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# THERMODYNAMIC PROPERTIES OF URANIUM DIOXIDE: ELECTRONIC CONTRIBUTIONS TO THE SPECIFIC HEAT

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It has recently been proposed that the anomalous specific heat of uranium dioxide be ascribed to the effect of electronic defects rather than Frenkel disorder on the union sub-lattice. We here present calculations showing that the entropy contribution from electronic defects is large enough to make a major contribution to the specific heat whereas the contribution from Frenkel defects is much smaller.

## 1. Introduction

Ther thermodynamic properties of solid and liquid phase uranium dioxide have been of considerable interest. Experiments show that there is an excess enthalpy above 1500 K giving rise to an anomalous increase in the solid state specific heat $C_p(s)$ (Browning et al. [1]; we are also indebted to Mr. Browning for an unpublished survey). Given the current precision of enthalpy measurements it is not possible to decide whether or not $UO_2$ shows a diffuse second-order transition, as do many fluorite lattice compounds; and so two quite different forms of the $C_p(s)$ versus temperature curve have been postulated.

The defect structure of this compound is clearly of considerable importance in this study. Catlow [2,3] has presented calculations suggesting that electronic disorder is more important in this compound than ionic disorder (here due to anion Frenkel defects). MacInnes [4–7] too has suggested the importance of electronic excitation is solid and liquid $UO_2$. He and his colleagues (MacInnes, Martin and Vaughan [8]) have discussed the implications in accident analysis. This view of electronic disorder is in sharp contrast to the proposed defect model of Szwarc [9], and Kerrisk and Clifton [10]. In this paper we present calculations of the thermodynamic properties of various defect systems present in $UO_2$ and so resolve the question of the source of the increase in $C_p(s)$.

## 2. The calculation

The general principles of the calculation will be described elsewhere (Harding et al. [11]); here we merely give a résumé.

We consider a cluster consisting of the defect and nearest neighbour ions embedded in a non-primitive repeating unit of the fluorite structure (usually the fcc cell is adequate). This unit is chosen to be sufficiently large so that none of the cluster ions are on the faces of the unit. The ions of the cluster are given the relaxed positions as calculated from a HADES run using the potentials of Catlow [2] shown in table 1. The phonon spectrum is calculated using this repeating unit and Catlow's potentials. Since a non-primitive cell is used the branches of the spectrum are folded back and so an adequate representation of the partition function may be obtained using the frequency spectrum seen at the point $\boldsymbol{k} = 0.0, 0.0, 0.0$ alone. Provided the non-primitive cell has all the symmetry elements of the primitive cell, this folding back will be performed in a consistent manner for all symmetry directions; this is the basis of the large unit cell method of Dobrotvorskii et al. [12]. In effect, we

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Table 1
Potential set for $UO_2$ used in the calculations

| | | |
|---|---|---|
| Ionic charge of U | $Z\|e\| = 4.0$ | |
| Repulsive potentials | | |
| U : O | $A_{12}$ (eV) | = 1217.8 |
| | $P_{12}$ (Å) | = 0.3871 |
| O : O | $A_{22}$ (eV) | = 22 764.3 |
| | $P_{22}$ (Å) | = 0.149 |
| | $C_{22}$ (eV/Å$^6$) | = 112.2 |
| Shell charges | $Y{+}\|e\| = 6.54$ | |
| | $Y{-}\|e\| = -4.4$ | |
| Shell-core | $K_+$ (eV/Å2) | = 103.38 |
| force constants | $K_-$ (eV/Å$^2$) | = 292.98 |

replace the integral over wavevector which appears in the partition function by a sum over branches at special points in the zone:

$$\frac{1}{\Omega}\int_0^\infty \mathrm{d}\boldsymbol{k}\,F(\boldsymbol{k}) \to \sum_i F_i(\boldsymbol{k}=0)\Big/\sum_i 1\,.$$

Further, since in this case all we are interested in is the difference between a value for the defect cluster and a value calculated for the perfect crystal; provided we calculate the perfect crystal using the same method and the same repeating unit as used for the defect cluster we can use non-primitive unit cells which do not all have all the required symmetry elements.

We thus approximate the partition function

$$\ln Q = \ln \Omega_0 - \frac{U_0}{k_\mathrm{B}T} - \int_0^\infty \mathrm{d}\boldsymbol{k} \sum_n \ln\left[1-\exp\left(-\frac{h\nu_{nk}}{k_\mathrm{B}T}\right)\right],$$

$$U_0 = E_0 + \int_0^\infty \mathrm{d}\boldsymbol{k} \sum_n \tfrac{1}{2}h\nu_{nk}\,,$$

(where $E_0$ is the internal energy and $\Omega_0$ the configurational term) as

$$\ln Q = \ln \Omega_0 - \frac{U_0}{k_\mathrm{B}T} - \sum_n \ln\left[1-\exp\left(-\frac{h\nu_{n0}}{k_\mathrm{B}T}\right)\right],$$

$$U_0 = E_0 + \sum_n \tfrac{1}{2}h\nu_{n0}\,,$$

and then calculate thermodynamic properties using the standard relations

$$S = Nk_\mathrm{B}T(\partial \ln Q/\partial T)_v + Nk_\mathrm{B}\ln Q\,,$$

$$A = -Nk_\mathrm{B}T\ln Q\,.$$

## 3. Calculations on the perfect lattice

Since we propose to use these potentials to obtain a frequency spectrum for the lattice it is of interest to see how well the phonon dispersion curves are reproduced. This has been done and the results compared with the measurements of Dolling et al. [3]. This is shown in fig. 1. The discrepancy between theory and experiment is of the order of 10% at worst and is usually considerably better. We have also calculated the perfect crystal entropy using various repeating units and these results are compared with the powder experiments of Huntzicker and Westrum [14] (fig. 2). Also we compare with the curve produced by the

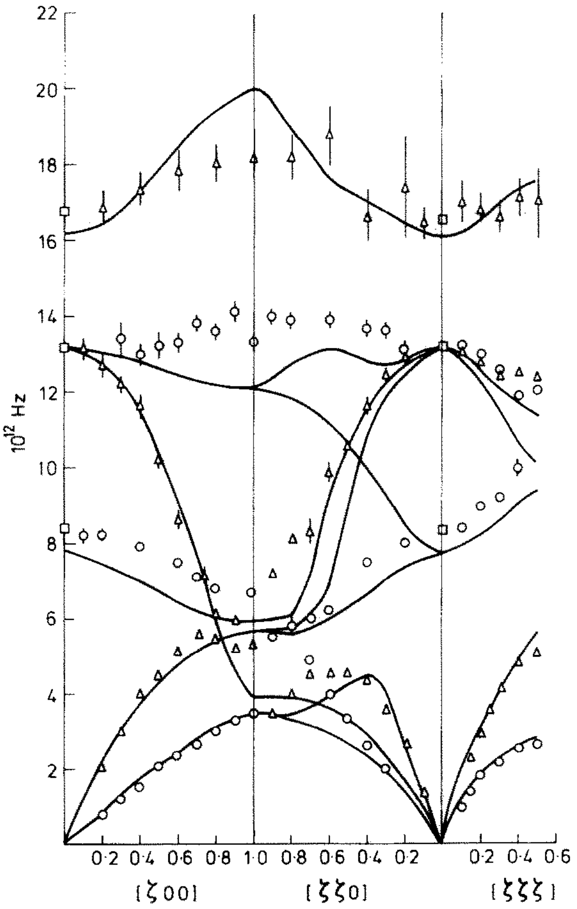

Fig. 1. Phonon spectrum of $UO_2$. The experimental data are from Dolling et al. [13]; the full lines are our calculations using Catlow's potential.

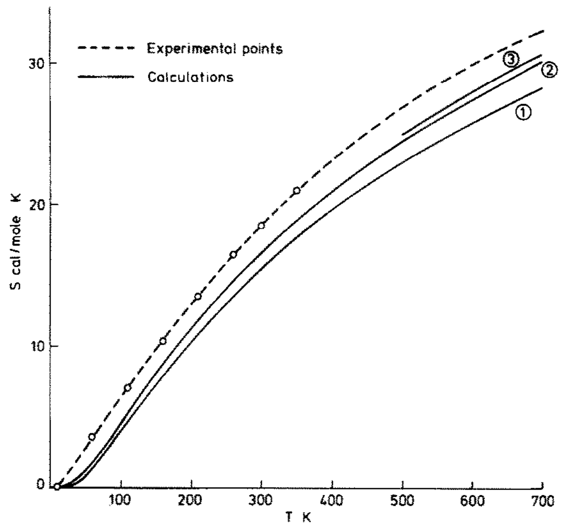

Fig. 2. Entropies for $UO_2$ in cal/mol · K from powder experiments and from theory. (1) Cell 2 × 2 × 2, sampled at $\boldsymbol{k}$ = (0, 0, 0). (2) Cell 2 × 2 × 2, sampled at $\boldsymbol{k}$ = (0, 0, 0), (1/2, 0, 0). (3) Cell 2 × 4 × 2, sampled at $\boldsymbol{k}$ = (0, 0, 0).

empirical equation of Kerrisk and Clifton [10] for $C_v$ using an Einstein-type model (fig. 3).

These results give some confidence that the method for calculating the partition function proposed in section 2 is giving proper weight to the physically important areas of $\boldsymbol{k}$ space.

## 4. Calculations on the electronic defects in $UO_2$

We shall consider the electronic defects using the small polaron model; that is to say that the electrons promoted from the valence hand are considered as localised on $U^{3+}$ cations. To make the necessary calculations we shall assume that the only effect of an electron leaving or being attached to a uranium ion is on the ion charge (i.e. we assume the uranium shell charges and the uranium–oxygen potentials are the same as in the perfect lattice).

We begin by calculating the Helmholz energy of formation and entropy of formation of the defect on the assumption that the defect density is sufficiently low so that the hole and electron states do not interact. The relevant data and results appear in tables 2 and 3. We have considered two estimates of the partition function: One where the $\boldsymbol{k}$ = (0.0, 0.0, 0.0) point alone is considered, and one where the $\boldsymbol{k}$ = (1.0, 0.0, 0.0) point is considered as well. The second calculation should be the more accurate. The first case (A) gives an entropy of formation of 9.1 cal/mol · K in the range 1800–3000 K and a Helmholz free energy of formation as shown in fig. 4. Case B gives a lower entropy of formation of 7.3 cal/mol · K and a correspondingly higher free energy of formation.

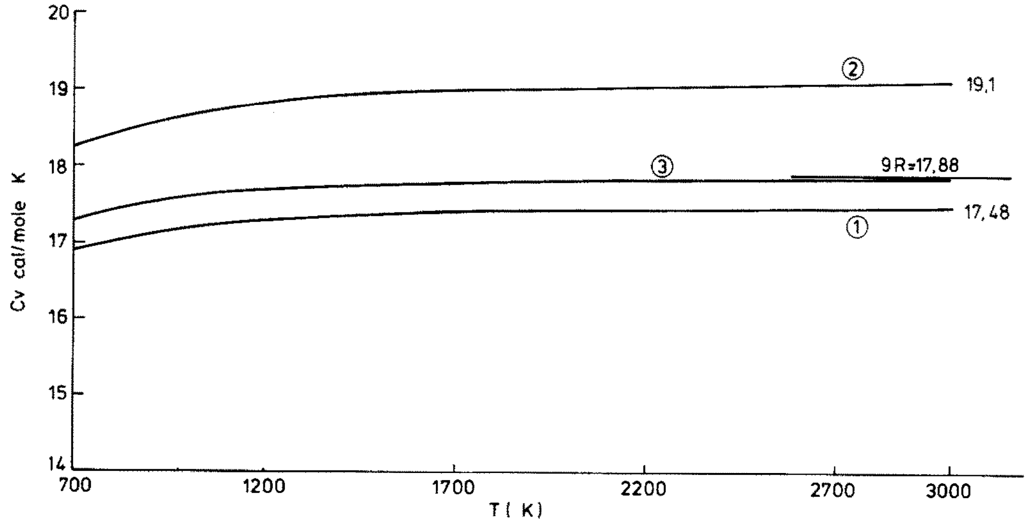

Fig. 3. Specific heat of $UO_2$ in cal/mol · K at constant volume, from Kerrick (1972) compared with theory. (1) Cell 4 × 4 × 2, sampled at $\boldsymbol{k}$ = (0, 0, 0). (2) Experiment; the Dulong–Petit limit is shown. (3) Cell 2 × 2 × 2, sampled at $\boldsymbol{k}$ = (1, 0, 0). Note that the origin does not correspond to $C_V$ = 0.

Table 2
Data for calculation of internal energy of electronic defects (Grant and Pyper [15])

Ionisation potential for $U^{4+} \rightarrow U^{5+}$ [I.P.(V)] = 46.57 eV
Ionisation potential for $U^{3+} \rightarrow U^{4+}$ [I.P.(IV)] = 31.86 eV

$\Delta U = \Delta U(\text{HADES}) + \text{I.P.(V)} - \text{I.P.(IV)}$

| | |
|---|---|
| Electron–hole pair | |
| (i) at infinite separation | 1.74 eV (per atom) |
| (ii) nearest neighbours along (100) direction | 1.64 eV (per atom) |
| (iii) nearest neighbours along (100) direction | 1.65 eV (per atom) |

For neither the $U^{3+}$ nor the $U^{5+}$ defect is there a recognisable local mode centred on the defects. However in both cases soft modes do appear. In the case of $U^{3+}$ a mode appears at 19 $cm^{-1}$ corresponding to a twisting motion of the oxygen sub-lattice about the defect. This mode also appears for the $U^{5+}$ defect at 49 $cm^{-1}$ and another mode involving the $U^{4+}$ ions appears at 56 $cm^{-1}$.

We also consider the case where electron and holes are localised close together. Here we consider a $U^{3+}$ ion and a $U^{5+}$ ion as nearest neighbours in the [110] direction in a cluster containing all the nearest neighbours to this defect. Here we must take a larger repeating unit (four fcc cells in square array in the (001) plane). Here we obtain an entropy of formation of 6.80 cal/mol · K for the temperature range. The value does not depend significantly on the orientation of the defect, and is little different from the case where the electron and hole are at large distances from one another.

Table 3
HADES calculation of internal energy of formation of defects

| | |
|---|---|
| Electron–hole pair | |
| (i) at infinite separation | −11.24 eV |
| (ii) nearest neighbours along (100) direction | −11.43 eV |
| (iii) nearest neighbours along (110) direction | −11.41 eV |
| Frenkel pair ($O^{2-}$ interstitial) | |
| (i) at infinite separation | 5.12 eV |
| (ii) nearest neighbours along (111) direction | 5.20 eV |
| Frenkel pair ($O^{-}$ interstitial) | |
| at infinite separation | 8.9 eV |
| Frenkel pair ($O^{0}$ interstitial) | |
| at infinite separation | 16.94 eV |

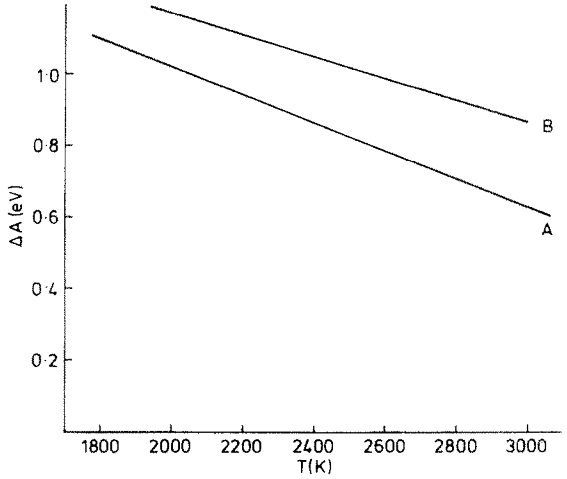

Fig. 4. Helmholz free energy of formation of the electron–hole pair assuming electron and hole are well separated. (A) Considering the $\boldsymbol{k}$ = (0.0, 0.0, 0.0) point only. (B) Considering the points $\boldsymbol{k}$ = (0.0, 0.0, 0.0) and $\boldsymbol{k}$ = (1.0, 0.0, 0.0).

From these figures we may readily obtain a value for the concentration of defects assuming the reaction

$$2\,U^{4+} \rightleftharpoons U^{5+} + U^{3+}$$

has reached equilibrium. We have

$$K_{eq} = \frac{[e][h]}{[U^{4+}]^2} = \frac{[e]^2}{[U^{4+}]^2} = \exp\left(-\frac{\Delta A}{k_B T}\right),$$

since the concentration of holes (or $U^{5+}$ ions) must equal the concentration of electrons ($U^{3+}$ ions). At a temperature of 2700 K we obtain a value for the equilibrium constant $2.73 \times 10^{-4}$, i.e. the concentration of electrons and of holes are both about 1.65%, and hence the total concentration of defects, counting both $U^{3+}$ and $U^{5+}$ is about 3.3%. A graph of this total concentration of defects over the temperature range of interest can readily be constructed (fig. 5).

It is clear that as the defect concentration mounts, the assumption implicit in the HADES calculation that the defect may be considered as enclosed in a block of pure (if distorted) crystal will break down; at these concentrations the effective elastic and

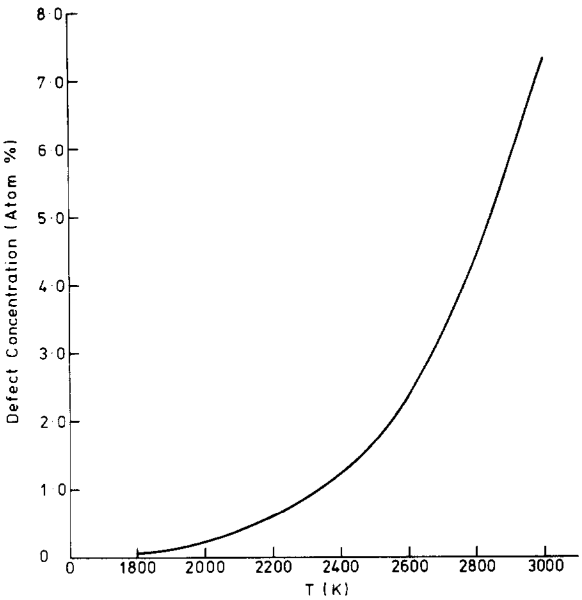

Fig. 5. Concentrations of electrons and holes, ignoring interactions and exclusion effects. The quoted concentration is $([U^{3+}] + [U^{5+}])/[U_{total}]$ in percent.

dielectric constants of the crystal will be different from the values used to obtain the potentials. In addition the expansion of the lattice at these temperatures will modify the results. For this reason it is hard to estimate our quantitative accuracy through the qualitative conclusions do not seem in doubt. Further calculations on these lines are desirable but the above is quite sufficient to indicate a considerable contribution from the electronic defects.

## 5. Calculations on the Frenkel defects on the oxygen sub-lattice

We now consider the effects of atomic defects on our predictions. The method of calculation is similar to that described in section 4. We consider the case where the vacancy and interstitial oxygen are isolated and where the interstitial is doubly charged. In this case the vibrational contribution to the entropy is negative, having a constant value of −1.0 cal/mol · K in the temperature range 2000–3000 K. Here there are two modes quite strongly localised on the defect, at 182 and 270 $\mathrm{cm}^{-1}$. The energy of formation of the defect is 5.1 eV per defect which gives a defect concentration of about $10^{-4}$ defects per lattice site.

It is clear that there are many more oxygen defects that might be considered, but on the basis of this one calculation it seems that the contribution of such defects to the anomalous specific heat will be much less than has been suggested. The atomic defect contribution may, however, be more significant close to the melting temperature.

## 6. Conclusions

The evidence from the anomalous specific heat of urania at high temperatures suggests that there is a source of entropy, of the order of 10 cal/mol · K. The calculations in this paper show that it is highly unlikely that Frenkel defects on the anion sub-lattice can provide more than a small proportion of this. However the contribution from electronic defects is large and could account for it. In the present paper we have considered only one small polaron reaction

$$2\,U^{4+} \rightarrow U^{3+} + U^{5+}\,.$$

It is apparent that there are others, which, although having a higher activation energy may make significant contributions close to the melting point. Also there is the configurational entropy term which we do not consider in this paper. With this in mind, we conclude that there is now strong evidence that electronic defects make a major contribution to the specific heat anomaly. A fuller analysis of the many contributions to the specific heat will be published separately [1].

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