Magnetic Resonance Absorption of Chromic Ammonium Alum*

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MEASUREMENTS of the paramagnetic susceptibility of some hydrated salts such as those of the iron group have been explained by the supposition that the lowest energy states of the paramagnetic ion are split by the large electric field created by the surrounding water molecules. This large field "freezes" the angular-momentum vector of the ion, leaving only the spin free to contribute to the paramagnetic and other properties of the crystal. There is, in addition, a small splitting of the lowest level of the order of several tenths of a wave number which makes itself felt in low temperature measurements on susceptibility and specific heat.

This small splitting has the consequence that the energy levels in a magnetic field are not those of a free spin but are displaced from these by amounts which depend upon the splitting in zero magnetic field. Therefore, at a fixed microwave frequency there are several values of the magnetic field at which the condition for resonant absorption is fulfilled. These values of the magnetic field lead directly to the nature and numerical value of the small splitting produced by the electrical field.

The method used in the work reported here is similar to that employed by Zavoisky[1] and Cumerow and Halliday[2] in that the d.c. magnetic field is applied perpendicular to the a.c. magnetic field. The a.c. frequency was 9375 mc/sec. The resonance absorption was observed by employing a magic tee essentially as an impedance bridge. The sample is placed in a resonant cavity on one arm of the tee, the symmetrical arm of which is loaded with a matched termination. The cavity consists of a shorted piece of wave guide provided with a sliding micrometer tuning screw. The cavity containing the sample is tuned with the d.c. field off, so that no power is detected by a low level detector crystal placed in the fourth arm of the tee. About one milliwatt of r-f power is absorbed by the sample. As the d.c. field is varied the resonance absorptions produce changes in the impedance of the loaded cavity which are indicated by the rectified current of the detector crystal. It can be shown that in this arrangement the rectified current is proportional to the absolute value squared of the susceptibility of the salt. The rectified currents are of the order of several microamperes.

An example of measurements made on chromic ammonium alum ($NH_4Cr(SO_4)_2 \cdot 12H_2O$) is shown in Figs. 1 and 2. Figure 1 shows the detector current as a function of the d.c. field for a powdered sample of 3 g. Figure 2 shows a similar curve for a sample consisting of four small single crystals all oriented with the d.c. field along one of the body diagonals of the face-centered cubic lattice. The position of the principal maxima shows the Lande g-factor to be 1.97 rather than 2.00, but this difference is of the order of the experimental error. The number and positions of the
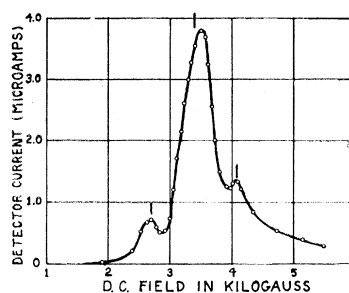

FIG. 1. Absorption curve for powdered chrome alum at a frequency of 9375 mc/sec. The vertical lines show the positions of the peaks computed with $g = 1.97$ and a zero-field separation of 0.15 cm^{-1}.
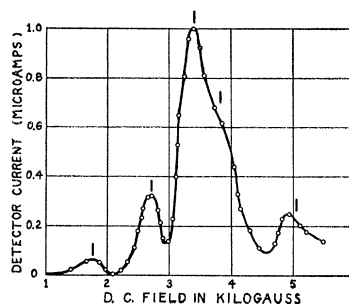

FIG. 2. Absorption curve for single crystals of chrome alum at a frequency of 9375 mc/sec. The vertical lines show the positions of the peaks computed with $g = 1.97$ and a zero-field separation of 0.15 cm^{-1}.

maxima can be explained on the basis that the small splitting is 0.15 ± 0.01 cm^{-1} and is produced by an axially symmetric electric field. The computed positions are shown on the figures. The spin of the Cr^{+++} ion being $\frac{3}{2}$, there are three groups of transitions possible in the case of the powder. Averaging the absorption over the various orientations of the axis of the electric field yields three different peaks as shown. In the orientation of the single crystals stated above there are two types of ions in the lattice; in one type the magnetic field is along the axis of the electric field, in the other the magnetic field makes an angle of 70°33' with the axis of the electric field. Consequently, six transitions are possible. Two of these, however, are superimposed, while a third is not completely resolved from these two. The result, 0.15 cm^{-1}, is somewhat different from the value 0.12 cm^{-1} deduced by Hebb and Purcell[3] for chromic potassium alum from measurements made on the specific heat in the neighborhood of 0.1°K.

The oscillator frequency has not been stabilized and consequently small frequency drifts occur which affect somewhat the reproducibility of the magnitude of the peaks. The positions of the peaks are reproducible within 50 gausses. The technique of the measurements is being improved to remove this difficulty.

[1] E. Zavoisky, J. Phys. U.S.S.R. 9, 211 (1945).
[2] R. L. Cummerow and D. Halliday, Phys. Rev. 70, 433 (1946).
[3] M. H. Hebb and E. M. Purcell, J. Chem. Phys. 5, 338 (1937).