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Paramagnetic Resonance of Ni^{++}, V^{++}, and Cr^{+++} in ZnF_2

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The millimeter wave paramagnetic resonance spectra of Ni^{++}, V^{++}, and Cr^{+++} have been measured in ZnF_2. Evidence was found that the extra charge of Cr^{+++} is compensated by an F^- ion, sitting on one of two available nonequivalent neighboring sites. The antiferromagnetic resonance line in NiF_2 which has been postulated by Moriya, is now expected to occur at 320 kMc/sec.

THE paramagnetic spectra of the ions Ni^{++}, V^{++}, and Cr^{+++} have been measured in the diamagnetic ZnF_2 lattice. They are described by the spin Hamiltonian

$$\mathcal{H}_s = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + g\beta \mathbf{H}\cdot\mathbf{S} + A\mathbf{I}\cdot\mathbf{S}.$$

The parameters for these ions are summarized in Table I. In Ni^{++}, V^{++}, and Cr^{+++}, spectrum A, the z axis is the [001] axis of ZnF_2 and the x axis follows [110]. In these spectra we do not know the sign of E. In Cr^{+++}, spectrum B, the z axis is in a (110) plane, 9° off the [$1\bar{1}0$] axis, and the y axis follows the [110] axis.

The Cr^{+++} spectra have previously been measured by Tinkham,[1] but we find 20% smaller zero field splittings than he predicted. We agree, however, with Tinkham's measurement of the directions of the main axes of the spin Hamiltonian, and also with his conclusion that they are due to the presence of an anion which compensates the excess charge on Cr^{+++}, and which can occupy either one of two nonequivalent positions. The fact that Cr^{+++} can be introduced in considerable amounts, together with recent measurements in CaF_2 [2] suggests F^- as the compensating ion.

The D term in Ni^{++} has been predicted by Stout[3] from susceptibility measurements. Moriya[4] has shown, that the Ni^{++} spins are aligned along the [110] axes of NiF_2, if $D>0$. He predicts an antiferromagnetic resonance to occur at $\nu=4E\langle S\rangle$. Here, $\langle S\rangle\approx 1.0$ is the expectation value of the spin. This resonance is now predicted at 320 kMc/sec. If VF_2 can be grown with the NiF_2 structure, then it should show a similar resonance at 28 kMc/sec. From crystal field theory we expect that the D and E terms should be proportional for V^{++} ($3d^3\,{}^4F$) and Ni^{++} ($3d^8\,{}^3F$), the proportionality factor being the square ratio of the spin-orbit couplings. This is seen to hold approximately. The same theory predicts a small anisotropy for g and A, and this effect as well as the structure of the Ni resonance due to the surrounding fluorine ions are now under study.

TABLE I. Summary of the ion parameters (in kMc/sec).

	D	E	g	A
Ni^{++}	125.5	80.1	2.33	
V^{++}	12.74	4.58	1.97	0.090
Cr^{+++} spectrum A	21.65	2.30	1.95	
Cr^{+++} spectrum B	21.35	2.75	1.97	

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