EPR of Gd^{3+} Impurities in a Host with Interconfiguration Fluctuations

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(Received 12 January 1978)

The EPR of Gd^{3+} impurities in the interconfiguration-fluctuation (ICF) host CePd$_3$ is reported. The observed linewidth is consistent with an intrinsic relaxation rate proportional to T, where the proportionality constant is 3 times *smaller* than in the isostructural non-ICF host YPd$_3$. Although contrary to what is suggested by simple fluctuation concepts, such an effect of ICF on the EPR linewidth is actually to be expected theoretically.

The problem of valence or interconfiguration fluctuations (ICF) in $4f$ systems near a configuration crossover has recently attracted much interest.[1-5] One possible probe of the fluctuation effects is provided by the EPR of an impurity with a well-defined magnetic moment, e.g., Gd^{3+}. At first sight one might expect the fluctuations to couple to the Gd moment, increasing the linewidth beyond that in a comparable normal-metal host.

Walsh *et al.*[6] studied the EPR of S-state ions in Gd$_x$Sm$_{1-x}$S and related systems. They found extreme g shifts as the configurational instability of Sm was approached from the Sm^{2+} side, but no observable EPR in the ICF state. Heinrich and Meyer[7] observed EPR in Gd$_x$Ce$_y$La$_{1-x-y}$Be$_{13}$, but only for small concentrations of the ICF impurity Ce. Huang and Sugawara[8] found EPR in Gd$_x$Tm$_{1-x}$Se with a large linewidth (≈ 400 Oe) which showed no significant variation in the experimental temperature range of 4 to 40 K; however, for reasons indicated below we believe that this width is actually due to inhomogeneity effects. Ours is thus believed to be the first observation of EPR of impurities in a concentrated homogeneous ICF host.

As ICF host we have chosen CePd$_3$, whose lattice constant, specific heat, and susceptibility all show anomalies of the type expected in an ICF system.[9] The lattice constant implies an average of about 0.5 $4f$ electrons per Ce ion. Inelastic neutron scattering,[10] which can be fitted by a dynamic susceptibility of Lorentzian form with half-width 0.02 eV, confirms that we have to do with dynamic fluctuations rather than a static, spatially inhomogeneous distribution of pure-configuration states. Since the high electronegativity of Pd normally causes the Pd $4d$ bands to be full in such intermetallics, it can be assumed that complications from $4d$ magnetism do not occur. This is supported by the normal susceptibility of the isostructural YPd$_3$.

Polycrystalline samples of Gd$_x$Ce$_{1-x}$Pd$_3$ were prepared by arc melting and annealed 24 hours at 700°C. Narrow x-ray lines confirmed that the metallurgy was good. EPR was observed at x and Q band in a total of 18 samples with 50 ppm $\leq x \leq 1\%$. The results were reproducible from sample to sample, except that larger x, which permitted the EPR to be followed to higher T, gave a somewhat larger linewidth at $T < 75$ K. The slope of linewidth vs T for $T \gtrsim 75$ K is independent of x within experimental error, indicating that a bottleneck effect[11] does not occur. Both the minimum width and the slope are unusually small for Gd^{3+} in a metallic host. The measured widths for two representative concentrations are shown in Fig. 1.

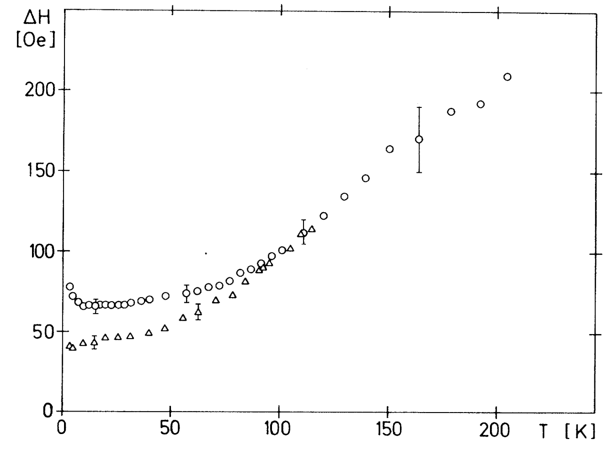

FIG. 1. EPR linewidth of Gd$_x$Ce$_{1-x}$Pd$_3$ as a function of temperature, at frequency 35.0 GHz. The symbols ○ and △ denote $x = 1\%$ and $x = 500$ ppm, respectively.

We interpret the observed width as an intrinsic relaxation width $H_{\rm int} = bT$, dominant for $T \gtrsim 75$ K, plus broadening at lower T from secondary mechanisms. The slope for $T \gtrsim 75$ K yields $b = 1.1 \pm 0.2$ Oe/K. A weak x dependence of the width for $T < 75$ K implies that some of the secondary broadening is due to Gd-Gd interactions, but we attribute most of it to the crystal electric field (CEF) splitting of Gd. Such a randomly oriented CEF is also expected to yield satellite lines[12] at sufficiently small T and x, which were in fact observed at liquid-helium temperatures for $x \leqslant 500$ ppm. A typical spectrum is shown in Fig. 2. The satellite positions imply a CEF parameter $b_4 = (20\ \text{Oe})g\mu_{\rm B}$ or a total zero-field CEF splitting of $(640\ \text{Oe})g\mu_{\rm B}$. Similar CEF broadening and satellite lines have been observed for Gd^{3+} in polycrystalline normal-metal hosts.[12]

The g shift $\Delta g = 0.030 \pm 0.005$ is about 3 times larger than would be permitted by the Korringa ratio appropriate to a normal-metal host.[13] However, it is very small compared to the g shifts of order 100% observed in hosts which are near a configuration crossover but still configurationally stable.[6]

For comparison we have also observed EPR of Gd^{3+} in the isostructural non-ICF host YPd_3. A bottleneck effect is again absent and the linewidth is linear in T at high T with slope $b = 3.2 \pm 0.2$ Oe/K. The g shift $\Delta g = 0.028 \pm 0.003$ yields a Korringa ratio $R \approx 0.2$, which is just the value to be expected in a normal-metal host with a large $5d$ density of states at the Fermi energy[13] from Y.

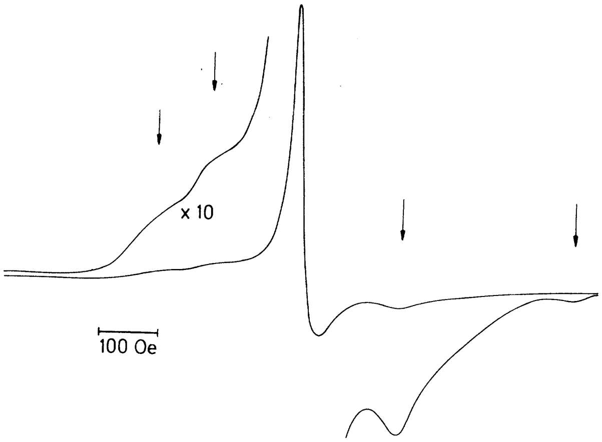

FIG. 2. EPR spectrum of $\text{Gd}_x\text{Ce}_{1-x}\text{Pd}_3$, for $x = 270$ ppm, at 1.6 K and frequency 9.3 GHz. Arrows indicate the positions of satellite lines corresponding to the CEF parameter $b_4 = 20\ \text{Oe} \cdot g\mu_{\rm B}$.

Although a complete theory of ICF systems is out of reach at present, we believe that the main features of our experimental results can correctly be understood with the help of simplified model calculations. First, we note that no bottleneck effect is to be expected in the EPR of Gd^{3+} in an ICF host, since the strong spin-orbit coupling in the ICF ions prevents the host from having a well-defined spin resonance.[14] In fact, experiments confirm that a small concentration of ICF ions is sufficient to destroy a bottleneck effect.[7] Having recognized this, we shall take no further explicit account of the orbital degrees of freedom. The essential feature of an ICF system is a large density of $4f$-like states in a narrow peak at the Fermi energy, and to describe this we represent the ICF ion by a spin-only Anderson model[15] with $U = 0$. This type of simplification has frequently been used in the past[3,5] and is reasonable in the present application, although we emphasize that a quantitative mapping onto the low-energy states of a model with realistic intra-ionic splittings fails because of subtleties in the statistics.[4,14] We further simplify by considering only a single ICF ion near the Gd impurity rather than an ICF lattice. "Low" and "high" T will be defined by comparison to Δ, the half-width of the $4f$ peak (with $\hbar = k_{\rm B} = 1$). The experimental value[10] $\Delta = 0.02\ \text{eV} = 230$ K implies that it is the low-T theory which is primarily relevant to our EPR experiments. The Gd moment, the Ce $4f$ electrons, and the conduction electrons will be denoted by μ, f, and k respectively.

Previous consideration[8] of EPR in ICF hosts has concentrated on relaxation of μ driven by an f-μ coupling, which can be attributed to indirect exchange and written $-2J_{f\mu}\vec{S}_\mu \cdot \vec{s}_f$. Simple fluctuation concepts combined with motional-narrowing arguments have sometimes been thought to imply that the corresponding relaxation rate should have the T-independent value[8]

$$1/\tau_{\mu f} \approx (J_{f\mu})^2/\Delta. \tag{1}$$

However, more careful consideration indicates that the relaxation rate at low T should be proportional to T, just as in a normal metal, and for essentially the same reason, namely the Fermi statistics of the excitations driving the relaxation.[4,14] Specifically, our simplified model yields

$$1/\tau_{\mu f} = (4/\pi)(J_{f\mu}/\Delta)^2 T \quad (\text{low } T), \tag{2}$$

$$1/\tau_{\mu f} = (J_{f\mu})^2/2\Delta \quad (\text{high } T), \tag{3}$$

where Eq. (2) assumes the $4f$ peak to be centered exactly at the Fermi energy.

In a normal-metal host, the dominant source of relaxation of a Gd^{3+} moment μ is the k-μ coupling, which can be attributed to contact exchange and written $-2J_{k\mu}\vec{S}_\mu\cdot\vec{s}$. where $\vec{s}$ is the conduction-electron spin density. In addition to calculating $1/\tau_{\mu f}$ for an ICF host, we should also examine whether ICF can modify the relaxation via the k-μ coupling—a possibility which does not appear to have been considered previously. In our simplified model, the latter relaxation rate can be written down in terms of matrix elements of the exact one-electron eigenstates, which in turn can be evaluated with the aid of one-electron Green's functions for which explicit solutions[15] are available. Reserving the details for a separate publication, we give here the result found for the low-T regime:

$$1/\tau_{\mu k} = \pi[2J_{k\mu}(1-z)\rho]^2 T \quad (\text{low } T), \tag{4}$$

where

$$z = \frac{\Delta^2}{(\epsilon_f - \epsilon_F)^2 + \Delta^2}\left[\frac{\sin(k_F R)}{k_F R}\right]^2.$$

Here ϵ_f is the position of the $4f$ peak, ϵ_F and k_F are the Fermi energy and momentum, ρ is the density of conduction-electron states per spin orientation, and R is the distance between Gd^{3+} and the ICF ion. This expression reduces to the usual Korringa rate for large R but decreases in oscillatory fashion as R becomes smaller vanishing completely at $R=0$ if $\epsilon_f = \epsilon_F$. The oscillations result from integrations of exponentials e^{ikR} weighted with Fermi functions, as is familiar, e.g., from Ruderman-Kittel theory. The relaxation decreases because mixing decreases the k amplitudes in the exact one-electron eigenstates of energy $\approx \epsilon_F$ near the ICF ion. (This statement is not in conflict with the Anderson compensation theorem,[15] which applies to the total density of k states without reference to a particular point of R space.)

In view of the simplifications in our model, and especially its inclusion of only a single ICF ion, Eq. (4) cannot be applied quantitatively to Gd in $CePd_3$. Nevertheless, we believe that it provides a qualitatively correct explanation of the observed tendency for ICF to reduce the relaxation rate of Gd^{3+} impurities in the experimental temperature range.[16]

In addition to the true relaxation broadening discussed above, inhomogeneity broadening may arise if the $4f$ ions of the host are not all equivalent. For example, if single configurations were stabilized on even a small fraction of the host ions, random effective fields are to be expected which would strongly broaden the EPR or render it unobservable. This is a likely explanation for the absence of an observable EPR[6] in chemically collapsed $Gd_xSm_{1-x}S$, where the finite concentration $x \gtrsim 0.15$ suggests large environmental effects. In TmSe, inequivalent Tm sites exist at least at low T by virtue of antiferromagnetic ordering.[5,17] Furthermore, inelastic neutron scattering[18] shows an unusually narrow extra line which can be followed up to 75 K, and which can most plausibly be attributed to the existence of stable configurations on a fraction of the Tm ions. It therefore seems likely that the large EPR linewidths[8] of Gd in TmSe are due to inhomogeneity fields associated with inequivalent sites rather than to ICF *per se*. Conversely, our observation of an unusually narrow EPR of Gd in $CePd_3$ can be taken as evidence that the latter is a highly homogeneous, nearly ideal ICF substance.

We are greatful to D. Wohlleben, T. Plefka, and M. Loewenhaupt for helpful discussions, and to the last for permission to quote his unpublished work. We thank O. L. T. de Menezes for his collaboration in the early stages of the experiments. This is a project of the Sonderforschungsbereich für Festkörperspektroskopie Darmstadt-Frankfurt, supported by the Deutsche Forschungsgemeinschaft.

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Dispersion of the Volume Plasmon of Silicon (16.7 eV) at Large Wave Vectors

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(Received 13 December 1977)

The dispersion of the volume plasmon of silicon at 16.7 eV has been measured with 50-keV electrons in the directions ⟨100⟩ and ⟨111⟩ up to the critical wave vector $q_c \simeq 1.1$ Å^{-1}. It shows a strong anisotropy. Along the ⟨100⟩ direction the q dependence could be measured up to large q vectors of ~ 2.4 Å^{-1}. At $q \gtrsim q_c$ the slope of the dispersion curve decreases strongly in a manner similar to what has been found earlier for Al and Be.

As is well known from different experiments, the position of the volume plasmon $\hbar\omega_p$ is displaced to higher energy values with increasing wave vector q approximately proportional to q^2 [see, e.g., Kloos[1] for details and further references]. This is in qualitative agreement with the approximation for $q < q_F$ (q_F Fermi wave vector),

$$\hbar\omega_p(q) = \hbar\omega_p(0) + \alpha(\hbar^2/m)q^2, \qquad (1)$$

obtained from the Lindhard function with $\alpha = \frac{3}{5}E_F/\hbar\omega_p(0)$. However, agreement is poor when one compares theoretical and experimental α values: e.g., α(obs) for Li, Na, and K are 0.22, 0.22, and 0.12, whereas α(calc) come out as 0.36, 0.31, and 0.28, respectively. The exchange correction[2] reduces the calculated values by about 10% which does not improve the agreement essentially. Recent measurements on monocrystalline materials, e.g., Al,[3] and PbS, PbTe, and PbSe,[4] showed that the dispersion coefficient α is a function of crystal direction $\langle hkl \rangle$. This indicates that the influence of the lattice potential on the dispersion of the volume plasmon has to be taken into account. Formula (1) is therefore only a rough approximation.

Concerning collective oscillations the valence electrons of silicon behave like those in Al: Although in Si the four valence electrons are bound (energy gap of ~ 1 eV), the volume plasmon energy of $\hbar\omega_p(0) \simeq 17$ eV is large enough to treat these electrons as nearly free; thus a large loss peak due to this volume oscillation is seen in the loss spectrum. It was therefore of interest to look at the dispersion behavior of this loss which had not yet been measured.

The measurements were performed with 50-keV electrons in transmission. The Si films, about 1000 Å thick, are monocyrstalline as demonstrated by electron diffraction patterns; they were made from thicker plates of Si monocrystals, thinned mechanically,[5] and then reduced to a thickness of $\sim 10^3$ Å by sputtering.[6] The results of our measurements are reproduced in Fig. 1 for the two crystal directions ⟨100⟩ and ⟨111⟩. Above $q \sim 0.6$ Å^{-1} the losses in the different directions are well separated so that two α's can be derived. The values of the dispersion coefficients in the ⟨100⟩ and ⟨111⟩ directions are $\alpha_{\langle 100 \rangle} = 0.41 \pm 0.01$ and $\alpha_{\langle 111 \rangle} = 0.32 \pm 0.02$ α of the nearly free electron gas has the value of $\alpha_{\mathrm{fr}} = 0.4$ [calculated with the electron density 2×10^{23} cm^{-3}, $E_F = 12.4$ eV, $\hbar\omega_p(0) = 16.6$ eV, and exchange correction]. This anisotropy is similar to that found for the substances mentioned above. However, one finds that the α value in Si has the highest value in the ⟨100⟩ direction whereas in Al this occurs for the ⟨110⟩ direction (Al: $\alpha_{\langle 110 \rangle} = 0.46$, $\alpha_{\langle 100 \rangle} = 0.40$). Thus Si behaves like PbS, PbSe, and PbTe, the