On the Magnetic Anisotropy of Caesium Hexachlorouranate(IV)

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Abstract

The magnetic susceptibility and anisotropy of the hexagonal salt Cs_2UCl_6 were measured from 80 to 300 K and found to be essentially independent of temperature. The results were interpreted using a parameterized crystal field model. *k* was found to be 0·93, but the $\angle C_3$–U–Cl deduced does not agree with the value known from the structure for any reasonable range of the crystal field parameter ρ_2. It is deduced that the next state, $\Gamma_4(O_h)$, above the ground Γ_1 state should be split by 50 cm^{-1}. This is in fair agreement with the value observed from the spectrum, 82 cm^{-1}.

It has been shown that the crystal field from an octahedral arrangement of ligand atoms about an f^2 ion leads to the non-degenerate level of Γ_1 symmetry in the O_h group lying lowest.[1] The magnetic susceptibility arising from this level is of the temperature-independent type, with a value of about 25×10^{-9} m^3 mol^{-1}, and is principally a consequence of interaction with the $\Gamma_4(O_h)$ state lying higher by some 1000 cm^{-1}. The magnetic susceptibility of Cs_2UCl_6 has been examined over the temperature range 4–300 K and shown to be in fair agreement with this picture, based upon calculations performed by means of a first-order perturbation treatment of crystal field effects within the ^3H term manifold.[2]

Cs_2UCl_6 crystallizes in the space group[3] $C\bar{3}_m$, with $Z = 1$. The UCl_6 octahedra are distorted by compression down a threefold axis, so that the angle $\angle C_3$–U–Cl is $58 \cdot 2 \pm 1 \cdot 5°$. The site symmetry for the uranium atom is D_{3d}. The C_3 axis of the UCl_6 octahedron is coincident with the unique c axis of the crystals. These considerations, together with the fact that fairly large crystals can be grown without much difficulty, makes the compound ideal for the study of the magnetic anisotropy of the U^{4+} ion in near octahedral site symmetry. Departure from strict octahedral symmetry is expected to split the degeneracy of the $\Gamma_4(O_h)$ level (amongst others) and the components should give different contributions to the susceptibility. Consequently, the magnetic susceptibility may be a function of direction in the crystal, and magnetic anisotropy may be present.

Results and Discussion

We found that the magnetic susceptibility of Cs_2UCl_6 is $24 \cdot 4 \times 10^{-9}$ m^3 mol^{-1} and the magnetic anisotropy $(\chi_\perp - \chi_\parallel)$ is $2 \cdot 63 \times 10^{-9}$ m^3 mol^{-1} at 300 K. The value

[1] Hutchison, C. A., and Candela, G. A., *J. Chem. Phys.*, 1957, **27**, 707.
[2] Candela, G. A., Hutchison, C. A., and Lewis, W. B., *J. Chem. Phys.*, 1959, **30**, 246.
[3] Siegel, S., *Acta Crystallogr.*, 1956, **9**, 827.

for the susceptibility agrees fairly well with an earlier report.[2] We found that both the susceptibility and the anisotropy rise slightly as temperature is lowered, the former steadily to 80 K, the latter steadily to c. 200 K and not thereafter. At 80 K the values were respectively $25 \cdot 1 \times 10^{-9} \, \text{m}^3 \, \text{mol}^{-1}$ and $2 \cdot 85 \times 10^{-9} \, \text{m}^3 \, \text{mol}^{-1}$. No explanation, apart from the possibility of an impurity obeying a Curie Law, is obvious to explain the changes with temperature. The 300-K values were chosen for comparison with theory. No major change in deductions takes place if the low temperature values are used.

From the magnetic susceptibility and anisotropy the principal susceptibilities parallel to ($\chi_{U\parallel}$) and perpendicular to ($\chi_{U\perp}$) the C_3 axis were deduced. These quantities were interpreted in terms of the theory for the perturbation of the states arising from the f^2 configuration in D_{3d} symmetry developed by one of us earlier for use in lanthanide element systems.[4] The full basis set was used as the restricted bases set of ^3H and ^3F gave suceptibilities approximately 15% lower than obtained by use of the complete f^2 configuration (for a representatives set of parameters, the ground state was 89% $^3H_4$ and 9% $^1G_4$). The theory involves the spin–orbit coupling constant for the U^{4+} ion ζ, the orbital angular momentum reduction factor k, and the crystal field parameters ρ_2, ρ_4, ρ_6 and θ and the interelectronic repulsion parameters F_2, F_4 and F_6. Here θ is nominally the angle $\angle C_3$–U–Cl. In principle, the parameters ζ, ρ_4, ρ_6, θ, F_2, F_4 and F_6 should be known from spectral and structural studies on Cs_2UCl_6 and other uranium(IV) compounds. However, unfortunately, there is not good agreement for many of these amongst various sources, and attempts by one of us[5] to use existing data in another connection emphasize the incompatibility. In particular, studies on lanthanide element systems show that it is not satisfactory to take θ as the physically determined angle $\angle C_3$–U–Cl; rather it is treated as an adjustable parameter in the theory. The procedure adopted was to take the most reasonable set of crystal field and interelectronic repulsion parameters which seemed to be available[6] and to use k, ρ_2 and θ as variables. The parameter set assumed was $\rho_4 = 2179 \, \text{cm}^{-1}$, $\rho_6 = 1914 \, \text{cm}^{-1}$, $F_2 = 182 \cdot 2 \, \text{cm}^{-1}$, $F_4 = 36 \cdot 9 \, \text{cm}^{-1}$, $F_6 = 3 \cdot 86 \, \text{cm}^{-1}$, $\zeta = 1796 \, \text{cm}^{-1}$.

Our magnetic anisotropy data required that the parameter k take on the value $0 \cdot 93 \pm 0 \cdot 01$, but do not give specific values for ρ_2 and θ. If a reasonable range for ρ_2 is taken to be 2000–4000 cm^{-1}, the experimental results are reproduced for θ lying between the respective extremes of $55 \cdot 95$ and $55 \cdot 40°$. From this treatment of our data a splitting of the $\Gamma_4(O_h)$ term of 50 cm^{-1} can be predicted, and a g value of $0 \cdot 810$ ($\rho_2 = 2000 \, \text{cm}^{-1}$) to $0 \cdot 725$ ($\rho_2 = 4000 \, \text{cm}^{-1}$) estimated. The splitting of the $\Gamma_4(O_h)$ term is approximately half that predicted on the basis of first-order perturbation theory and emphasizes the importance of crystal field mixing of the $\Gamma_3(D_{3d})$ levels as well as the contribution to the susceptibility from matrix elements of the type

$$\langle \Gamma_1 | \hat{L} + 2\hat{S} | \Gamma_3 \rangle$$

which are allowed in D_{3d} symmetry but forbidden in O_h symmetry.

[4] Gerloch, M., and Mackey, D. J., *J. Chem. Soc. A*, 1970, 3030; Gerloch, M., and Mackey, D. J., *J. Chem. Soc. A*, 1971, 2605.

[5] Mackey, D. J., unpublished data.

[6] Johnston, D. R., Ph.D. Thesis, University of California at Los Angeles, 1967.

The spectrum of Cs_2UCl_6 has been examined in some detail, including polarized single crystal studies at very low temperatures.[6] The $\Gamma_4(O_h)$ state is observed to be split by 82 cm^{-1} giving a $\Gamma_3(D_{3d})$ state at 897 cm^1 and a $\Gamma_2(D_{3d})$ state at 979 cm^{-1}. In view of the limited reliability of the crystal field and interelectronic repulsion parameter sets for the U^{4+} ion the agreement between the observed splitting of the $\Gamma_4(O_h)$ state and that deduced from the magnetic anisotropy can be regarded as, if not satisfactory, at least encouraging. Also, although the g value for the $\Gamma_3(D_{3d})$ state probably is not subject to experimental confirmation, it allows, in principle, a separation of the parameters ρ_2 and θ.

Although the limits placed upon the angle θ by the X-ray structure determination (θ_{exp}) are not close, they do not encompass the value (θ_{calc}) required to reproduce the magnetic data. The magnetic data is very sensitive to the departure of θ_{calc} from the value for a regular octahedron, $54\cdot75°$, so that only a very slight compression of the octahedron (θ_{calc} c. $55\cdot7°$) is required. Experimentally, the octahedron is rather more compressed, with $\theta_{exp} = 58\cdot2°$. This disagreement has been noted in the application of the crystal field model used here to the magnetic properties of some lanthanide ion compounds.*

Experimental

Cs_2UCl_6 was prepared as described earlier[7] and was obtained as a fine green powder. This was dissolved in a minimum amount of water and crystals of up to 5 mm were grown by slow evaporation under an atmosphere of nitrogen.

The magnetic susceptibility and anisotropy of the powder was determined over the temperature range 80–300 K on equipment which has been described previously.[8–11] The absolute values of the quantities were estimated to be accurate to $\pm2\%$, and their relative values at different temperatures to $\pm0\cdot5\%$. The magnetic susceptibility was corrected for the presence of the diamagnetic atoms by use of a standard compilation.[12] The magnetic anisotropy was not corrected for the possible anisotropy of the diamagnetic constituents as that was considered to be negligibly small in a compound in which the symmetry is so close to cubic.

Acknowledgments

* See ref. 4 and subsequent papers in *J. Chem. Soc. A* and *J. Chem. Soc., Dalton Trans.*

[7] 'Gmelin's Handbook of Inorganic Chemistry' 1936, **55**, 227.

[8] Engelhardt, L. M., and Figgis, B. N., *J. Chem. Soc. A*, 1968, 1258.

[9] Krishnan, K. S., and Banerjee, S., *Phil. Trans. Roy. Soc. A*, 1935, **234**, 265.

[10] Gordon, D. A., *Rev. Sci. Instrum.*, 1958, **29**, 929.

[11] Fleishmann, C. W., and Turner, A. G., *Rev. Sci. Instrum.*, 1966, **37**, 73.

[12] Konig, E., 'Landholt–Bornstein. II. Atomic and Molecular Physics, 2, Magnetic Properties of Coordination and Metal-Organic Compounds' (Springer: Berlin 1966).