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Letters to the Editor

Paramagnetic Resonance Absorption in Uranium (III) Chloride and the Nuclear Spin of Uranium-235†

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GHOSH, Gordy, and Hill[1] have reported observations of electronic magnetic resonance in powdered compounds of U but no measurements on single crystals are reported in the literature. We have observed resonance absorption in single crystals of anhydrous UCl_3 diluted with $LaCl_3$. The anhydrous $LaCl_3$ was prepared by the method of Anderson and Hutchison[2] and the UCl_3 as described by Handler and Hutchison.[3] The crystals were grown by a method similar to that developed by Gruen.[4] Measurements have been made at frequencies of about 8700×10^6 cycles/sec (at 20°K) and $23\,000\times10^6$ cycles/sec (at 4.2°K) with crystals containing approximately 2 mole percent U in La and also with others between 10 and 100 times more dilute. In all, an intense absorption is observed from the $^{238}U^{3+}$ ions with the axially symmetric g-values

$$g_{\parallel}=4.153\pm0.005, \quad g_{\perp}=1.520\pm0.002.$$

These are close to the values

$$g_{\parallel}=3.991, \quad g_{\perp}=1.769$$

measured[5] for $NdCl_3$ and not far from those[6] for $Nd(C_2H_5SO_4)_3\cdot9H_2O$.

The structures of UCl_3 and the isomorphous $LaCl_3$ have been determined by Zachariasen.[7] The point symmetry at the metal ion is C_{3h}, the same as in the lanthanide ethyl sulfates, and the theory developed by Elliott and Stevens[8] for the latter should apply to the anhydrous trichlorides. If the three magnetic electrons in U^{3+} are $5f$ electrons, the ground state would be the same ($^4I_{9/2}$) as for Nd^{3+}, $4f^3$, and the resonance absorption must arise from the Kramers doublet:

$$\cos\theta\,|J_z=\pm7/2\rangle+\sin\theta\,|J_z=\pm5/2\rangle.$$

The resonance results suggest that the electronic structures of U^{3+} and Nd^{3+} are essentially the same, confirming the conclusion reached earlier[3] from static field susceptibility data.

In the more concentrated crystals, the absorption by the $(U^{235})^{3+}$ is observed, employing U of normal isotopic composition. With the c-axis parallel to $\mathbf{H}_{DC}$, three hyperfine structure components are observed on either side of the main $(U^{238})^{3+}$ line, two central components being obscured by this intense line and a satellite structure which accompanies it. The spin of U^{235} is clearly 7/2 and

$$A=0.0176\pm0.0001\ \text{cm}^{-1},$$
$$B=0.00568\pm0.00003\ \text{cm}^{-1}.$$

In the perpendicular orientation, the satellite structure is more complicated and spread over a wider range of fields permitting observations of only the two outermost components. Conflicting values of the spin have been reported on the basis of optical data.[9] From the foregoing results we find that

$$g_{\perp}A/g_{\parallel}B=1.13,$$

whereas for Nd^{+3} the value[6] of this quantity is 1.12, indicating that in U^{3+} the mixing with other J's or with higher configurations is small[10] and of about the same amount as in Nd^{+3}.

The value of the nuclear magnetic moment may be estimated for U^{235} in a manner similar to that described by Bleaney[11] for the rare earths, although this method is less reliable for $5f$ electrons and probably gives too large a value of $\langle r^{-3}\rangle$. Employing the value, 1300 cm^{-1}, for ζ given by Eisenstein and Pryce[12] for NpO_2^{++} and the value, 1700 cm^{-1}, given for U^{3+} by Jorgensen,[13] one obtains 0.38 and 0.31 nuclear magneton, respectively, as the values of the moment.

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