Paramagnetic Resonance of Eu^{2+} Dissolved in Yb Metal

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The paramagnetic resonance of Eu^{2+} dissolved in Yb metal was measured between 1.6 and 77°K. The g value is $g=1.970\pm0.005$, displaying a g shift outside the experimental error. The increase in linewidth with temperature is $dW/dT=24\pm4$ G/°K independent of the Eu concentration. Assuming that this is caused by the Korringa mechanism, this temperature-dependent linewidth yields a g shift of $|\Delta g|=0.031$. From the g shifts, the exchange integral between the Eu spins and the conduction electrons is derived as $J=-0.02$ eV.

I. INTRODUCTION

MEASUREMENTS of electron spin resonance (ESR) of local moments in metals can be used to study the exchange interactions of these moments with the conduction electrons.[1] This exchange interaction has two effects: (a) It shifts the value of the g factor relative to the value of the same moment in a diamagnetic ionic environment by a mechanism analogous to that which is responsible for the Knight shift of NMR lines in metals. The magnitude of this shift is proportional to the magnitude of the exchange interaction and estimates of the exchange integral between the local moment spin and the conduction electrons can be obtained from the g shift. (b) Because of this coupling of the local moment to the conduction electrons, relaxation can take place between the two systems and this can produce a temperature-dependent ESR linewidth, analogous to that observed via the Korringa mechanism in NMR experiments in metals. Again from that temperature dependence the magnitude of the exchange interaction can be obtained. As has been pointed out,[2] ESR experiments are supplementary to nuclear resonance and magnetic measurements for better understanding the interaction mechanism in metals.

The ESR of Mn^{2+} and Gd^{3+} in a metallic environment has been investigated by various authors.[3–10] Measurements of Eu^{2+} have so far only been performed in Eu metal[11] and $EuAl_2$,[12] and in both cases no measurable g shift has been detected. Mössbauer measurements[13] on the alloy series Eu_xYb_{1-x} $(0\leq x\leq 1)$ indicated that Eu dissolved in Yb exhibits a local moment and therefore ESR measurements should be possible. In this communication the results of these measurements are reported.

II. EXPERIMENTAL

Samples of 1, 3, and 10% Eu dissolved in Yb were prepared by melting the stoichiometric amounts of the constituents in an argon atmosphere. X-ray fluorescence measurements and microprobe analysis showed that the Eu was well dispersed and that the samples exhibited no detectable inhomogeneities. The measurements were performed with a standard Varian-ESR spectrometer at $f=9.3$ kMc/sec and $f=35$ kMc/sec in the temperature range from 1.6 to 77°K. The samples had the form of thin plates and were polished under oil before each measurement in order to have as little oxidation as possible. Measurements were made with the dc field parallel and perpendicular to the sample plates in order to be able to correct for demagnetization effects. The magnetic field was calibrated with a nuclear resonance probe.

III. EXPERIMENTAL RESULTS

Figure 1 shows an ESR curve of Eu_1Yb_{99} measured at a frequency of $f=35$ kMc/sec at 1.6°K. This curve shows the asymmetric lineshape typical for ESR signals in metallic samples.[7] The curves of the other samples show the same general shape and they all were analyzed with the procedure outlined by Peter *et al.*[7]

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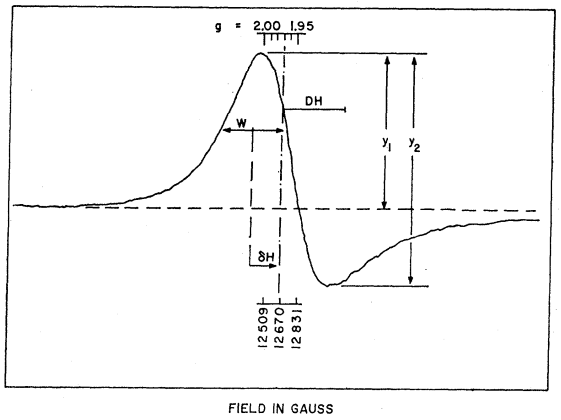

FIG. 1. ESR line of $Eu_{0.01}Yb_{0.99}$ at 1.6°K; $f=35$ kMc/sec. For the notation see Ref. 7.

Because of the low concentration, magnetization effects are negligible in the measurement shown in Fig. 1 and this curve therefore gives directly the g factor of Eu^{2+} in Yb metal as $g=1.970\pm0.005$ (see Fig. 2). This yields a g shift of $\Delta g=-0.023\pm.0005$ if we take the g value of Eu^{2+} in CaF_2 ($g=1.9926\pm0.0003$) as reference for an ionic crystal.[14]

The measurements of the samples with the higher concentrations showed the same result, but were a little less accurate than those with the 1% sample. There were yet slight indications that at higher concentrations the g factor increased, but these effects were still within the experimental error. The linewidth W (for a definition of W see Fig. 1) as a function of temperature is shown in Fig. 3. This figure shows, that for all cases above a certain temperature the linewidth increases linearly with the temperature, and that the slope of the curves is the same for all concentrations and frequencies with an average value of $dW/dT=24\pm4$ G/°K.

IV. INTERPRETATION OF RESULTS

A. General

Yb is divalent and in the diamagnetic $^1S_0$ ground state (closed $4f$ shell) as can be inferred from magnetization[15,16] and specific heat measurements.[17] Yb metal therefore exhibits only the Pauli paramagnetism of the conduction electrons. Eu is also divalent in Eu metal, with an $^8S_{7/2}$ ground state ($4f^7$ configuration).[18] Therefore we can assume that the band structures in these two metals are roughly the same as is also the case for those of Gd and Lu metals.[10] The dissolving of Eu in Yb metal will therefore certainly not produce any large perturbations in the host lattice and band structure. The exchange interaction derived below between the Eu^{2+} ion and the conduction electrons in Yb metal should therefore be roughly the same as in Eu metal.

The observed resonances are most certainly due to Eu^{2+} dissolved in Yb metal because all possible impurities would give different resonances or none at all:

Eu_2O_3: Ground state $^7F_0$ gives no resonance.

EuO: Has a Curie temperature of 69°K and gives a very different type of resonance in the temperature interval studied.[19]

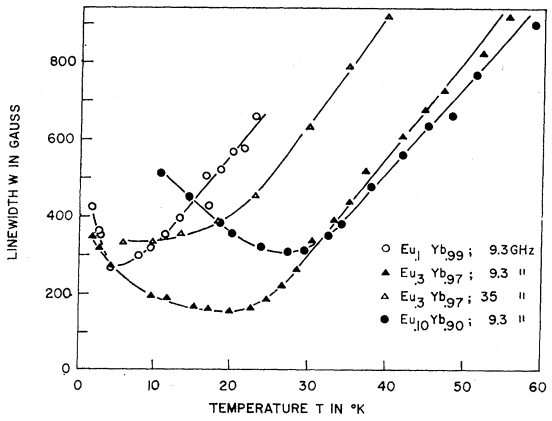

FIG. 3. Linewidth W (for a definition see Ref. 3) as a function of temperature for the Eu_xYb_{1-x} alloys ($0\leq x\leq1$).

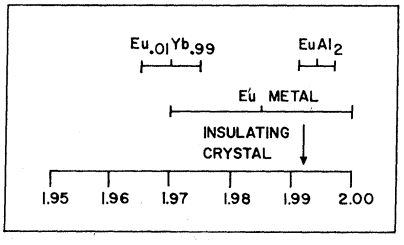

FIG. 2. g factor of the Eu^{2+} ion in a metallic environment.

Yb_2O_3: Gives broad anisotropic resonances.

It should be stressed that the observed resonance has the typical form expected for an ion in metallic environment.

Also, Mössbauer-effect measurements of the samples with the 22-keV γ line of Eu^{151} show that the samples do contain Eu in its metallic form (isomer shift -0.83 cm/sec). Traces of EuO and Eu_2O_3, which have a very different isomer shift, could not be detected; of course this cannot rule out the presence of these impurities because of the limited sensitivity of the Mössbauer measurement.

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B. g Shift

In order to evaluate the exchange integral from the g shift we follow Peter *et al.*[1] The exchange Hamiltonian between a spin $\mathbf{S}_n$ at the lattice site $\mathbf{R}_n$ with a conduction-electron polarization $\boldsymbol{\sigma}(\mathbf{x})$ at the site $(\mathbf{x})$ can be written as

$$\mathcal{H}_{ex}=-(1/n_0)J\mathbf{S}_n\cdot\boldsymbol{\sigma}(\mathbf{x})\cdot(\mathbf{R}_n-\mathbf{x}), \tag{1}$$

where n_0 is the number of the lattice sites per unit volume and J is the exchange integral. This exchange interaction produces a g shift Δg of the ESR line as compared to its position in a diamagnetic environment:

$$\Delta g=\chi_e J/n_0 g_e\mu^2 B, \tag{2}$$

where χ_e=conduction-electron susceptibility, and $g_e=g$ factor of the conduction electrons. (χ_e can be measured experimentally.)

In the case of Yb metal such a measurement is difficult because of the magnetic impurities generally present in the samples. We have therefore deduced χ_e from the specific heat measurements of Lounasmaa.[17] Morrison and Newsham[19] get from an analysis of these measurements from the linear term $\gamma\gamma T$ a value of $\gamma=2.90\pm0.05 mJ/\text{mole}(°\text{K})^2$. Assuming a free electron gas in Yb metal the following two relations hold:

$$\chi_e=\tfrac{1}{2}g_e^2\mu_B^2 N(E_F), \tag{3a}$$

$$\gamma=(\pi^2/3)k^2N(E_F)(A/\rho), \tag{3b}$$

where A is the atomic weight, ρ the density, and $N(E_F)$ the density of states at the Fermi surface. From these equations we get

$$\chi_e=0.46\times10^{-6}\ \text{cm}^3/\text{g}.$$

This value may be compared with $\chi_e=0.5\times10^{-6}$ cm^3/g and $\chi_e=0.2\times10^{-6}$ cm^3/g which can be both taken from Fig. 2 of Ref. 15. These two different values result from the measurements of Lock[16] and Schieber *et al.*,[15] respectively. In both cases the authors say nothing about the diamagnetic correction and imply possible impurities of other rare earths which may violently influence the measurement. Therefore, we think that the value derived from the specific heat measurements is the most accurate one. With the above value for χ_e we finally obtain $J=-0.02$ eV for Eu^{2+} in Yb metal. This derivation of J includes several approximations. First, it was assumed that there is no exchange enhancement of the conduction electron susceptibility in Yb metal. This is a reasonable assumption because we know of no experiments indicating a sizeable exchange enhancement. Second, the assumption of a free electron gas in Yb is certainly very questionable. This is especially so because the conduction electrons in Yb metal have a pronounced d character. But as long as χ_e has not been measured accurately, we have to rely on the present estimate.

C. Linewidth

The linewidth varies linearly with temperature, independent of concentration ($dW/dT=24\pm4$ G/°K), and we therefore assume that it is caused by a relaxation of the spins to the conduction electrons. This implies that the conduction electrons are always in thermal equilibrium with the lattice and that there is no bottleneck between the conduction electrons and the lattice as was recently observed by Gossard *et al.*[6] for Mn in Cu. In this case we can use the Korringa relation[20] which gives the following relation between the g shift and the linewidth

$$\left(\frac{\Delta g}{g}\right)^2=\frac{DH}{T}\frac{\mu_B}{\pi k g_s} \tag{4a}$$

$$=\frac{dW}{dT}\times0.94\frac{\mu_B}{\pi k g_s}. \tag{4b}$$

DH in this notation is the halfwidth of halfpower of the absorption part of the resonance line in Fig. 1; $DH=0.94W$ can be obtained from Ref. 7. The derivation of Eq. (4) implies that T_1 and T_2 are equal.[21] Relation (4) gives a g shift of $\Delta g=0.031$ in good agreement with the direct measurement. If there are no accidental cancellations of errors introduced by the various approximations then this result shows that neglecting the exchange enhancement is a very reasonable approximation in our case.

At low temperatures the linewidth shows a different behavior as can be seen from Fig. 3. We attribute this to correlations between the spins because of the exchange coupling; a similar trend has been observed for Gd dissolved in various hosts.[7,8]

V. DISCUSSION

Any information from NMR and ESR measurements in rare-earth metals, alloys, and intermetallic compounds has to be inspected with extreme caution because of the complex band structure in these materials.[10] The conduction bands in most of these materials are of mixed s and d character with certainly some $4f$ character present. Because it is very difficult to estimate the magnitude of the different contributions, one usually talks in terms of effective properties into which all the different contributions have been lumped together. Therefore, these quantities can only be regarded as order-of-magnitude estimates. A g shift in a metallic system can only be measured if there is no bottleneck present.[21] The temperature dependence of the linewidth has been found to be independent of Eu concentration in this experiment, thus indicating the absence of any bottleneck and the validity of the analysis of the preceding paragraph.

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The conduction electron-Eu exchange integral of $J=-0.02$ eV determined in this measurement is of the right order of magnitude as that obtained for the electronically similar compound $GdAl_2$ (Ref. 12) ($J=-0.03$ eV from the g shift and $J=-0.26$ eV from Knight shift measurements). The difference in the exchange integrals should not be taken too seriously. Both types of experiments measure the s-f exchange interaction at a different site; it is known that this interaction is strongly r and g dependent, thus making the difference in these values understandable. The negative sign and the magnitude of the exchange integrals agree with theoretical estimates from calculation which take band mixing into account.[22,23] These analyses show that, while a pure s band of course leads to a positive J, the interaction with the d bands is responsible for the negative sign.

It is surprising that the alloy series $Gd_xLu_{1-x}(0\leq x\leq 1)$, which one would expect to give similar results as the Eu_xYb_{1-x} series, because of the electronically related structure (only one conduction electron more per constituent), yields a *positive* g shift and hence a positive exchange integral of $J=+0.07$ eV[10]. This result is difficult to understand in the light of the calculations of Ref. 22. It should also be mentioned that the g values of the pure metals (Gd: $g=1.94\pm0.02$; Eu: $g=1.985\pm0.015$) are in both cases different from those of the dilute samples. This shows that the conduction electron distribution gets disturbed by a magnetic neighbor. In the Eu_xYb_{1-x} alloys one can estimate the g shift produced by the $6s$ electrons only by making use of the measured hyperfine fields at the Eu nucleus. According to Davidov and Shaltiel[2] the following relation holds:

$$H_1^{\mathrm{hf}}=\frac{\Delta g}{g}\frac{A}{g_I\mu_n}\langle S\rangle, \tag{5}$$

where H_1^{hf}=hyperfine field at the nucleus due to the conduction electron polarization induced by the ionic spin $\langle S\rangle$, $A/g_I\mu_n$=hyperfine field per unit spin, $\langle S\rangle$=expectation value of the spin of the magnetic ion. Relation (5) holds for the s and d electrons of the conduction electrons separately.

In the Eu_xYb_{1-x} alloys one can estimate the s contribution to the conduction-electron density. Mössbauer-effect measurements determine, via the isomer shift, only the s-electron density at the nucleus. Making use of the fact that the shielding by $5d$ electrons is small,[15] the isomer shift in this alloy shows that the s-electron density is about half a $6s$ electron as compared with trivalent or divalent Eu compounds.[13] Gossard *et al.*[24] arrive at a similar conclusion because they find that the amplitude of the $6s$ electron density at the nucleus in metallic Yb has to be reduced to about 30% of its free-ion value, which would again indicate about half a $6s$ electron in the Yb metal conduction band. These estimates indicate that the d-electron contributions of H^{hf}, which has been determined in Ref. 13 as 190 kOe, are not important, and we will therefore completely neglect them in this order of magnitude estimate. The value of $A/g_I\mu_n$ can be taken as $6.05.10^6$ Oe from the work of Gossard *et al.*[24] This gives $\Delta g=+0.02$ for the contribution of the s electrons to the g shift in Eu_xYb_{1-x} and $J_{f-5d}\approx-0.03$ eV.

The estimate just performed is only given to stimulate further work in this direction and to show that we are dealing here with different contributions of equal magnitude making the determination of exact and accurate values very difficult.

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