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Letters to the Editor

Nuclear Magnetic Resonance in Paramagnetic Iron Group Fluorides

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FOLLOWING the initial observation[1] of nuclear magnetic resonance of F^{19} in MnF_2, in which fractional displacements of the resonance as large as 8% were observed, we have continued these studies in CoF_2, FeF_2, NiF_2, CrF_3, FeF_3, and CuF_2. Except for CrF_3, where no displacements were observed, all the resonances were shifted to lower fields.

The shifts of the F^{19} resonances from ω/γ^{19} in spherical-shaped single crystals of CoF_2 and FeF_2 with H_0 parallel to [001] are plotted *vs* temperature in Fig. 1. In both cases we have included the corresponding susceptibilities[2] arbitrarily normalized at the highest temperature measured. As in MnF_2,[3] ΔH and $\chi_{\parallel}$ coincide for FeF_2 (a similar observation was drawn from the measurements on powdered NiF_2) but a large discrepancy is to be noted in CoF_2. With H_0 in (001), the resonance fields *vs* angle measured from [100] were recorded and are plotted in Fig. 2. It is to be noted that both the shift and the anisotropy in the shift are larger for $Co(F^{19})_2$ than for $Fe(F^{19})_2$. Similar measurements have been made with H_0 in (110) in which the displacements exhibit 180° symmetry rather than the 90° symmetry shown in Fig. 1. In CoF_2 the two resonances were resolved at room temperature and 16 Mc/sec, whereas in FeF_2 they were resolvable only at 90°K.

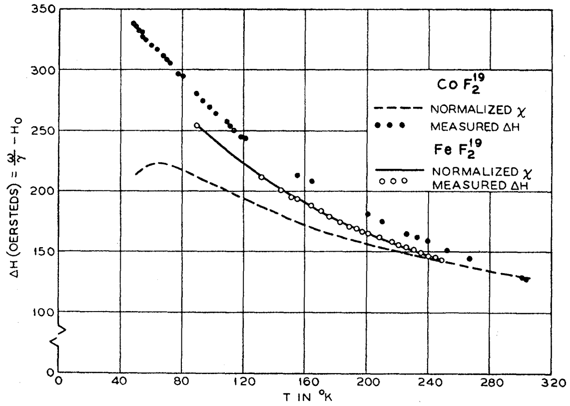

FIG. 1. The shift of the F^{19} resonance *vs* temperature, $H_0 \parallel [001]$ in CoF_2 and FeF_2. The solid curves are the corresponding normalized susceptibilities.

The large shifts and their angular dependences are explained by electron transfer from the F^- to the paramagnetic ion as was the case in MnF_2.[1] The unpaired electron remaining on the F^- has a time-average spin polarization proportional to $\langle S\rangle$, the spin polarization of the magnetic ion. The hyperfine interaction of the unpaired electron shifts the resonances to a frequency[3,4]

$$\omega=\gamma\left[\sum_{ij}\left(H_i-\frac{A_i^j}{\gamma\hbar}<S_i>^j\right)^2\right]^{\frac{1}{2}}, \tag{1}$$

where i refers to the three principal directions, j to the three nearest magnetic ions, and A_i^j is the principal value of the hyperfine interaction constant resulting from an electron being transferred to the jth magnetic ion with the external field in the ith direction.

Unlike MnF_2, where $\langle S_i\rangle$ is simply related to the measured susceptibility, FeF_2 and particularly CoF_2 present difficulties. In FeF_2 one must subtract from the susceptibility the orbital contributions which can be estimated by the departure of the electronic g from the free-electron value. Analyzing the data along the lines suggested by Tinkham,[5] as modified in reference 3, we find that the percentage of s character of the covalent bond (transferred electron) is $(0.47\pm0.04)\%$.

In CoF_2 the susceptibility deviates from the Curie-Weiss law because of thermal excitation to low-lying electronic states with different orbital contributions. The interpretation of the hyperfine interaction in this compound will be presented at a later date. At 77°K and 300°K the shapes and widths of the two resolved lines were measured. Although the less displaced line was symmetric and close to Lorentzian in shape, the other was asymmetric.

The resonance in a powder sample of anhydrous NiF_2 was studied from 75.5°K to 300°K. Unlike CoF_2, FeF_2, and MnF_2, where the temperature variations of the displacements and then anisotropies are continuous before disappearing abruptly at the antiferromagnetic transition temperatures, in NiF_2 an anomalous increase in line width was observed, in a small temperature range, before the resonance disappeared at T_n. This effect may be associated with the small ferromagnetic moment previously[6] noted in susceptibility measurements.

In powder samples of CuF_2 and FeF_3, the shifts at room temperature were 0.47% and 1.2% respectively. In CrF_3, however, where the $3d^3$ electrons are all in $d\epsilon$ orbitals, the shift of the fluorine resonance was less than 0.03%, reflecting the absence of σ bonding.

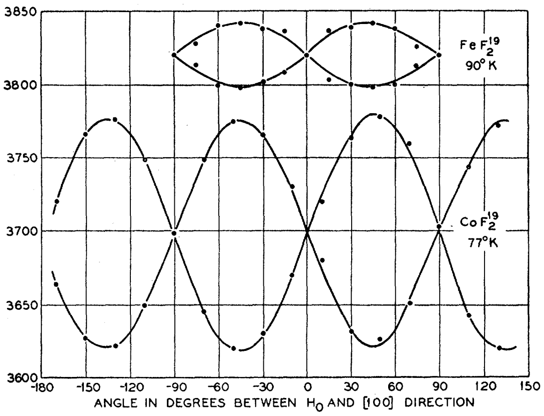

FIG. 2. The fields for resonance *vs* angle, measured from [100], with H_0 in (001) in CoF_2 (at 77°K) and in FeF_2 (at 90°K). In both sets of data the frequency was 16.230 Mc/sec corresponding to an undisplaced F^{19} resonance field of 4052 oersteds.

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Nuclear Magnetic Resonance in CoF_2 and FeF_2

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SHULMAN and Jaccarino[1] have recently observed nuclear magnetic resonance of F^{19} nuclei in MnF_2. They found a much greater "paramagnetic shift" than one would calculate from magnetic dipole fields of the manganese ions, and they explained it by overlap of the magnetic electrons onto the fluorine nuclei. Bleaney[2] also calculated the shift, using overlap parameters derived by Tinkham.[3] These were obtained from measurements of the fluorine hyperfine structure in the paramagnetic resonance spectrum of Mn^{++} ions in ZnF_2. Tinkham also made measurements of this hyperfine structure in the paramagnetic resonance spectra of Co^{++} and Fe^{++} in ZnF_2. We have measured the "paramagnetic shift" of the field in which nuclear magnetic resonance of F^{19} occurs in CoF_2 and FeF_2 in order to see if these can be correlated with Tinkham's results.

Bleaney has shown that the resonance frequency ν in a field H is given by

$$h\nu = g_N\beta_N H(1+\alpha)$$

[this is Bleaney's Eq. (2) with a sign correction],

$$\alpha = (1338\chi/g)\textstyle\sum_N A^N,$$

where χ is the susceptibility of the salt per mole, g is the spectroscopic splitting factor, and A^N is the hyperfine structure coupling constant between the fluorine nuclear spin $\mathbf{I}$ and the electronic spin $\mathbf{S}$ (the interaction being $\sum_N \mathbf{I}\cdot A^N\cdot\mathbf{S}$). The sum is taken over all ions in the crystal, but as the three nearest ions have by far the largest coupling constant they will contribute most to the shift. For a spherical specimen the more distant ions will give a contribution approximately cancelling the demagnetizing field, which may therefore be neglected.

The main features of our results in CoF_2 and FeF_2 are similar to those of Shulman and Jaccarino and the paramagnetic shifts observed are of the same order of magnitude. When H is in the *ab* plane there are two resonances, corresponding to inequivalent sites, which are coincident in the *a* and *b* directions and have a maximum separation $(H\Delta\alpha)$ at 45° to these axes. The mean paramagnetic shift parameter in this plane has been called α_{ab} and that for the *c* direction α_c. There is only one resonance for all orientations in the *bc* plane. Our measurements were made at 30 Mc/sec at two temperatures above the antiferromagnetic transition temperature. No resonance was observed at 90°K in FeF_2 or at 20°K in CoF_2. The antiferromagnetic transition temperatures are variously given as 90°K for FeF_2 and 50°K for CoF_2,[4] and 78°K for FeF_2 and 38°K for CoF_2.[5] The single-crystal specimens we used were not spherical, but as their dimensions in three mutually perpendicular directions were nearly equal, it is assumed that the field inside them is the same as it would be for a spherical sample (the correction will in fact be small as $\chi_{\mathrm{vol}} \sim 4\times10^{-4}$ cgs). There will, however, be a contribution of a few gauss to the line width due to lack of field homogeneity over the specimen.

The shift parameters α obtained from our measurements are given in Table I. The values of $\alpha_c/\chi_{\parallel}$, $\alpha_{ab}/\chi_{\perp}$, and $\Delta\alpha/\chi_{\perp}$ are approximately independent of temperature. The susceptibilities are given by de Haas and Schultz,[6] and Stout and Matarrese.[7]

TABLE I. Observed and calculated values of the paramagnetic shift parameter α.

		$\alpha_c\times10^3$		$\alpha_{ab}\times10^3$		$\Delta\alpha\times10^3$	
Salt	Temp. °K	Meas.[a]	Calc.[b]	Meas.[a]	Calc.[b]	Meas.[a]	Calc.[b]
FeF_2	300	36.2	41 ±3	30.3	38 ±7	9.6	2 ±8
	195	49.1	57 ±5	39.0	51 ±9	11.8	3 ±12
CoF_2	300	35.8	19 ±3 (31 ±5)	30.7	19 ±3 (23 ±4)	15.2	4 ±4 (5 ±5)
	90	79.7	37 ±5 (61 ±9)	82.0	52 ±7 (63 ±9)	33.6	11 ±7 (13 ±9)
MnF_2	77			72.0[c]	77 ±6[d]	19.6[c]	7 ±8

[a] The error in the measurements of $\alpha\times10^3$ and $\Delta\alpha\times10^3$ in FeF_2 and CoF_2 is ±1.3 on all values.

[b] CoF_2 values are calculated by using Tinkham's *g* values (unbracketed) and Nakamura and Taketa's *g* values (bracketed).

[c] Shulman and Jaccarino's experimental results without a demagnetising correction.[1]

[d] Bleaney's calculated value.[2]