PHYSICAL REVIEW VOLUME 96, NUMBER 1 OCTOBER 1, 1954

Paramagnetic Resonance in Uranium Salts*

S. N. Ghosh,† Walter Gordy, and D. G. Hill‡
Department of Physics, Duke University, Durham, North Carolina

(Received November 5, 1953; revised manuscript received July 2, 1954)

Paramagnetic resonance has been observed in U^{+3} and U^{+4} ions in powdered samples of UF_3 and UF_4, respectively. The resonance curve in UF_3 was found to be asymmetric, with two unresolved peaks yielding $g_\perp \approx 2.1$ and $g_{\parallel} \approx 2.8$. The resonance is broad and weak; the over-all half-width is about 5 kilogauss at room temperature. The curve obtained for UF_4 is symmetric and yields $g = 2.1_5$. Its half-width is about 3.5 kilogauss at room temperature. Although the resonance in UF_3 appeared somewhat stronger at liquid air than at room temperature, that in UF_4 could be detected only at room and at elevated temperatures. The results favor the interpretation that the two unpaired electrons in U^{+4} are $6d$ electrons, that the crystalline field in UF_4 is essentially cubic, and that either the lowest component of the Stark multiplet is a nonmagnetic singlet or that the electrons have a high degree of antiferromagnetic alignment. The results on UF_3 show that the crystalline field has an axially symmetric component.

THE magnetic properties of the uranium compounds are of special interest because of the light they throw on the electronic structure of the uranium atom and its ionized forms. Numerous measurements have been made on the magnetic susceptibilities of the uranium salts.[1] Supplementary information from paramagnetic resonances is obviously desirable, but previous attempts to observe such resonances in a large number of uranium salts have met with failure.

We have been able to detect paramagnetic resonance at microwave frequencies in both UF_3 and UF_4 at room temperature, but only in UF_3 at the temperature of liquid air. Both resonances were abnormally weak and broad. The reported detection[2] of resonance in UF_4 at liquid air temperature proved to be erroneous. The spurious signal was caused by the increased instability of the balanced wave-guide bridge when the cell was cooled by liquid air. With the more stable spectrometer employed in the later work, the resonance in UF_4 could be detected at room or at elevated temperatures, but not at the temperature of liquid air. That in UF_3 appeared to be slightly stronger at liquid air than at room temperature, as mentioned in the preliminary report. Attempts made to detect paramagnetic resonance in UCl_4 at 90°K and at 300°K were unsuccessful. The spectrometer employed was the balanced microwave bridge type described by Lancaster and Gordy.[3] All measurements were made at frequencies near 30 kMc/sec on samples in powder form. The results are summarized in Table I. The samples, which were obtained from the Oak Ridge National Laboratory, had an estimated purity better than 99 percent.

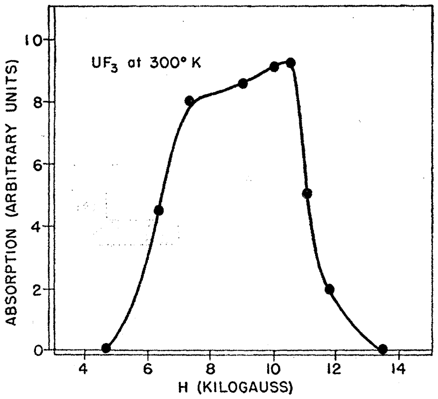

FIG. 1. Paramagnetic resonance in UF_3 powder at 30 kMc/sec and room temperature.

UF_3

Figure 1 shows the resonance curve obtained for UF_3 powder at room temperature. The curve is noticeably asymmetric, with its highest peak on the high field side. A plausible interpretation of the asymmetric shape is that the internal field around the U^{+3} ion has a cylindrically symmetric component which resolves the g factor into distinguishable components parallel ($g_{\parallel}$) and perpendicular ($g_\perp$) to the axis of the field symmetry. In a powder where all orientations of the polycrystalline axes are equally probable, the $g_\perp$ has for geometric reasons the greater weight. From the stronger peak we tentatively assign $g_\perp = 2.1\text{–}2.2$, and from the position of the shoulder on the low-field side $g_{\parallel} = 2.8\text{–}2.9$, approximately.

At the temperature of liquid air the strength of the absorption in UF_3 appeared to be greater than at room

TABLE I. Summary of results.

Substance	Ion	g factor	Half-width kilogauss
UF_3	U^{+3}	$g_{Av} = 2.4 \begin{cases} g_\perp = 2.1-2.2 \\ g_{\parallel} = 2.8-2.9 \end{cases}$	5.0 (unsymmetrical)
UF_4	U^{+4}	2.1_5	3.5 (symmetrical)
UCl_4	U^{+4}	Resonance not observed	

---

* This research was supported by the U. S. Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command.

† Now at the Air Force Cambridge Research Center.

‡ Department of Chemistry, Duke University, Durham, North Carolina.

[1] J. K. Dawson, Nucleonics **10**, 39 (1952).

[2] Ghosh, Gordy, and Hill, Phys. Rev. **87**, 229 (1952).

[3] F. Lancaster and W. Gordy, J. Chem. Phys. **19**, 1181 (1951).

temperature, but the amount of increase could not be quantitatively measured. Although the curve shows the same tendency for doubling at the lower temperature, the peak on the high-field side appears to be stronger relative to that on the low-field side (see Fig. 2). The average g factor obtained for the lower temperature is slightly higher than that for room temperature, but this may be a spurious effect resulting from the change in shape of the curve upon cooling. From such broad and asymmetric curves it is obviously not possible to obtain anything but approximate g values.

The U^{+3} ion has three unpaired electrons. The orbitals which they occupy are uncertain. Dawson[1] has reviewed the evidence from magnetic susceptibilities for uranium and related elements, and he concludes that the $5f$ and $6d$ shells are very close in U^{+3}. It is possible that the ground state represents an admixture of these states. The present results are not sufficient to resolve the question of the ground state. They do show that the unpaired electrons are not in orbitals which are effectively shielded from the crystalline field effects. Considerable internal Stark interaction is evident. Evidently, the orbital motions are not completely quenched by the internal field since the observed g factor is different from the free spin value of 2.

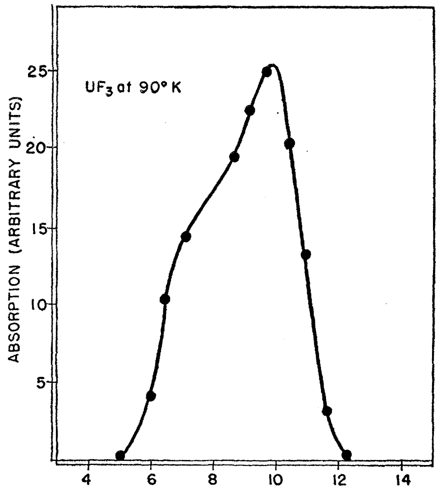

FIG. 2. Paramagnetic resonance in UF_3 powder at 30 kMc/sec and liquid air temperature.

Even if there were no spin-orbit decoupling, the internal field could resolve the g factor into distinguishable $g_\perp$ and $g_{\parallel}$ components. In the latter case, the vector $\mathbf{J}=\mathbf{L}+\mathbf{S}$ is resolved into components J_z along the axis of symmetry z of the crystalline field as in certain of the rare earth salts.[4] The observed transitions then occur between certain of the J_z levels which happen to be populated at room temperature and which are degenerate, or nearly degenerate, in the absence of an external field. Also the selection rules must allow transitions between the particular levels considered, which in general means that $J_z=J_z'\pm 1$.

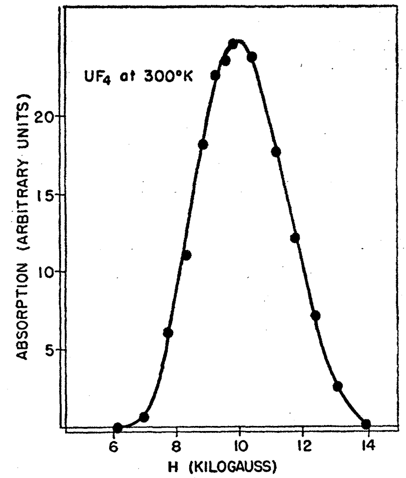

FIG. 3. Paramagnetic resonance in UF_4 powder at 30 kMc/sec and room temperature.

It is possible that the resonances which we observed in UF_3 arise from two sets of electronic levels which are sufficiently close for both to be populated significantly at room temperature. This might explain the variation in the shape of the resonance curves upon cooling. Measurements on single crystals of UF_3 at different orientations are highly desirable, but we have not been able to obtain such crystals.

UF_4

The curve observed for UF_4 is symmetric (see Fig. 3) and yields a g value of 2.1_5. The resonance was easily observed at temperatures of 300, 420, and 450°K, but it could not be detected at the temperature of liquid air. Unsuccessful attempts were made to detect resonance in UCl_4 at room temperature.

In the U^{+4} ions there are only 2 unpaired electrons. According to the Seaborg,[5] representation of the ground state of the uranium atom $5f^36d7s^2$, the unpaired electrons would be expected to reside in the $5f$ orbitals. From a consideration of the available magnetic susceptibility data, Dawson[1] has concluded, however, that they are probably $6d$ electrons. The present paramagnetic resonance results tend to confirm Dawson's conclusions. The observed g factor is essentially isotropic and near the free spin value of 2. This suggests that the orbital motions are effectively quenched by an internal field of cubic symmetry.

The fact that the resonance in UF_4 could not be observed at liquid air temperature, together with the fact that it is not as strong at room temperature as would be expected from its width, suggests either that the resonance arises from electrons which are not in the lowest level of the Stark multiplet or that there is

---

[4] R. J. Elliott and K. W. H. Stevens, Proc. Phys. Soc. (London) **A64**, 205 (1951).

[5] G. T. Seaborg, Nucleonics **5**, 16 (1949).

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 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.

---

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

PHYSICAL REVIEW VOLUME 96, NUMBER 1 OCTOBER 1, 1954

Paramagnetic Resonance in Chromous Sulfate Pentahydrates

KAZUO ONO, *Institute of Science and Technology, University of Tokyo, Tokyo, Japan*
SHOICHIRO KOIDE AND HISAO SEKIYAMA, *College of General Education, University of Tokyo, Tokyo, Japan*
AND
HIDETARO ABE, *Institute of Science and Technology, University of Tokyo, Tokyo, Japan*

(Received April 30, 1954)

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.

PARAMAGNETIC 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 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.

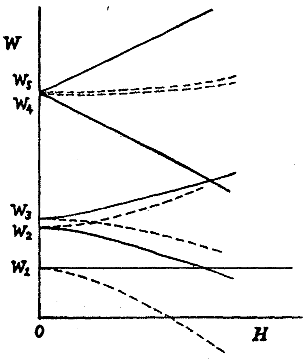

FIG. 1. Relative positions of the lowest energy levels of the Cr^{++} ion in $CrSO_4 \cdot 5H_2O$. The full lines are those for $\mathbf{H} \| z$ axis and the dashed lines for $\mathbf{H} \| y$ axis.

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

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

where D and E are constant parameters, β the Bohr