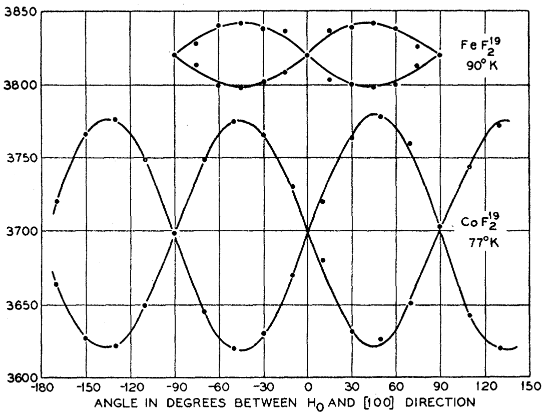

FIG. 2. The fields for resonance *vs* angle, measured from [100], with H_0 in (001) in CoF_2 (at 77°K) and in FeF_2 (at 90°K). In both sets of data the frequency was 16.230 Mc/sec corresponding to an undisplaced F^{19} resonance field of 4052 oersteds.

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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 $\chi_{\text{vol}}\sim 4\times 10^{-4}$ 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.

		$\alpha_c\times 10^3$		$\alpha_{ab}\times 10^3$		$\Delta\alpha\times 10^3$	
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 $\alpha\times 10^3$ and $\Delta\alpha\times 10^3$ 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]

Comparison of the observed shifts with Tinkham's results is rather more indirect than for MnF_2 because the presence of induced dipoles (which give rise to temperature-independent terms in the susceptibility) makes the net spin component $\bar{S}$ in any direction no longer proportional to the susceptibility. This effect is probably not too serious in FeF_2, where Tinkham indicates that the only low-lying levels are the five spin states ($S=2$). These have an over-all splitting of about 50°K, and it should be a reasonable approximation at our temperatures to assume that the susceptibility and $\bar{S}$ are proportional to one another. Tinkham measures only A_z^{I} and A_z^{II} but the other values can be estimated using Tinkham's Eq. (II, 9) and the values for A_σ and A_π he gives for MnF_2. This gives

	x	y	z	
A^{I}	23	24	25	$\times 10^{-4}$ cm^{-1}.
A^{II}	22	18	16	

Nirra and Oguchi[8] interpreted the susceptibility in undiluted FeF_2 using $g_{\parallel}=2.45$ and $g_{\perp}=2.24$. If these values are used instead of Tinkham's, all values of α and $\Delta\alpha$ are reduced by about 9%.

In common with the MnF_2 values, the predicted shifts are a few percent larger than the observed shifts. This is probably due to the fact that in these salts the separation of the fluorine from its neighboring paramagnetic ion is about 5% greater than it is in ZnF_2, so that the s-electron overlap, and hence the values of A^N, are expected to be smaller. Both salts have a much larger $\Delta\alpha$ than is predicted. This could be due to the fact that the distance to the nearest fluorine neighbors I changes less than that to the fluorine neighbors II so that an increase in the ratio $A^{\mathrm{I}}/A^{\mathrm{II}}$ may occur leading to an increased anisotropy.

In the case of CoF_2 the assumption that $\bar{S}$ is proportional to the susceptibility is probably a very poor one, especially as the specific heat data of Stout and Catalano[5] suggest that another doublet state lies some 240°K above the ground doublet. Also it is difficult to know what g values to use as Tinkham[3] and Nakamura and Taketa[9] give widely differing results. Tinkham's g values, measured in a diluted salt, differ greatly from 2, and he explains these values by assuming a ground state with large admixtures of several free ion states. Nakamura and Taketa estimate their g values by fitting the susceptibility of the concentrated salt theoretically on the assumption that the ground state is an orbital singlet, with small admixtures of other states, so that their values are close to 2. This theory would require considerable modification to fit the diluted salt. Values of α have been calculated by using both sets of g values. Tinkham was unable to distinguish between the hyperfine structures of the two bonds and gives only an average $A_y=32$ and $A_z=21(\times 10^{-4}\ \mathrm{cm}^{-1})$. These suggest that A^N in terms of real spin is isotropic ($A^N=14\times 10^{-4}\ \mathrm{cm}^{-1}$) and hence one can estimate $A_x=16\times 10^{-4}\ \mathrm{cm}^{-1}$ using Tinkham's g values. The large discrepancy between the measured and calculated values of α is not unexpected since the treatment is very approximate.

In both salts the signal/noise ratio is proportional to H_1 ($\gamma^2 H_1^2 T_1 T_2' \ll 1$); and the line width, measured between points of maximum slope, is about 27 gauss and is independent of temperature. This is close to the value of 28.5 gauss given for MnF_2.

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Photoelectroluminescence with Visible Response

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PHOTOELECTROLUMINESCENCE[1] has been reported for the phosphor ZnS:Mn,Cl.[2] It is the purpose of this letter to report on the recent observation of this phenomenon in the luminescent materials ZnS:As,Cl and ZnS:P,Cl. In contrast to the manganese-activated phosphor, the spectral responses are much broader and extend well into the blue region of the visible spectrum. Similarly, however, the photoelectroluminescent emission intensity exceeds the intensity of the radiation incident on the phosphor. Consequently, the energy for emission originates primarily from the electric field to which the phosphor is subjected, and not from the incident radiation. The steady irradiation brings about and maintains the conditions for electroluminescence. Though the efficiency of the electroluminescence is still rather low, the improvement in spectral response and the increased energy gains make these phosphors of interest from the standpoint of solid-state light amplification.

The phosphors are formed as thin, continuous layers by the vapor reaction method.[3] The electrodes for application of voltage consist of a transparent TiO_2 coating on one side and a metallic film on the other. The dotted curves of Fig. 1 compare the arsenic and