Observation of a Positive Hyperfine Field for Dilute Fe Impurities in Ca

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The magnetic hyperfine field for isolated Fe impurities in Ca metal has been measured as a function of temperature (86 K $\leq T \leq$ 300 K) by use of the technique of perturbed angular distributions. The data indicate the presence of an unquenched orbital local moment. This is the first such observation for Fe impurities in any metal host. The results could not be explained by the assumption of a purely ionic configuration for the impurity and are interpreted in terms of the Friedel-Anderson model.

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In this Letter we report on the first observation of a positive hyperfine field for an isolated Fe impurity in a metal host. The system studied was *Ca*Fe. This system had never been investigated before because the low solubility[1] of Fe in Ca made it inaccessible to the standard techniques used to study local magnetism such as the Mössbauer effect and NMR. For this work we used the method of perturbed angular distributions (PAD), whose recent applications to this field are described in our earlier work.[2,3] This method introduces extremely low impurity concentrations ($<$ 1 ppm) and makes it possible to probe a wide variety of host-impurity combinations. The *Ca*Fe system is particularly interesting since the positive hyperfine field indicates the existence of an unquenched local orbital moment. This is a rare phenomenon for *d*-shell impurities in nontransition metals[4] and has successfully been explained in only one other system, *Au*Co.[5] From the analysis of many *f*-shell impurity systems and the results for Co in Au it was assumed that the orbital local moment could survive only if the impurity electrons maintained an ionic configuration. We will show that this need not be true for Fe in Ca and that the data can be explained within the context of the Friedel-Anderson model.[6,7]

The Fe probe used for these experiments was the $I^{\pi} = 10^{+}$ isomer of ^{54}Fe,[8] whose lifetime, $\tau_m = 515(5)$ ns, and nuclear moment, $g = +0.7281(10)$,[3,9] make it well suited for the study of small hyperfine fields. The ^{54}Fe nuclei were produced in a 1-mg/cm^2 Sc foil via the reaction ^{45}Sc(^{12}C, $2np$)^{54}Fe with a 39-MeV, pulsed ^{12}C beam ($\tau = 2.0$ μs, full width at half maximum = 2 ns) from the model FN tandem Van de Graaff accelerator of the State University of New York at Stony Brook. The beam momentum served to make the product nuclei recoil into a ≥ 0.999 pure Ca backing which was mechanically sandwiched between the Sc target and a 0.30-mm Pb sheet. The Ca backing was prepared by evaporation from ≥ 0.99-purity commercial-grade Ca which was preheated in vacuum to remove the major impurity, Mg. Its thickness, 1.4 mg/cm^2, was chosen so as to stop all the Fe recoil nuclei ($E_{\text{recoil}} \sim 9$ MeV) but not the direct beam which was stopped in the Pb. The target assembly was mounted on a Cu finger attached to a CryoTip Joule-Thomson expansion device, and the temperature could be varied from 84 to 300 K. A transverse magnetic field, $B = 0.7516(1)$ T, was applied and the Larmor precession of the angular distribution of the 411-, 1130-, and 1408-keV γ-ray transitions was observed by two NaI(Tl) detectors placed at $\pm 135^{\circ}$ to the beam direction.

To enhance the Larmor oscillations and eliminate the nuclear lifetime, the ratio

$$R(t) = \frac{Y(+135^{\circ}) - Y(-135^{\circ})}{Y(+135^{\circ}) + Y(-135^{\circ})}$$

was formed from the normalized γ-ray yields, $Y(\theta_i)$, in each detector. The data were then analyzed by fitting with the function

$$R(t) = \tfrac{3}{4} b_2 G_2(t) \sin(\omega_L t + \theta), \qquad (1)$$

where $\omega_L = g\mu_N H(T)/\hbar$, μ_N is the nuclear magneton, $H(T)$ is the time-averaged total magnetic field at the nucleus, b_2 is the angular distribution coefficient,[2] and $G_2(t)$ is a function described by Dafni *et al.*[10] which accounts for any static weak electric field gradients present near the probe.

Figure 1 shows the data obtained at two different temperatures. The dashed vertical line was drawn to emphasize that the frequency increases with a decrease in temperature, in contrast to that observed for Fe in Pt,[2] Cu, Au, Bi, and other hosts where a local moment is formed.[3]

Figure 2(a) is a plot of ω_L as a function of inverse temperature. The solid line is a fit by a

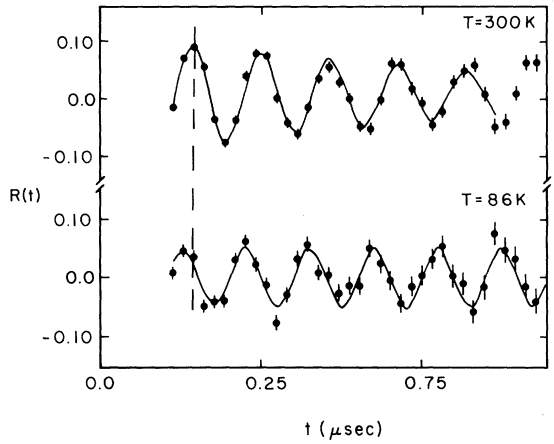

FIG. 1. Ratio functions for Fe in Ca.

Curie law, $\omega_L = \alpha + \beta/T$, with the values $\alpha = 27.62(8)$ Mrad/s and $\beta = +0.262(13) \times 10^3$ K Mrad/s. It can be shown that in this temperature region $\mu B \ll kT$ and the Curie parameters can be expressed as[2]

$$\alpha = \omega_0(1+\Delta K), \quad \beta = [\omega_0 \mu' H_{hf}'(J'+1)]/3kJ', \quad (2)$$

where $\omega_0 = \mu_N g\, B/\hbar$; J' is some effective electronic spin with associated moment, μ', and total hyperfine field, H_{hf}'; and ΔK is the temperature-independent component of the frequency shift. Substituting the experimental values for α, β, and g we obtain

$$\mu' H_{hf}[(J'+1)/J'] = +446(26) \text{ kOe } \mu_B$$

and $\Delta K = +0.054(5)$. These large positive values indicate that the orbital angular momentum for Fe in Ca is not quenched. For the case of AuCo, the only other instance where a positive hyperfine field was observed for a $3d$ impurity in a nontransition metal, the data were explained by assuming a pure ionic configuration for the Co impurity.[5] We attempted a similar analysis for Fe in Ca. By means of the formalism of Ref. 5, with minor modifications to account for the larger spin of the Fe ion, the data were fitted by expressions for the frequency shift and hyperfine fields derived from energy levels obtained by diagonalizing the Hamiltonian

$$H = \mu_B(L_z + 2S_z)B + DqV_{cf} - \lambda \vec{L} \cdot \vec{S}. \quad (3)$$

The crystal-field and spin-orbit parameters, Dq and λ, respectively, were constrained to the physical limits, $Dq \leq 0.083$ eV and $\lambda \leq 0.033$ eV. No reasonable fit could be obtained for either a +2 or +1 charge-state configuration [see Fig. 2(b)].[11]

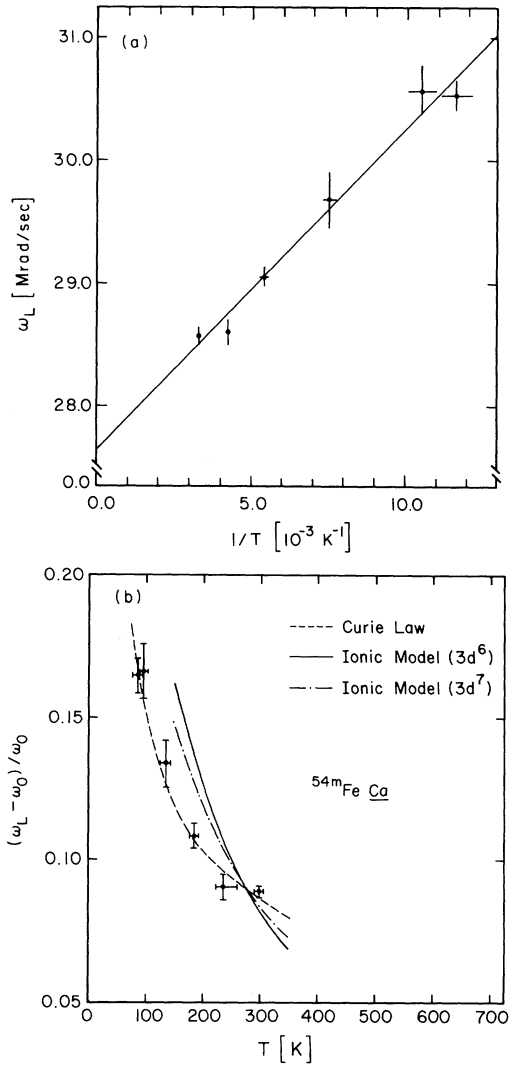

FIG. 2. (a) ω_L vs $1/T$ [$B = 0.7616(1)$ T]. (b) Best fits to the data for $(\omega_L - \omega_0)$ vs T. ($\lambda = -200$ K, $Dq = 500$ K.)

On the other hand, the data could be explained with an analysis based on a modified Friedel-Anderson model, which includes the crystal-field potential.[6,7] With the assumption of near-integral occupation numbers for the electronic states,[12] the valence of the Fe impurity was taken as approximately +2, the same as for the Ca host. The spin and the effective orbital angular momentum of the impurity are therefore $S \sim 2$ and $\tilde{L} \sim 1$. The total time-averaged hyperfine field can be written as

$$H(t) = [\mu_s H_s(S+1)/S + \mu_l H_o(\tilde{L}+1)/\tilde{L}]/3kT, \quad (4)$$

where μ_s and μ_l are the spin and orbital electron magnetic moments and H_s and H_o are the spin

and orbital hyperfine fields. The spin-orbit interaction was neglected since for $3d$ elements $\Delta/\lambda \gg 10$ (see Fig. 3).

Setting $H(T) = [+446(26)\ \text{kOe}\ \mu_B]/3kT$ and using $H_o \leq +635$ kOe,[13] we obtain $H_s/\mu_B \gtrsim -35$ kOe/μ_B. This value, though large when compared to the calculated field, $H_s/\mu_B = -120$ kOe/μ_B,[5] is not unusual. Typical fields measured for Cr and Mn ions in nontransition-metal hosts range from -80 to -30 kOe/μ_B.[13] Neither has an orbital contribution to the hyperfine field since Mn is an S-state ion and Cr is in the l_g crystal-field ground state. The observed reduction in the magnitude of the spin hyperfine field was explained by Hirst as due to an impurity-induced dynamic polarization of the conduction electrons parallel to the external field.[13]

Figure 3 shows an energy diagram for the virtual levels of an Fe impurity in Ca metal consistent with our results. The energy scale is drawn relative to the Fermi energy, E_F. The values of the Coulomb and exchange integrals, U and J, are fairly host independent and were

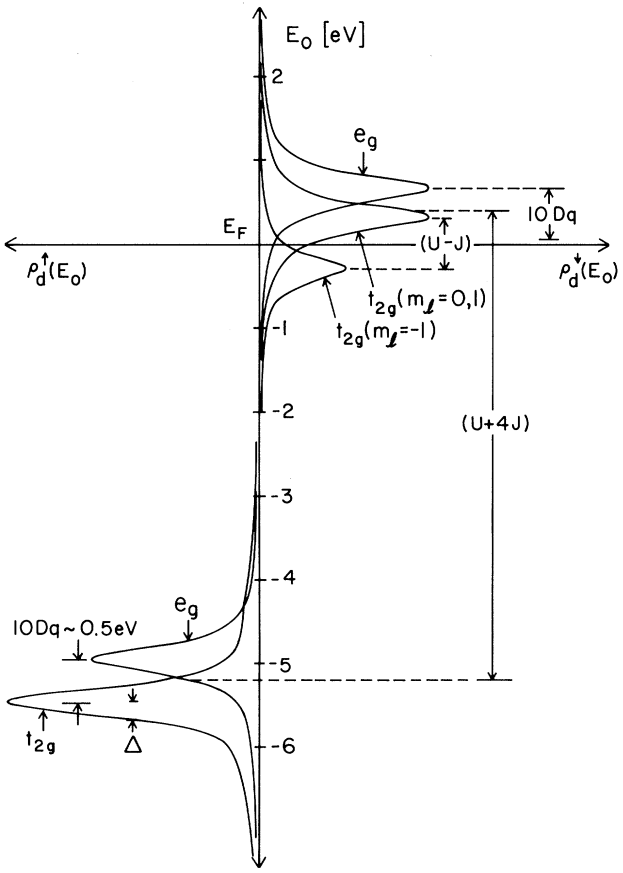

FIG. 3. Virtual level diagram for Fe in Ca.

obtained from the data of Fe in Cu.[12] From the figure it can be seen that an orbital moment for a $3d$ impurity can exist only when the virtual level width is less than the larger of the two quantities, $U-J$ or the crystal-field splitting. Since either of these is much weaker than the Coulomb repulsion between electrons of opposite spin, this condition is much harder to satisfy than that for the existence of a spin-only local moment.

The temperature-independent frequency shift, ΔK, can have both spin and Van Vleck orbital components. For Fe in Ca it can be shown that the spin component, mostly due to the Knight shift and diamagnetic correction, is only $+0.0047$,[3] and can be neglected. The Van Vleck frequency shift from the single d electron whose orbit lies close to E_F (see Fig. 3) is given by[14]

$$\Delta K = 2\frac{H_{orb}}{|\tilde{L}|}\frac{\mu_B}{10Dq}|\langle t_{2g}|L_z|e_g\rangle|^2. \quad (5)$$

Substituting the previously defined values for H_o and ΔK into Eq. (5) we obtain a crystal-field splitting of $10Dq \leq 0.5$ eV. To account for the observed orbital moment of CaFe this value also implies a virtual level width, $\Delta \leq 0.5$ eV. These results are surprising within the context of the Friedel-Anderson model where $\Delta = \pi|V_{dce}|^2\rho(E_F)$[6] is given by the host density of states at the Fermi energy, $\rho(E_F)$, and the interaction matrix element between the $3d$ and the conduction electrons, V_{dce}. From specific-heat measurements it is known that the $\rho(E_F)$ for pure Ca is approximately 5 times larger than that for Cu, Ag, and Au where no orbital moment was found.[2,3] This is consistent with the NMR measurements on CuFe which give $10Dq \sim 0.5$ eV and $\Delta \sim 0.7$ eV.[12]

A possible explanation for our results may be that the Fe impurity is probing an effective local density of states in Ca which is very different from that of the bulk. Band-structure calculations[15] have shown that the unoccupied d band in Ca produces anomalously large fluctuations in $\rho(E_F)$, leading to a small level width Δ and the existence of a local moment.

A narrow Δ can also be achieved by a reduction in $|V_{dce}|^2$. An explanation for this process based on the impurity-host volume mismatch is given by Kornrumpf, Nishiyama, and Riegel.[16]

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