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Origin of Nuclear Magnetic Resonance Shifts in Paramagnetic MnF_3

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The nuclear magnetic resonance of F^{19} in MnF_3 has been observed and shifts from the normal resonance field of several percent have been measured. The shifts are paramagnetic, and it is shown that the mechanism of electron transfer cannot account for a shift in this direction. However, the results could be explained by covalent bonding between fluorine and manganese.

INTRODUCTION

PREVIOUS nuclear magnetic resonance (NMR) investigations of paramagnetic transition element fluorides[1,2] have shown the F^{19} resonances to be displaced from the normal resonance field, ω/γ_N, by as much as twelve percent. These observations have been explained by considering hyperfine interactions to exist between the fluorine nuclei and the magnetic electrons. The free fluorine ion ($2s^2 2p^6$) is diamagnetic and can have no hyperfine interaction with the F^{19} nucleus. However, in a paramagnetic solid the surrounding ions may alter the ground-state ion configuration and a hyperfine interaction can result. It has been shown that these interactions depend upon the spin orientation of the magnetic ion and that the NMR shift can be represented by a tensor hyperfine interaction of the form $\mathbf{I}\cdot\mathbf{A}\cdot\langle\mathbf{S}\rangle$. The hyperfine interaction constants A can be used as a measure of the degree to which the magnetization is localized on the fluorine ions.

There are several mechanisms which might create paramagnetism at the fluorine site. The two most apparent are, first, the transfer of an electron from the fluorine ion to the metal ion and, second, the formation of covalent bonds between the two ions. In this article we shall present the results of an NMR study of MnF_3, which, when taken in conjunction with earlier investigations,[2] shows that the mechanism of electron transfer cannot be responsible for the NMR shifts while covalent bonding could explain the experiments. The basis for distinguishing between the alternative explanations is the direction of the F^{19} shift in MnF_3; namely, whether it is paramagnetic or diamagnetic. The spin orientation of a transferred electron will be determined by Hund's rule. (This assumes that the paramagnetic free-ion states are still a good approximation to the actual state in the presence of crystalline fields and covalent bonding.) If the magnetic ion has less than a half-filled d shell, then the transferred electron's spin will be parallel to the magnetic electrons while for a d shell which is not less than half filled the transferred electron will have its spin antiparallel to those of the magnetic ion. On the other hand, covalent bonding will always remove an electron whose spin is antiparallel to the magnetic electrons.

The electron responsible for the hyperfine interaction with the F^{19} nucleus is the one left behind, unpaired, on the fluorine. For covalent bonds this electron will always be parallel to the magnetic electrons; consequently the F^{19} resonance will always be shifted *paramagnetically*. If the d shell is at least half-filled, the theory of electron transfer also predicts a paramagnetic shift of the fluorine resonance. However, if the d shell is less than half-filled, the electron transfer mechanism predicts a *diamagnetic* shift. All of the iron group fluorides in which shifts have previously been observed[2] have contained at least five $3d$ electrons and it was not possible to distinguish between these two mechanisms on the basis of the sign of the NMR shift. For this reason MnF_3 with a $3d^4$ (one less than a half-filled shell) configuration of the magnetic ion provides the first opportunity to distinguish between these two mechanisms.

The NMR shift in MnF_3 is observed to be *paramagnetic*, inconsistent with the predictions of the electron transfer hypothesis. It is consistent with covalent bonding or with any other mechanism which requires that the electron removed from the fluorine ion always has a spin direction antiparallel to the magnetic ion.

EXPERIMENTAL

Measurements were made with a Varian Associates variable frequency NMR spectrometer at frequencies from 2 Mc/sec to 16 Mc/sec. The MnF_3 sample was a powder, from Allied Chemical and Dye Company, a chemical analysis of which showed that the percentages of manganese and fluorine by weight were close to the calculated values of 49.0% and 51.0%, respectively. MnF_3 is not very stable, decomposing readily to yield MnF_2 and free fluorine. There was an undisplaced fluorine resonance the intensity of which increased with time if the sample was exposed to air. In contrast to the displaced resonances, this undisplaced line was quite sensitive to the sample's previous history, could readily be saturated and was relatively narrow. It was weakest in our purest sample and undoubtedly is due to a decomposition by-product. The displaced resonances were similar to those observed in other iron group fluorides in that they were broad, with short values of T_1 indicated, since they could not be saturated. They were shifted by several percent from the normal resonance field of ω/γ_N to lower fields, the absolute shift at

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[1] R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

[2] Jaccarino, Shulman, and Stout, Phys. Rev. **106**, 602 (1957).

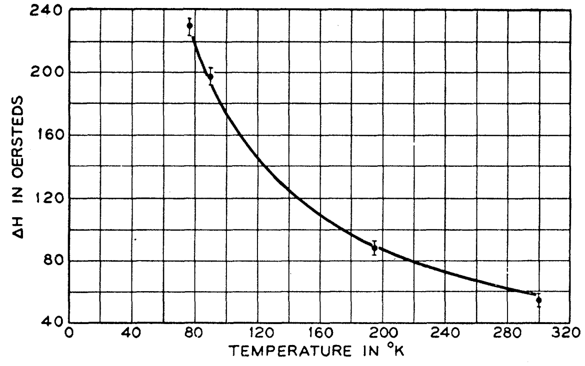

FIG. 1. Measured values of the NMR shift, ΔH, plotted *vs* temperature at a frequency of 16.23 Mc/sec. The solid curve is a best fit of Curie's law to the experimental points.

any temperature being proportional to the magnetic field while the fractional shift increased as the temperature was lowered. The resonance shift is plotted as a function of temperature in Fig. 1. We have fitted the experimental points by Curie's law which is shown as a solid line. Bozorth has measured[3] the susceptibility of our sample. Between 77°K and 300°K the temperature region plotted in Fig. 1, he showed that Curie's law was an accurate representation of the susceptibility. The slope of susceptibility *vs* temperature showed that the Curie constant, C, corresponded to 4.9 Bohr magnetons, which had been reported[4] previously on the basis of a room temperature measurement. This is the value expected from a ^5D state in which orbital contributions are quenched.

The frequency for resonance, including the indirect hyperfine interaction, is[1,2]

$$\omega=\gamma_N\left[\sum_i\left(H_i-\sum_j\frac{A_i^j}{\gamma_N\hbar}\langle S_i\rangle^j\right)^2\right]^{\frac{1}{2}},\qquad(1)$$

where i and j refer to the principal directions and magnetic nearest neighbors ions, respectively, and A_i^j and $\langle S_i\rangle^j$ are the respective jth hyperfine component and spin polarization along the ith direction. The "spin-only" characteristic of the NMR shifts predicts the identical temperature dependence of the shifts and susceptibility shown in Fig. 1. The magnitude of the isotropic contributions to the hyperfine interaction in $\mathrm{MnF_3}$ indicates 0.3% $2s$ character in the unpaired electron.

Line widths of shifted resonances in powders have contributions from two sources, the natural line width and the width arising from anisotropy in the shifts as a result of the superposition of the resonances corresponding to all possible crystalline orientations. Since the second contribution is field-dependent, it can be eliminated and the line width that would be observed in a single crystal can be determined. In Fig. 2 we plot δH (the separation between derivative extrema) as a function of H_0. The line width asymptotically approaches 9.5 oersteds which we assume to be the width one would find in a single crystal. This width is presumably due to nuclear dipolar broadening since it should be approximately equal to the calculated nuclear dipolar width of 10 oersteds in $\mathrm{MnF_2}$.

From this measurement we determine that $T_2 \cong 2\times10^{-6}$ second if we assume a Gaussian-shaped line, while T_1 is bounded by T_2 on one side and by our inability to saturate the resonance on the other; i.e., $4\times10^{-6}<T_1<10^{-4}$ sec.

CHEMICAL AND MAGNETIC PROPERTIES

Hepworth and Jack[5] have determined the crystal structure of $\mathrm{MnF_3}$ to be monoclinic, in which each manganese is octahedrally surrounded by six fluorines which occur in pairs at 2.09 A, 1.91 A, and 1.79 A. The octahedra are connected by their corners so that there are two unique combinations of Mn—F—Mn bonds, namely 1.91 A–1.91 A and 1.79 A–2.09 A, there being twice as many of the latter. In conjunction with Nyholm,[4] they claim that the single d_γ electron of $\mathrm{Mn^{+3}}$ is localized in the longest bond and is responsible for its length. This means that our results are inconsistent with the proposed model if one considers that the single d_γ electron is localized along one bond direction. However, the d_γ orbitals are not localized as completely as Hepworth, Jack, and Nyholm have indicated and one must look to some intermediate degree of localization to explain both the anisotropic bond lengths and the NMR shifts.

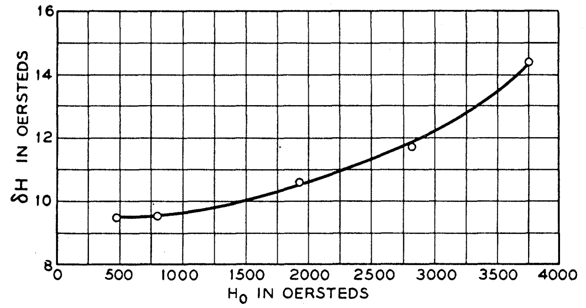

FIG. 2. Measured values of δH, the distance in oersteds between the derivative extrema, plotted *vs* the external magnetic field at $T=300$°K.

The displaced fluorine resonance was very broad (its total spread was roughly equal to the displacement of the center) so that it is quite possible that one-third of the fluorines were displaced less that the remaining two-thirds. It would be very difficult to show this, however, even if a single crystal of $\mathrm{MnF_3}$ were available, since the low symmetry would not allow complete resolution of the fluorine lines.

ACKNOWLEDGMENTS

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[3] R. M. Bozorth (private communication).

[4] Hepworth, Jack, and Nyholm, Nature **179**, 211 (1957).

[5] M. A. Hepworth and K. H. Jack, Acta Cryst. **10**, 345 (1957).