of the sensitivity of E_{exc}, the interconfiguration excitation energy, to local disorder that could be, for example, due to the presence of vacancies or other crystallographic defects. The actual line shape of the spectrum depends upon the relative magnitudes of the following energies: the excitation energy E_{exc}, the width δ of the localized $4f$ level [or the valence fluctuation temperature $T_{sf}=h/(\tau_{sf}k_B)$], and the inhomogeneous spread Δ of E_{exc} arising from disorder in the sample. In the fast fluctuation limit and with Δ small, there is almost no variation of the resonance width as a function of temperature.

We had reported[5] recently $EuNi_2P_2$ to be an intermediate valence system. We have now performed extensive Mössbauer investigations on this material and have observed a line broadening as a function of temperature in the interval 1.4—300 K. In this paper we wish to present these results and demonstrate that this behavior of the linewidth cannot be understood in terms of the known sources of line broadening.

II. EXPERIMENTAL

The material $EuNi_2P_2$, both in the form of single-crystal platelets and polycrystalline powders, was prepared following the procedure suggested in the literature.[6,7] Small single crystals were obtained by carefully cooling the melt in a tin flux. Polycrystalline samples were synthesized by heating together stoichiometric amounts of Eu, Ni, and P in a sealed quartz tube. The x-ray powder diffraction of the samples gave identical patterns corresponding to the $ThCr_2Si_2$ structure (space group D_{4h}) and showed that they were single phase. The lattice constants ($a=3.911$ Å and $c=9.482$ Å) of the tetragonal unit cell agreed very well with those reported in the literature.[6] $GdNi_2P_2$, the other material used in this work as a reference, was also prepared by heating the constituents directly in a quartz tube. The lattice constants of this material were also in good agreement with literature.[6,7]

^{151}Eu Mössbauer measurements on $EuNi_2P_2$ were made using 200 mCi $^{151}Sm_2O_3$ source. A conventional cryostat was used to study the temperature dependence of the Mössbauer resonance in the temperature interval 1.4—300 K. The IS values reported here have been expressed with respect to Sm_2O_3. ^{155}Gd Mössbauer measurements were also performed on $GdNi_2P_2$ as a function of temperature. $GdNi_2P_2$ provides us with a good reference to estimate the lattice contribution to the electric field gradient. Magnetic susceptibility was measured in the same temperature interval and in applied fields of about 3 kG using a Faraday microbalance.

III. RESULTS

Figure 1 shows the Mössbauer spectra of $EuNi_2P_2$ at various temperatures of specific interest in the interval 1.4 to 300 K. A very noticeable feature of these spectra is the absence of an additional component which has been ob-

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served, for instance, in $EuCu_2Si_2$ and $EuPd_2Si_2$—the two very well studied mixed-valence systems with the same structure. This component is usually weak ($\sim$10–15% of the main line) and is believed to arise due to the disorder in the near-neighbor shells of Eu. The absence of this weak component in $EuNi_2P_2$, therefore, is an indication that a crystallographic order of high degree exists in this material. This is consistent with the fact that $EuNi_2P_2$ is more like a chemical compound unlike $EuCu_2Si_2$ and $EuPd_2Si_2$. As a consequence of this, we expect that in $EuNi_2P_2$, Δ may not be appreciable.

The observed spectra are fitted to a single Lorentzian with Γ, the full width at half maximum (FWHM), and S, the isomer shift, as variable parameters. It may be noted that even though the fit is not good around the tail region of the spectra, this inadequacy of the fit does not affect the systematics of the temperature dependence of S and Γ. The spectra are characterized by a temperature dependent S ($S = -6.3$ mm/s at 300 K and -4.25 mm/s at 1.4 K), which is intermediate between that typically observed for divalent (~ -8 to -12 mm/s) and trivalent ($\sim$0 to $+4.5$ mm/s) europium ionic states. Furthermore no hyperfine splitting was discernible even at 1.4 K. These observations clearly suggest that Eu is in an intermediate valence state in $EuNi_2P_2$. The temperature dependence of S over the entire temperature interval studied here is shown in Fig. 2. It may be noted that the overall variation of S in $EuNi_2P_2$ with temperature is much smaller than that in $EuCu_2Si_2$ and $EuPd_2Si_2$, suggesting that the variation of the average valence of europium is also much smaller.

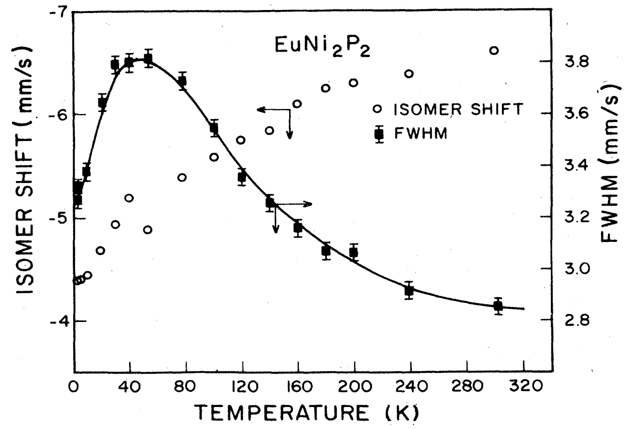

FIG. 2. Temperature dependence of the width (▮) and the isomer shift (○) of the Mössbauer line. The smooth line drawn through the data points (▮) is a guide to the eye. The error in the isomer-shift values is smaller than the size of the circle (○).

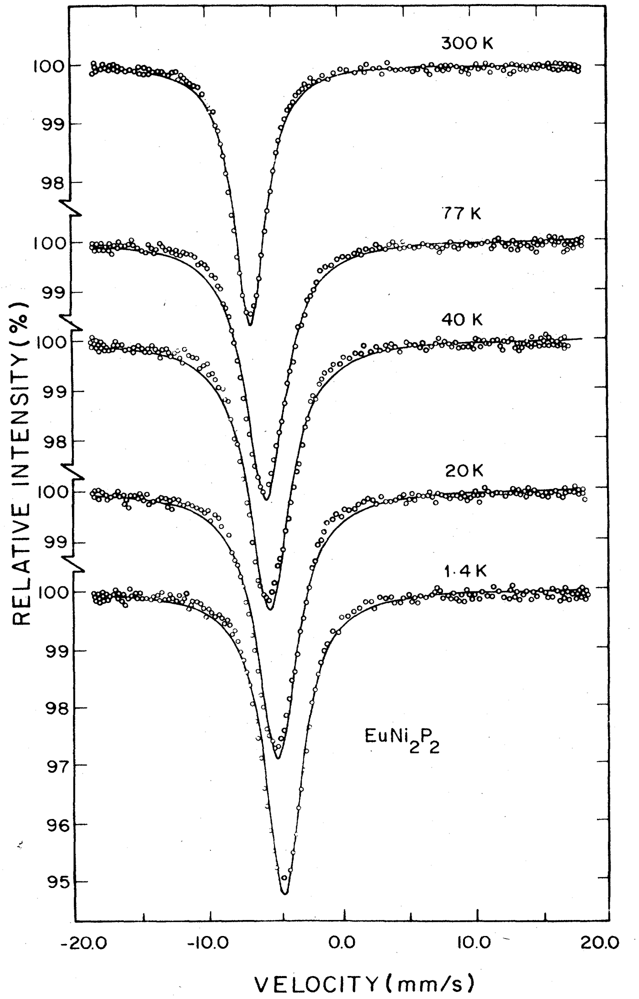

FIG. 1. Mössbauer spectra of ^{151}Eu in $EuNi_2P_2$ at various temperatures. The solid lines are single Lorentzian fits to the data points.

Figure 2 also shows Γ as a function of temperature. It is interesting to note that above 40 K, Γ increases progres-

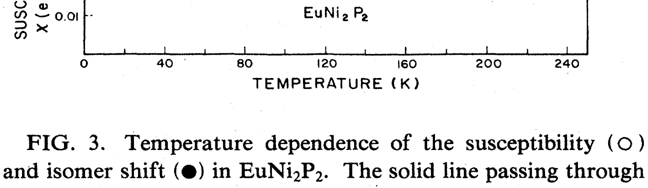

FIG. 3. Temperature dependence of the susceptibility (○) and isomer shift (●) in $EuNi_2P_2$. The solid line passing through the susceptibility data is a fit using Eqs. (1) and (2). The solid line passing through the isomer-shift data is generated using Eqs. (1) and (3b) with $E_{exc} = 160$ K and $T_{sf} = 80$ K obtained from the susceptibility fit. The broken line shows the temperature dependence of the average valence $\bar{V}$, Eq. (4).

sively as the sample is cooled; it exhibits a maximum in the neighborhood of 40 K and then decreases again as the temperature continues to drop further down.

Magnetic susceptibility $\chi(T)$ of the sample, measured as a function of temperature, is displayed in Fig. 3. The low-temperature behavior of $\chi(T)$ is typical of a mixed-valence material—it saturates below $\sim$40 K and does not diverge as $T \rightarrow 0$. It is clear that such a temperature dependence of susceptibility cannot arise if Eu were in a stable divalent state. In addition, no hyperfine field was observed in our Mössbauer spectra even at 1.4 K. This clearly rules out any magnetic ordering in the sample at least down to 1.4 K which is consistent with the mixed-valence nature of the sample. The results of independent runs on samples drawn from different batches were in excellent agreement.

IV. DISCUSSION

A. Susceptibility and the isomer shift

The interconfiguration fluctuation gives rise to broadening of the $4f$ levels. While calculating various thermodynamic quantities, the level width is taken into consideration by introducing[2,8] an effective temperature T^* (of the ions) that is different from the lattice temperature T. Following Franz *et al.*,[8] T is replaced by

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

where T_{sf} is the width (in units of temperature) of the $4f$ level. All the sublevels belonging to the two configurations $4f^6$ and $4f^7$ are assumed to be broadened by the same amount. The occupation probabilities $P_2(E_{\rm exc}, T^*)$ and $P_3(E_{\rm exc}, T^*)$ of the 2^+ and 3^+ configurations—which may simply be written as P_2 and P_3—are given by

$$\frac{P_2}{P_3} = \frac{8\exp(-E_{\rm exc}/k_B T^*)}{1+3\exp[(-480\ {\rm K})/T^*]+5\exp[(-1330\ {\rm K})/T^*]+7\exp[(-2600\ {\rm K})/T^*]} , \tag{1}$$

where $E_{\rm exc}$ is the excitation energy of the $4f^7$ configuration with respect to the ground-state level ($J=0$) of $4f^6$ configuration and $P_2 + P_3 = 1$.

The magnetic susceptibility for such a system is given by

$$\chi(T) = P_2\chi_2(T^*) + P_3\chi_3(T^*) , \tag{2}$$

where $\chi_2(T^*)$ is the Curie susceptibility of $4f^7$ ions and $\chi_3(T^*)$ is the Van Vleck susceptibility of $4f^6$ ions at effective temperature T^*. A very good fit for $\chi(T)$ is obtained with $E_{\rm exc}/k_B = 160$ K and $T_{sf} = 80$ K as shown in Fig. 3. The analysis of $\chi(T)$, therefore, fixes the values of $E_{\rm exc}$ and T_{sf} and suggests that these two quantities are temperature independent in $\rm EuNi_2P_2$. However, an explicit and strong temperature dependence of $E_{\rm exc}$ and T_{sf} had been considered in the recent mixed-valence studies[9] of $\rm EuCu_2Si_2$. It must also be pointed out that we did not have to introduce Δ here as was done, for example, in the case of $\rm EuPd_6B_4$.

For the case $\Delta = 0$, the resonance absorption intensity is given by

$$I(\omega) = \frac{\Gamma/\pi}{\Gamma^2 + [\omega - S(E_{\rm exc}, T^*)]^2} \tag{3a}$$

with

$$S(E_{\rm exc}, T^*) = P_2 S_2 + P_3 S_3 . \tag{3b}$$

Here S_2 and S_3 are the isomer shifts of the divalent and trivalent states and ω represents the photon energy. Usually one chooses S_2 and S_3 as the isomer shifts observed experimentally in isostructural materials with europium in pure divalent and trivalent states. One also prefers choosing those materials as references whose cell volumes are close to the cell volume of the material under consideration, as there are volume effects on the isomer shift.[10] In our case, however, the freedom of independently choosing S_2 and S_3 is limited as $E_{\rm exc}$ and T_{sf} have already been fixed. The isomer shift calculated from Eq. (3b) with $S_2 = -8.8$ mm/s and $S_3 = +0.4$ mm/s agrees reasonably well with the experimental data as shown in Fig. 3. In view of the fact that isomer shift of europium in divalent state could be in the range -8 to -12 mm/s and in the trivalent state could be in the range of 0 to $+4$ mm/s,[11] the values of S_2 and S_3 obtained in our above analysis are not unreasonable. It may be noted from Fig. 3 that the calculated shifts are not in good agreement for temperatures around 40 K. The values agree fairly well again at low temperatures (below 10 K). The temperature variation of the average valence $\bar{V}(T)$ is obtained from the relation

$$\bar{V}(T) = 2P_2 + 3P_3 \tag{4}$$

and is shown in Fig. 3. It is clear that $\bar{V}(T)$ varies between 2.25 (at 300 K) and 2.50 (at 1.4 K). A very noticeable feature of this system which distinguishes it from other Eu-based mixed valence systems and which has important bearing on the valence fluctuation phenomenon is the following: The mixed-valence materials involving Eu ions known so far tend to approach a low-temperature ground state wherein Eu is close to being trivalent. $\rm EuNi_2P_2$ is the first Eu-based material which exhibits strong mixed valence ($\bar{V} \simeq 2.5$) even as $T \rightarrow 0$. The ground state of this system is, therefore a truly quantum-mechanical mixed-valence state.

B. Linewidth

The behavior of the linewidth of the Mössbauer resonance with respect to temperature is anomalous as it is difficult to account for in terms of the known sources of line broadening as discussed below.

(i) The rapid fluctuation between two valence states with isomer shifts S_2 and S_3 gives rise to a single line of width Γ given by[3]

$$\Gamma=\Gamma_0+\pi(S_2-S_3)^2\tau_{sf}[1-(P_2-P_3)^2]\ . \tag{5}$$

This expression predicts an increase in Γ as the difference between P_2 and P_3 decreases, i.e., we get a maximum width $\Gamma_{\max}$ given by

$$\Gamma_{\max}=\Gamma_0+\pi(S_2-S_3)^2\tau_{sf} \tag{6}$$

as P_2 and $P_3 \to 0.5$. Thus one may expect a change in the linewidth simply because of the changes in P_2 and P_3. However, the magnitude of this change also depends upon T_{sf} through the relation to τ_{sf}. In our case the value of T_{sf} $(=80\ \mathrm{K})$ and its temperature independence corresponds to a variation in Γ which is not appreciable. Further, in this system, the limiting value of P_3 is ~ 0.5 and therefore this mechanism cannot produce the drop of the width which is observed below 40 K.

(ii) In $\mathrm{EuPd_6B_4}$, much more pronounced temperature dependence of the linewidth has been reported and explained[4] as a consequence of relatively large Δ. Even though our susceptibility analysis indicates that $\Delta \simeq 0$, we investigated if a reasonable value of Δ could explain the observed behavior of Γ in $\mathrm{EuNi_2P_2}$. Following Felner and Nowik,[4] the intensity $I(\omega)$ of the resonance absorption in the presence of Δ is given by

$$I(\omega)=\int_{-\infty}^{\infty}\left[\frac{\Delta/\pi}{\Delta^2+(E-E_{\mathrm{exc}})^2}\right]\times\left[\frac{\Gamma/\pi}{\Gamma^2+[\omega-S(E,T^*)]^2}\right]dE\ . \tag{7}$$

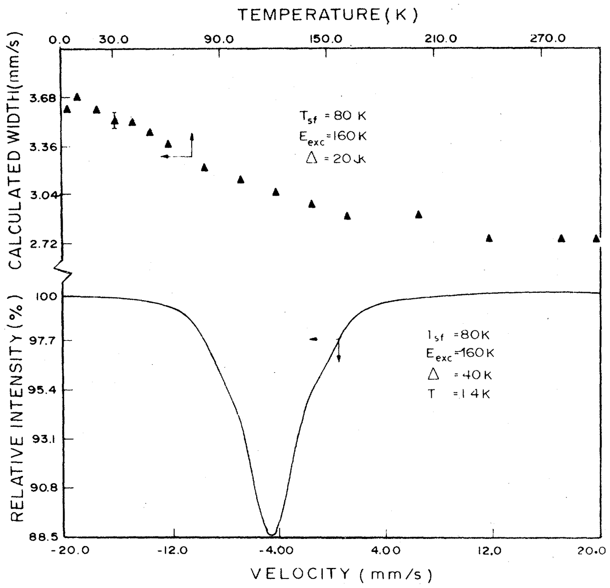

FIG. 4. Results of the calculations of the width (▲) of the line for the parameters $T_{sf}=80$ K, $E_{\mathrm{exc}}/k_B=160$ K, and $\Delta/k_B=20$ K [see expression for $I(\omega)$, Eq. (7), in the text]. Vertical bar represents the computational resolution for the calculated width. The lower part of the figure shows a simulated spectrum for $\Delta/k_B=40$ K, with other parameters being the same. One sees clearly a distortion in the simulated line shape suggesting that $\Delta=40$ K is too high an inhomogeneous spread in E_{exc}. Compare the observed spectra in Fig. 1.

Spectra were generated for various values of Δ using Eq. (7). Small values of Δ such as 5 or 10 K do not lead to any appreciable variation of linewidth. Figure 4 gives the calculated variation of Γ for $\Delta=20$ K. It is clear from Fig. 4 that although the calculated Γ does increase with decrease of temperature, however, it saturates as $T \to 1.4$ K and does not exhibit the experimentally observed drop at low temperatures $(1.4\ \mathrm{K}<T<40\ \mathrm{K})$. Higher values of Δ $(>20\ \mathrm{K})$ lead to excessive distortion in the line shape (Fig. 4) which is not the case in $\mathrm{EuNi_2P_2}$.

(iii) The possibility of unresolved quadrupole-split resonance lines contributing to the observed linewidth cannot be ruled out. We, in fact, get a better fit with the observed spectra if the possibility of quadrupole interactions is allowed (Fig. 5). The quadrupole interaction $e^2qQ(T)$ obtained from this analysis is shown as a function of temperature in Fig. 5. Thus, if the observed linewidth variation is to be associated with the variation of $e^2qQ(T)$, it would imply that $e^2qQ(T)$ exhibits a very unusual behavior. One observes, generally, either a monotonically increasing or decreasing variation of e^2qQ with temperature.[12]

In order to obtain an estimate of the lattice contribution to the electric field gradient (EFG) at the Eu-nucleus (with Eu in trivalent state) we studied ^{155}Gd Mössbauer resonance in $\mathrm{GdNi_2P_2}$ (whose cell constants are very close to those of $\mathrm{EuNi_2P_2}$) and obtained e^2qQ at the Gd site to be $+1.51$ mm/s at 25 K. From this it is possible to

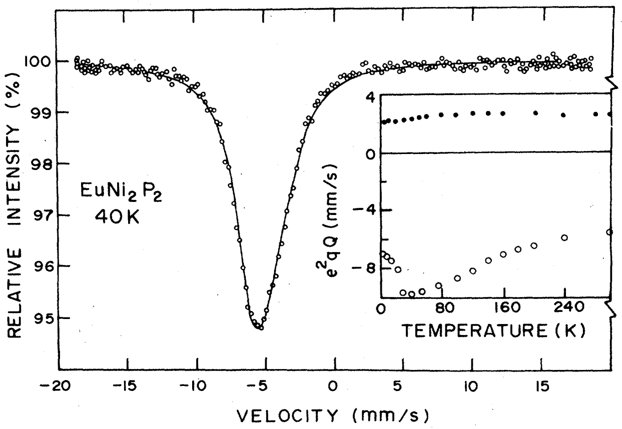

FIG. 5. Spectrum at 40 K fitted with quadrupole interaction (QI), e^2qQ, as an adjustable parameter and with a fixed resonance linewidth. One gets a better fit with QI than without QI (see spectrum at 40 K and the solid line representing the single Lorentzian fit in Fig. 1). Inset shows the temperature dependence of e^2qQ extracted (○) from such an analysis of the line shape. It is to be compared with the calculated (●) values of e^2qQ as explained in the text.

evaluate the lattice and the intraionic contributions to the EFG at the Eu nucleus when Eu is divalent and trivalent. Our calculations show that the net EFG—which includes contribution from the lattice and from $J=0,1$, and 2 states—in the trivalent configuration is of opposite sign with respect to that when Eu is in divalent state. Figure 5 shows $e^2qQ(T)$ calculated using the relation[3,13]

$$e^2qQ(T)=P_2[e^2qQ(T^*)]^{2+}+P_3[e^2qQ(T^*)]^{3+} \ . \quad (8)$$

It is clear from Fig. 5 that both the magnitude and the relative variation with temperature of the calculated $e^2qQ(T)$ are not in agreement with $e^2qQ(T)$ extracted from the line-shape analysis. It may be mentioned here that the relation of the type given above was found to account for the variation of $e^2qQ(T)$ of copper isotopes in $EuCu_2Si_2$ (Ref. 13) very satisfactorily. Thus, either (1) quadrupole interactions themselves are inadequate to account for the observed variation of linewidth or (2) the processes which induce the quadrupole interactions and their temperature dependence in $EuNi_2P_2$ are not understood properly.

A phase transition as the cause of the observed line broadening seems to be rather unlikely as in mixed-valence systems it would lead to a change in the valence state of the rare-earth ion (in this case the Eu ion) giving rise to a change in the magnetic susceptibility of the sample which is not observed in this case.

Thus, the origin of the unusual variation of the Mössbauer resonance width in $EuNi_2P_2$ is not clear. One is motivated to consider new mechanism(s) of line broadening which either do not contribute significantly in the cases reported in literature earlier or get masked by effects such as inhomogeneous spread of E_{exc}.

V. CONCLUSIONS

The magnetic susceptibility and the Mössbauer isomer-shift measurements suggest that $EuNi_2P_2$ has a truly quantum-mechanical mixed-valence ground state. The linewidth of the Mössbauer resonance absorption exhibits an anomalous temperature dependence in that it cannot be explained either as a consequence of slowing down of the valence fluctuations, or the presence of inhomogeneous spread of E_{exc}, the interconfiguration excitation energy, or the unsplit quadrupole components. Detailed measurements of Eu L_{III} edge and low-temperature x-ray diffraction measurements are in progress which should be of importance in getting further insight into this anomalous behavior of $EuNi_2P_2$.

ACKNOWLEDGMENTS

We are very grateful to Professor R. Vijayaraghavan for his kind encouragement and very valuable advice throughout the course of the present work.

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