PARAMAGNETIC RESONANCE IN A QUASI SINGLE CRYSTAL OF CrCl₃

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Paramagnetic resonance in a quasi-single-crystal of $CrCl_3$ has been measured at room temperature at a frequency of 36,000 Mc/sec. An anisotropy of the g factor has been observed ($g_\perp = 1.989 \pm 0.001$; $g_\parallel = 1.984 \pm 0.001$) which is accompanied by a change in the width of the absorption line $\Delta H_\perp = (98 \pm 2)$ oe; $\Delta H_\parallel = (140 \pm 5)$ oe.

ANHYDROUS chromic chloride has several times been studied by means of the electron paramagnetic-resonance (e.p.r.) method (cf., for example, references 1 and 2). As far as we know, however, polycrystalline specimens were used in all cases. This can evidently be explained by the fact that it is impossible to grow sufficiently large single crystals of this compound.

Chromic chloride has a hexagonal layer-like lattice in which the chromium atoms form layers bounded on both sides by layers of chlorine atoms.[3] $CrCl_3$ crystallizes in the form of small flakes whose surfaces are parallel to the chromium and chlorine layers. It is, therefore, natural to assume that a $CrCl_3$ specimen consisting of a number of flakes laid on each other possesses the main properties of an axially symmetric single crystal.

The e.p.r. of such quasi-single-crystal specimens of $CrCl_3$, consisting of three to five flakes, was studied at 36,000 Mc/sec at room temperature by a previously described method.[4] As a result of the measurements we obtained the following values of the g factor and widths of the e.p.r. lines:

$$g_\perp = 1.989 \pm 0.001, \qquad g_\parallel = 1.984 \pm 0.001,$$

$$\Delta g = 0.005 \pm 0.002, \qquad \Delta H_\perp = (98 \pm 2)\ \text{oe},$$

$$\Delta H_\parallel = (140 \pm 5)\ \text{oe}.$$

Thus, it can be seen that in the quasi single crystal of $CrCl_3$ a marked anisotropy of the g factor is observed which is accompanied by a change in the width of the resonance curve (the width of the curve was measured at the half-height of the intensity).

One can speak of several possible reasons leading to a change in the width of the e.p.r. line in the directions parallel and perpendicular to the symmetry axis of the crystal. It is known, for instance, that although fine splitting in undiluted salts is averaged out by exchange interactions, the fine structure does contribute to some extent to the broadening of the e.p.r. line.[6] It would, however, be incorrect to assume that the difference of this contribution for different directions determines the observed line widths in $CrCl_3$, since in experiments conducted at frequencies differing by more than a factor of 3500 the widths of the e.p.r. lines are approximately the same: at 10 Mc/sec (reference 1), and 9308 Mc/sec (reference 2) in polycrystals ΔH is 132 and 148 oe respectively. The widths obtained from our measurements at 36,000 Mc/sec do not exceed these values.

The observed widths of the e.p.r. lines also cannot be explained by a difference in the dipole-dipole interactions in the investigated directions. Actually, the widths calculated from Van Vleck's formula,[5] assuming that the line has a Gaussian shape, are 900 oe in a constant magnetic field parallel to the symmetry axis of the crystal, and 1030 oe for the two directions of H_0 perpendicular to this axis. Such a large discrepancy in the observed and calculated widths indicates the presence of strong exchange interactions between the Cr^{3+} ions which has already been previously noted.[2]

On the other hand, a comparison of the calculated and measured values of ΔH allows us to assume that the directional dependence of the e.p.r. line width in $CrCl_3$ is due to the anisotropy of exchange interactions. The same conclusion could have been reached from a consideration of the structure of $CrCl_3$: neighboring Cr^{3+} ions belonging to the same layer are at a distance of 3.5 A from each other, while the distances between nearest Cr^{3+} ions of neighboring layers are 6.1 A. However, there remains here the unestimated role of the chlorine ions through which a superexchange may occur.[7] Employing the approximate formula, proposed by Anderson and Weiss[6]

$$\Delta\omega = [^{10}/_3 \, \Delta\omega_p^2]/\omega_e,$$

where ω and ω_p are the observed and dipole-dipole half-widths of the e.p.r. lines at the half-height of the intensity, it is possible to estimate the frequencies ω_e of the exchange interactions: the exchange frequency in the direction perpendicular to the symmetry axis of the crystal $\omega_{e\perp}$ = 3.2 × 10^{11} cps, while $\omega_{e\parallel}$ = 1.7 × 10^{11} cps.

The above method of investigation can also be applied to other substances with a layered structure.

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56