in Gd. Further theoretical work, including calculations for La, and other rare-earth metals, is in progress to answer this and other questions.

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LOCALIZED MOMENTS OF MANGANESE IMPURITIES IN FERROMAGNETIC IRON

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Most studies of hyperfine fields in ferromagnetic transition-metal alloys have been concerned with the spatial distribution of the fields and little attention has been given to the thermal variation of the latter. Recently,[1] however, it has been observed that the temperature dependence of the Mn^{55} nmr frequency ν_T in a dilute (1.5% Mn) ferromagnetic FeMn alloy departs markedly from that of the magnetization σ_T of the Fe host. In particular, ν_T decreases much more rapidly than σ_T as may be seen in Fig. 1 where ν_T/ν_0 (open circles) and σ_T/σ_0 are plotted vs T/T_c.

We show here that an adequate explanation of the course of the Mn nmr may be obtained from the following assumptions: First, ν_T is proportional to the thermal average of the Mn moment $\langle S_T \rangle$; second, the Mn moment is localized, with a magnitude S that is independent of temperature; third, the thermal average of the Mn moment is taken over its levels in the exchange field of the iron H_T^{Mn}; fourth, H_T^{Mn} is substantially weaker than that exchange field H_T^{Fe} which acts between the iron ions. From this we conclude that little, if any, of the Mn magnetization is induced by the iron host. As such the experiment and its interpretation provide information about the magnitudes of S and H_0^{Mn} and constitute the first example of a magnetized localized state in a ferromagnetic transition metal.

The simplest quantitative expression of these ideas is to equate ν_T/ν_0 with the Brillouin function $B_S(y)$, with

$$y = \frac{g\beta S}{kT} H_T^{\mathrm{Mn}}, \tag{1}$$

and $H_T^{\mathrm{Mn}} = H_0^{\mathrm{Mn}} \sigma_T/\sigma_0$. Then for various values of S and particular choices of $\zeta \equiv g\beta S \times H_0^{\mathrm{Mn}}/kT_c$, families of curves may be generated, examples of which are shown in Fig. 2 for $S = \frac{1}{2}$ and $S = \frac{5}{2}$ for the values of ζ indicated. It is immediately apparent that the general shape of these curves, particularly for $0.5 < \zeta < 1$, resemble the behavior of the experimental data of Fig. 1. In particular, for $S = \frac{3}{2}$ and $H_0^{\mathrm{Mn}} = 3.7\times10^6$ Oe ($g = 2.00$), a best fit to the experimental data could be obtained for which the average deviation $\Delta < 0.5\%$. Less satisfactory agreement was found for $S = 1$ ($\Delta > 1\%$) and for other half-integral values of S the fits were noticeably poorer.

The question arises why so simple an approach appears to give an adequate description of the thermodynamic behavior of a strongly coupled localized state in a metal. The use of such naive molecular-field concepts can be given a certain degree of respectability, at least within the framework of the Heisenberg ferromagnet. The work of Wolfram and Calloway[2] on spin impurities in ferromagnets shows that a resonant state may be associated with the impurity and that if it is formed low (energetically) in the spin-wave band, it may be quite sharp. This reflects the fact that the short spin waves to which it couples readily are far away in energy. There will be associated with a narrow level a large enhancement of the density of states at that energy. At the same time if one examines the Green's function theory of ferromagnetism,[3,4] which seems to be successful in predicting the temperature dependence of the magnetization, it appears that the recipe used to find σ_T is actually the following: One calculates the mean occupation number of the excited levels of the system (what these are taken to be distinguishes different Green's function theories) and equates this to the occupation number of a fictitious Bose oscillator with level spacing E. The magnetization is then given as a Brillouin function of E/kT. In the impurity problem, then, it follows that if the resonant level is sufficiently sharp the enhanced density of states will make E just the energy at which the level forms. We have made Green's function calculations of this kind and find that a fit to the data slightly inferior to that shown in Fig. 1 may be obtained for $S=1$. However, the most important conclusion reached from these calculations is that only for values of $H_0^{\mathrm{Mn}}/H_0^{\mathrm{Fe}} > 0.5$ would one expect even a qualitative agreement with the molecular-field approach for $S=1$ or $\frac{3}{2}$.

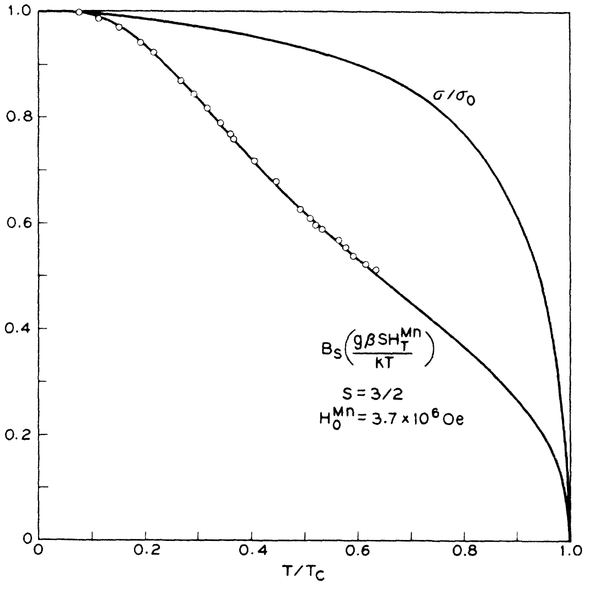

FIG. 1. Open circles: ν_T/ν_0 vs T/T_c for the Mn^{55} nmr in 1.5 % Mn in ferromagnetic iron (see reference 1). A value of 239 Mc/sec was chosen for ν_0 and a value of 1020°K for T_c for this alloy. The line passing through the data is obtained from the theory outlined in the text for the values of S and H_0^{Mn} shown. The reduced magnetization σ_T/σ_0 for pure iron is also given.

The fact that a negligible part of the Mn magnetization is induced via the polarization of conduction electrons implies that the hyperfine field $|H_0^{\mathrm{hf}}| = 227$ kOe is produced mainly by the Mn d electrons. If we neglect orbital contributions to g and H_0^{hf} then the observed value is fortuitously close to that expected from d-spin core polarization if $S=1$ and somewhat smaller if $S=\frac{3}{2}$. This suggests that H_0^{hf} is negative, a result not yet verified experimentally.

The fact that a large moment (2-3 Bohr magnetons) resides on the Mn atom and that the change in the total magnetization per Mn impurity $d\mu/dc \simeq -2.11$ Bohr magnetons[5] requires that a sizeable decrease in the magnetization of neighboring iron ions must take place. This has important bearing on the interpretation[6,7]

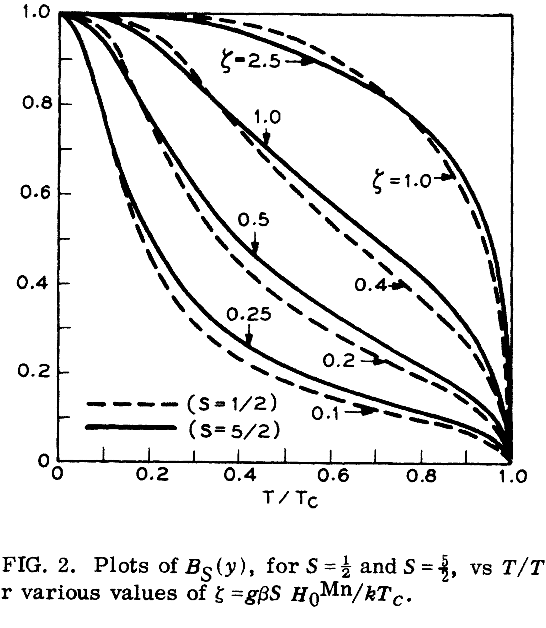

FIG. 2. Plots of $B_S(y)$, for $S=\frac{1}{2}$ and $S=\frac{5}{2}$, vs T/T_c for various values of $\zeta = g\beta S\, H_0^{\mathrm{Mn}}/kT_c$.

of the magnetization distribution on Fe ions adjacent to a Mn impurity. Lastly, it is of interest to note that the corresponding measurements of the temperature dependence of the V^{51} nmr (1% V in Fe)[1] do not admit of the simple interpretation given here but rather suggest that a considerable portion of the V magnetization is not local in origin.

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PARAMAGNETIC RESONANCE ABSORPTION IN AN OPTICALLY EXCITED STATE IN $CaF_2:Dy^{2+}$ †

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We have observed paramagnetic resonance absorption in a metastable state of $Dy^{2+}:CaF_2$ populated by optical pumping. Paramagnetic resonance of optically excited states in solids has been observed in $Cr^{3+}:Al_2O_3$ (ruby) using optical detection methods[1] and by direct absorption in certain organic compounds which have metastable triplet states with lifetimes of the order of seconds.[2] However, this is the first time to our knowledge that spin-resonance absorption has been directly observed in an optically excited state of an ionic crystal.

Extensive theoretical and experimental optical work has been done on the crystal-field-split components of the lower two spin-orbit terms ($^5I_7$ and $^5I_8$) of this ion in calcium fluoride.[3,4] The level diagram for these states is shown in Fig. 1 along with the broad $4f$-$5d$ absorption bands which can be used to pump these ions into the metastable $^5I_7$ $(T_1^{(2)})$ state. Also paramagnetic resonance studies of the $^5I_8$ $(T_1^{(1)})$ and $^5I_8$ $(E^{(2)})$ states have been done previously by one of us.[5]

Normally the rare-earth ions go into calcium fluoride in the trivalent state; we reduced our crystals, doped with either natural dysprosium or isotopically pure (~90%) dysprosium-164, which is spinless, by using the recently developed technique of high-temperature electrolysis.[6,7]

The samples used in the experiments on the optically excited state $^5I_7$ $(T_1^{(2)})$ were single crystals 0.5 cm square by 1.3 cm long and contained 0.05% natural dysprosium, of which about 70% of the ions were reduced. They were placed against the side wall of an X-band cavity operating in the TE_{101} mode. To be able to optically pump the crystal, many slots were cut into the wall parallel to the current flow to affect the cavity Q as little as possible. The pump lamp was a 600-watt iodine-vapor

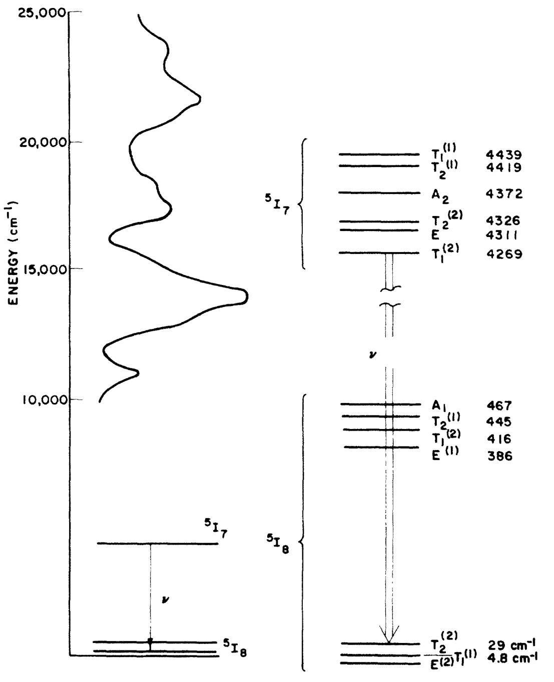

FIG. 1. Energy levels of $CaF_2:Dy^{2+}$.