a high degree of antiferromagnetic alignment. In a private communication Herzfeld[6] has informed us that magnetic susceptibility data obtained by him can best be interpreted on the assumption that the lowest state in UF_4 is single and hence could not give rise to paramagnetic resonance. Our results might be interpreted on the assumption that the lowest state is a "nonmagnetic" singlet and that it is the only state significantly populated at the temperature of liquid air. The weakness of the resonance observed at room temperature would then be attributed to the relatively low population of the "magnetic state" at room temperature. The observed magnetic state would lie above the nonmagnetic ground state by kT or more (where T is the room temperature, $kT \approx 200$ cm^{-1}).

Our failure to detect resonance in UCl_4 may be a result of the internal crystalline field splittings. This does not mean that the crystalline field splitting in

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[6] We are indebted to Dr. C. M. Herzfeld for communicating his results to us before publication.

UCl_4 would necessarily be larger than that in UF_4 and hence, that the magnetic state would be less populated. The failure to detect resonance in UCl_4 could be caused by too short a relaxation time (line too broad to detect), which might result from a closer spacing of the Stark multiplet.

The most likely cause of the weakness of paramagnetic resonance in UF_3 and UF_4 and the failure to detect resonance in other uranium salts is strong exchange interaction which could cause significant antiferromagnetic alignment of the electron spins. Many of the uranium salts, including the ones investigated here, have been found to have relatively large Weiss constants.[1] Paramagnetic resonance studies on magnetically diluted salts are needed, and are being planned.

Dr. E. E. Schneider, at our request, has checked the existence of paramagnetic resonance in both UF_3 and UF_4 at room temperature. He used a method of detection which depends on magnetic modulation. We wish to thank him for this assistance.

Paramagnetic Resonance in Chromous Sulfate Pentahydrates

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Paramagnetic resonance absorption in single crystals of chromous sulfate pentahydrate has been observed at room temperature and at wavelengths of 11 mm, 6.5 mm, and 5.4 mm. The result shows that this crystal has a structure similar to that of copper sulfate pentahydrate. The observed data have been analyzed by the so-called spin Hamiltonian, and the parameters determined have been found to be quite consistent with the values of the spin-orbit coupling constant and the spin-spin interaction constant obtained from spectroscopic data.

P ARAMAGNETIC resonance absorption in single crystals of chromous sulfate pentahydrate has been investigated at room temperature and at wavelengths of $\lambda = 11$ mm, 6.5 mm, and 5.4 mm. Few measurements have heretofore been made of the magnetic properties
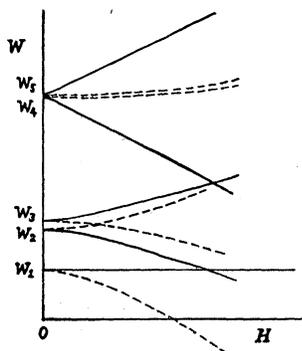
FIG. 1. Relative positions of the lowest energy levels of the Cr^{++} ion in $CrSO_4$ $\cdot 5H_2O$. The full lines are those for $H\|z$ axis and the dashed lines for $H\|y$ axis.

of the Cr^{++} ion, because the Cr^{++} ion, especially in aqueous solution, has a strong tendency to oxidize. The specimens were, therefore, prepared in an evacuated vessel. Large crystals were obtained, which were blue and transparent. This crystal is triclinic and each unit cell seems to contain two unequivalent ions.

The ground state of the free Cr^{++} ion is $3d^4\,^5D$. The fivefold orbital degeneracy is split by the cubic component of the crystalline field into a lower doublet Γ_3 and an upper triplet Γ_5, both of them being split into singlets by the additional rhombic component. These circumstances are the same as in the case of the $3d^9\,^2D$ ion (Cu^{++}). The fine structure Hamiltonian for the lowest spin quintuplet becomes

$$\mathcal{3C} = D(S_z^2 - \tfrac{1}{3}S(S+1)) + E(S_x^2 - S_y^2)$$
$$+ \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z), \quad (1)$$

where D and E are constant parameters, β the Bohr

magneton, g the g factor, and $\mathbf{H}$ is the applied magnetic field. Since D is comparable to $g\beta H$ in this case, the spacings of the spin quintuplet vary with H in a complicated way as shown in Fig. 1. The transition $W_2 \leftrightarrow W_1$ can be observed when $\mathbf{H}$ is parallel to the z axis and that between $W_2 \leftrightarrow W_3$ when $\mathbf{H}$ is applied in the xy plane. The transition $W_2 \leftrightarrow W_3$ is energetically possible in the case of $\mathbf{H} \| z$, but is forbidden by selection rules. Examples of the angular dependence of the resonance field are shown in Fig. 2 and Fig. 3. In Fig. 2, the magnetic field is in the yz plane with $\lambda = 5.4$ mm, and in Fig. 3, $\mathbf{H}$ lies in the z_1z_2 plane (the subscripts 1 and 2 indicate the two dissimilar ions, respectively) with $\lambda = 6.5$ mm. In these figures, dashed lines are used to indicate that the resonance absorption is small. We can see in Fig. 3 that the angle α between the two z axes is 86°. This angle is just the same as that obtained by one of the present authors[1] for copper sulfate.
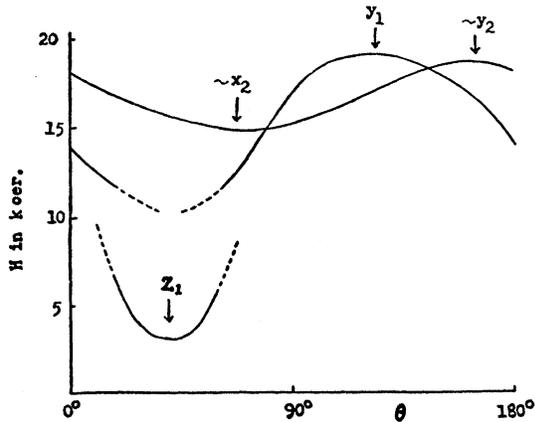
FIG. 2. The angular dependence of the resonance field in the z_1-y_1 plane with $\lambda = 5.4$ mm. x_1, y_1, z_1 and x_2, y_2, z_2 indicate the rhombic axes of the crystalline fields corresponding to the two kinds of ions, respectively.

Using some appropriate approximations, it can be shown that

$$D = -3(l^2 - m^2)\left(\frac{\lambda^2}{\Delta E} + \rho\right),$$

$$E = -2\sqrt{3}\,lm\left(\frac{\lambda^2}{\Delta E} + \rho\right),$$

$$g_x = 2 - 2(l - \sqrt{3}m)^2\lambda/\Delta E, \tag{2}$$

$$g_y = 2 - 2(l + \sqrt{3}m)^2\lambda/\Delta E,$$

$$g_z = 2 - 8l^2\lambda/\Delta E,$$

where λ is the spin-orbit coupling coefficient, ρ is the spin-spin coupling constant between $3d$ electrons, ΔE is the spacing between Γ_3 and Γ_5, and l and m satisfy the relations

$$2lm/[\sqrt{3}(l^2 - m^2)] = E/D, \quad l^2 + m^2 = 1. \tag{3}$$

[1] K. Ono (unpublished work).
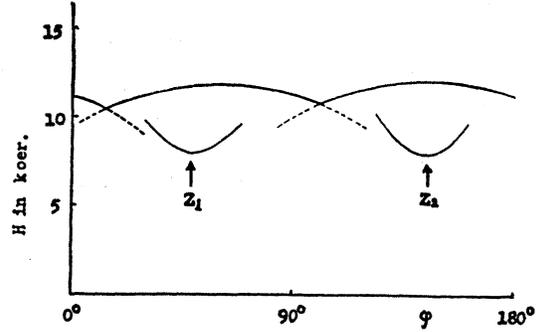
FIG. 3. Angular dependence of the resonance field in the $z_1 - z_2$ plane with $\lambda = 6.5$ mm.
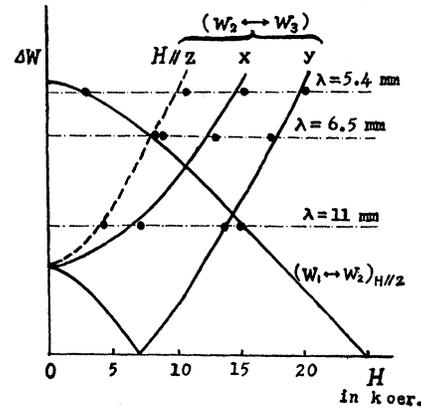
FIG. 4. ΔW as a function of H. The full lines indicate the theoretical values and the circles the experimental ones.

The best agreement of the experimental resonance frequencies with the calculated ones is obtained by taking $|D| = 2.24$ cm^{-1} and $|E| = 0.10$ cm^{-1} for both dissimilar ions. Since the g's are considered to be very close to 2 on account of the smallness of the spin orbit coupling constant compared to ΔE, the above calculation was tentatively made by assuming $g_x \doteq g_y \doteq g_z \doteq 2$. Spectroscopic data indicated $\lambda = 58$ cm^{-1} and $\rho = 0.42$ cm^{-1} for the free Cr^{++} ion.[2,3] These values are quite consistent with the values of $|D|$ and $|E|$ determined above, if we assume $\Delta E = 10\,000$ cm^{-1}. In the above formula we have two alternative cases, i.e., $l \simeq 1$, $m \simeq 0$ and $m \simeq 1$, $l \simeq 0$. Since copper sulfate corresponds to the former, it is reasonable to assume that for chromous sulfate it is also the case. Then we obtain $g_x \doteq g_y = 1.99$ and $g_z = 1.95$, and these values improve the agreement between the calculated and the observed ΔW (see Fig. 4). We have made preliminary measurements of the anisotropy of the static susceptibility of this crystal. The results are consistent with the anisotropy espected from the above values of D and the g's.

The authors' thanks are due to Professor H. Kumagai for his continuous encouragement.

[2] O. Laporte, Z. Physik 47, 761 (1928).
[3] M. H. L. Pryce, Phys. Rev. 80, 1107 (1950).