Structural Transitions in UCl₄ Anticipating Melting

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Abstract

A structural transition in UCl₄ has been found by differential enthalpic analysis at about 821 K, just below the melting point of 861 K. Refinements of the $I4_1/amd$ structure [$M_r = 379\cdot84$, $a = 8\cdot3531$ (3), $c = 7\cdot6982$ (5) Å] by neutron powder profile analysis at 5, 298 and 849 K ($R_I = 5\cdot56$, $5\cdot45$, $10\cdot82\%$ respectively) indicate that the almost flat UCl₄ tetrahedra commence hindered rotation before moving off the crystal lattice at the melting point.

Introduction

At ambient temperature, UCl₄ is tetragonal $I4_1/amd$ and is isostructural with ThCl₄, PaCl₄ and NpCl₄. Mooney (1949) found by X-ray diffraction that each metal atom is coordinated with eight chlorine atoms, but that four chlorine atoms, forming an extremely squashed tetrahedron, or kinked square, are significantly closer to the uranium. Taylor & Wilson (1973) found, by neutron powder diffraction, that the eight U–Cl distances are more nearly equal, though four are still significantly shorter. There has been some discussion in the literature about the nature of the bonding and the eightfold coordination of uranium in these compounds (Mucker, Smith, Johnson & Elson, 1969, and references cited therein). In this paper we will show, by studying the temperature dependence of the structure, that UCl₄ is essentially a simple molecular solid, with rigid UCl₄ units remaining intact through a phase transition which anticipates the transition to the molten state.

We have previously studied the temperature dependence of a number of transuranic halides, and have found that in most cases structural transitions occur before such compounds melt. The nature of these transitions depends on whether the bonding is covalent or ionic. For example, in Na₂UBr₆ the Na⁺ ion becomes free to move between equivalent lattice sites at the first transition, making the material a superionic conductor (Bogacz, Bros, Gaune-Escard, Hewat & Taylor, 1980). The U–Br are, however, covalent and remain intact even when at higher-temperature transitions the UBr₆ octahedra begin hindered rotation (Hewat, Taylor, Gaune-Escard, Bros, Szczepaniak & Bogacz, 1984).

Information about the nature of the bonds in UCl₄ and insight into the melting mechanism can therefore be obtained by looking for premelting structural transitions in this material.

Differential enthalpic analysis (DEA)

The enthalpy of a phase transition can be accurately determined with our high-temperature Calvet microcalorimeter used as a differential enthalpic analyser (Fouque, Gaune-Escard, Szczepaniak & Bogacz, 1978). Very small and closely spaced thermic effects can be identified owing to the very slow scanning rate (less than 1 K h⁻¹), the large number of thermocouples surrounding the sample, and the large sample volume (3 cm³). The apparatus is calibrated using the Joule effect or the melting of suitable reference materials. Absolute values for the enthalpies of phase transitions, and therefore the entropies, can be obtained, as has been successfully demonstrated for many materials, and in particular for the uranium compounds Na₂UBr₆ (Fouque *et al.*, 1978), UBr₄ (Fouque, Bros, Gaune-Escard, Szczepaniak & Bogacz, 1980), UI₄ (Bros, Fouque, Gaune-Escard, Szczepaniak & Bogacz, 1982) and Li₂UBr₆ (Bogacz, Szczepaniak, Bros, Fouque & Gaune-Escard, 1984).

Fig. 1 shows the thermogram obtained for UCl₄ on heating; it exhibits three distinct regions:

(1) from 298 to 821 K, the base line is flat and parallel to the time axis, showing no thermal effects;

(2) at 821 K, a small endothermic effect begins, and lasts until 843 K;

(3) at 861 K, the compound begins to melt, producing a large endothermic effect.

The endothermic effect at 821 K indicates that a structural transition probably anticipates the melting point by about 40 K; the exact melting point is, however, difficult to assess because of the slow initial rise of the thermal flux dQ/dT, possibly due to other premelting effects. The total enthalpy associated with the structural and melting transitions is 44·6 kJ mol^{-1}. It should be noted that we can resolve only a single thermal effect before melting, while other authors have seen two in the same temperature range (Pascal, 1960).

It should also be noted that some transitions have been found at 19 K (Mulak & Zolnierek, 1976) and at 70 K (Khan Malek, Delamoye, Hussonnois & Guibé, 1980) based on magnetic susceptibility measurements.

Neutron powder diffraction

A second identical sample, sealed in a 12 mm diameter quartz glass tube, was examined on the high-resolution neutron powder diffractometer $D1A$ at the Institut Laue–Langevin (Hewat & Bailey, 1976). A vanadium furnace, contributing no lines itself to the diffraction pattern, allowed examination from ambient temperature up to the melting point. With a wavelength of 1·909 Å, the diffraction patterns were recorded at 298 and 849 K from 6 to 161° 2θ in steps of 0·05°, each run taking about 22 h. For the 5 K run, the sample was transferred to a He gas flow cryostat; only 2 h were available for the data collection at this temperature, resulting in slightly less precise results. The Rietveld profile refinement program (Rietveld, 1969; Hewat, 1973) was used to analyse the data.* No radical difference was apparent between the diffraction patterns at these temperatures, though of course the intensity of the high-temperature pattern is much reduced by thermal atomic motion (Fig. 2). The calibration of the neutron furnace (±5 K) is not as precise as that of the calorimeter, but the highest temperature surely exceeds 821 K, where the thermal

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* A list of observed and calculated intensities for each profile point of the 5 K refinement has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43474 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
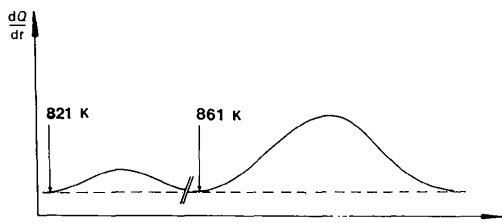

Fig. 1. Differential enthalpic analysis thermogram of UCl₄: thermal flux dQ/dt (arbitrary units) versus time t (min). The mass of the sample was 4·0666 g.

effect commences. Shorter preliminary runs at 778, 818, 828, 833 and 838 K had also failed to show any radical change in the pattern, as did a later run near 861 K, when the sample showed signs of melting. The phase transition cannot then involve a major rearrangement of the structure, as was immediately obvious, for example, in Na₂UBr₆ (Hewat et al., 1984).

At 295 K, our refinement (Table 1) is in excellent agreement with the results of Taylor & Wilson (1973), though our parameters are considerably more precise, and we were able, above ambient temperature, to refine anisotropic Debye–Waller factors. We see the same anisotropy in the motion of the chlorine atom as was found by Mucker et al. (1969) in ThCl₄ by single-crystal X-ray diffraction. This atom has a much larger motion in directions perpendicular to the U–Cl bond than along the bond (Fig. 3). Mucker et al. (1969) attributed this anisotropy in ThCl₄ to easy vibrations in and out of the z-axis channels between chlorine atoms. Our interpretation is different, and forms the basis of our explanation of the phase transition in UCl₄.

At 849 K, well above the transition temperature recorded by DEA, we find that the same structure fits the data very well. However, there are important
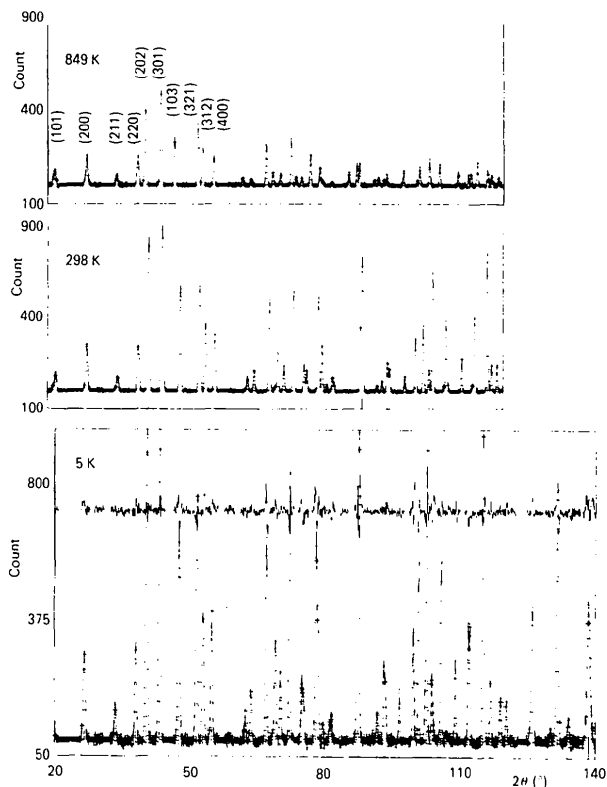

Fig. 2. Observed and calculated neutron powder diffraction profiles for UCl₄ at 849, 298 and 5 K, and a difference profile at 5 K. There is no radical change at the transition temperature 821 K, except for the strong reduction in intensity owing to thermal disorder at high temperature.

Table 1. *Parameters describing the structure of* UCl_4 *at 5, 298 and 849 K with calculated e.s.d.'s in parentheses, and earlier results for comparison*

The coordinates y, z are fractions of the cell edges, and the B_{ij} factors (Å^2) are defined by the Debye–Waller factor $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$, where $\beta_{ij}=\frac{1}{4}a_i^*a_j^* B_{ij}$ depends on the reciprocal-lattice lengths a_i^*. R_I is the R factor for integrated intensities, about twice the usually quoted R factor for structure factors.

Parameter†	Mooney	Taylor & Wilson	5 K	298 K	849 K
$c/a^{(1)}$	0.9025 (20)	0.9032 (10)	0.8947 (1)	0.9014 (1)	0.9216 (1)
$y(Cl)^{(2)}$	0.281	0.3125 (5)	0.3112 (1)	0.3113 (1)	0.3089 (2)
$z(Cl)$	0.917	0.9261 (5)	0.9237 (2)	0.9254 (1)	0.9284 (43)
$B(U)^{(3)}$	0	0.8 (2)	0.1 (2)	0.8	3.9
$B_{11}(U)$			—	0.4 (1)	1.7 (2)
$B_{33}(U)$				1.7 (1)	8.2 (4)
$B(Cl)$	0	1.9 (1)	1.0 (1)	1.8	5.7
$B_{11}(Cl)$			—	3.0 (1)	7.8 (2)
$B_{22}(Cl)$			—	0.5 (1)	1.8 (1)
$B_{33}(Cl)$			—	2.0 (1)	7.5 (1)
$B_{23}(Cl)$			—	0.2 (1)	0.5 (1)
$b(U)$		0.84	0.84	0.84	0.84
$b(Cl)$		0.96	0.99 (1)	0.96 (1)	0.98 (1)
R_I (%)		12	5.56	5.45	10.82
U–Cl (Å)	2.41	2.638 (1)	2.632* (1)	2.632 (1)	2.624 (1)
	3.09	2.869 (1)	2.873 (1)	2.877 (1)	2.930 (1)
Cl_1–U–Cl_1 (°)			92.63 (1)	92.56 (1)	92.50 (3)
Cl_1–U–$Cl_2^{(4)}$ (°)		65.3 (2)	65.78 (3)	65.63 (2)	65.64 (3)
		69.4 (2)	69.48 (4)	69.39 (2)	69.24 (3)

† Notes: (1) *cf.* $c/a=0.9012$ (13) (Yoshimura, Miyake & Imoto, 1971). (2) Uncorrected for libration (calculated bond lengths are therefore slightly underestimated especially at high temperature). (3) Corrected for absorption (Hewat, 1979) by adding $\Delta B=0.4\ \text{Å}^2$ to all refined B_{ii} parameters. (4) Calculated for comparison with Taylor & Wilson only. These angles have no special physical significance according to our interpretation, since the Cl_1 and Cl_2 atoms are on different UCl_4 molecules. The Cl_1–U–Cl_1 intramolecular angle remains constant with temperature.

changes in the parameters on heating. The c axis expands anisotropically, with $c/a = 0.90$ at room temperature becoming 0.92 at high temperature; the four
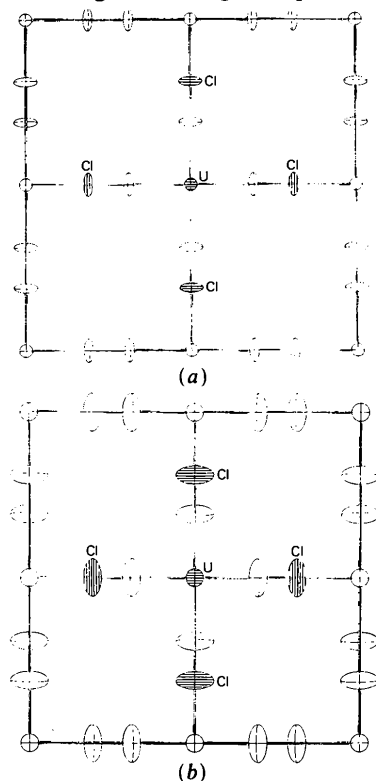

Fig. 3. *ORTEP* plot (Johnson, 1965) showing the thermal ellipsoids for 50% occupation in the (001) projection of UCl_4 at (*a*) 298 K and (*b*) 849 K, indicating rotation of the UCl_4 tetrahedra about the (001) axis.

shortest U–Cl bonds remain constant at 2.63 Å, but the second four increase from 2.87 to 2.95 Å; the anisotropic motion of the chlorine atom becomes very large in directions perpendicular to the U–Cl bonds with $B_{11}(Cl) = 8\ \text{Å}^2$; and finally the entire UCl_4 molecule vibrates strongly along z [large $B_{33}(U) = B_{33}(Cl) = 8\ \text{Å}^2$], with an average displacement of 0.32 Å.

All four of these observations suggest that the highly squashed UCl_4 tetrahedron may rotate about the 4_1-fold crystal axis at high temperature. Such a rotation would be hindered, in the sense that most of the time the molecule would be aligned in one of two orientations with U–Cl bonds projected along the a or b axes, and cooperative in the sense that rotations of adjacent UCl_4 molecules would be co-related. A single 90° rotation of the molecule at $(0,\frac{1}{2},\frac{1}{4})$, for example, would bring the chlorine atoms of this molecule into closer contact essentially along the z axis with the chlorine atoms on the molecule 0,0,0 (b.c.c.). Such oppositions must of course occur at the boundaries of regions of counter rotation, since the co-relation length for rotation will be finite. Counter rotations would then force the molecules apart along z, expanding the z axis as observed.

Molecular rotation about the z axis would also result in strong vibration of the entire UCl_4 molecule along z [large $B_{33}(U) = B_{33}(Cl)$] whenever rotations of overlapping molecules are not synchronized. This is also observed at high temperature (Table 1).

A further consequence of UCl_4 rotation and the resulting expansion along z would be an increase in the second-neighbour U–Cl distance (from uranium

to chlorine atoms on adjacent molecules), while the closest U–Cl distance (from uranium to chlorine atoms on the same molecule) would remain unchanged, again as observed.

Diffraction data can only tell us the average structure of this material, but all four observed changes in this average structure (strong vibration of Cl perpendicular to the UCl bond, expansion of the c axis, vibration of the entire molecule along c, and constancy of the U–Cl bond lengths within a molecule) strongly suggest that the phase transition observed by DEA can only involve the onset of hindered rotation of UCl$_4$ molecules about their unique z axis.

Many examples of such phase transitions involving hindered rotations are known, the most famous examples being the ammonium halides, where the NH$_4$ tetrahedra commence rotation even at low temperature. Levy, Sanger, Taylor & Wilson (1975) have found similar hindered rotations commencing at high temperature in halide octahedra such as MoF$_6$, and no doubt many others will be found when structural measurements close to the melting point become more common. Such dynamic disorder, though strongly suggested by the present elastic diffraction measurements, could only be proved using inelastic scattering techniques.

Apart from offering an explanation for a phase transition in this class of materials, we have also demonstrated that such compounds form essentially simple molecular structures made from UX$_4$ units. In fact, these UCl$_4$ units probably remain intact even in the liquid phase. This simple molecular picture contrasts with the more complex coordinations previously suggested for uranium in such compounds.

Finally, at the other extreme, we might have expected that at least one more phase transition would lower the symmetry at low temperature. The volume of the structure could be reduced by a static co-related tilting of the tetrahedra, with the chlorine atoms moving toward the z-axis channels, and such cooperative static rotations of tetrahedra are well known (e.g. in BiVO$_4$; David, Glazer & Hewat, 1979). However, in the case of UCl$_4$ the structure remains tetragonal down to the lowest temperatures.

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The Incommensurate Structure of Mullite by Patterson Synthesis

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Abstract

The incommensurate structure of a mullite, Al$_2$[Al$_{2+2x}$, Si$_{2-2x}$]O$_{10-x}$, with $x = 0.40$, has been solved by the analysis of Patterson functions constructed from satellite intensity data collected by single-crystal X-ray diffractometry. The analysis shows that the incommensurate modulation is comprised of two sets of ordering patterns (difference structures) which have different symmetries, and which are modulated in quadrature through the crystal. One difference

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