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ANHARMONIC SPECIFIC HEAT OF SOLID UO_2

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The specific heat of UO_2 and related fluorite crystals contains a contribution from the anharmonic motion of the anion. We evaluate this term using thermodynamic perturbation theory and known parameters from neutron experiments. It is negligible (less than 2% of the total observed) up to 1273 K for UO_2, the highest temperatures for which anharmonicity parameters are known. Extension of the scattering experiments to higher temperatures will be necessary before anharmonic contributions to the specific heat anomaly can be assessed reliably and their importance relative to other conjectured mechanisms, notably electronic disorder, adjudged.

1. Introduction

Following the first attempted explanation [1] in terms of Frenkel defects of the anomalously large specific heat, $C_p(T)$, observed [2] in UO_2 between about 1300 K at its melting point (3100 K), an alternative possibility involving properties only of the perfect lattice was indicated by Hoch [3]. In view of the high temperatures involved, he argued that contributions from *anharmonic* lattice vibrations can no longer be ignored (as they often can be at lower temperatures), and he succeeded in fitting the then existing data to the following T-dependence:

$$C_p(T) = 3nRD(\theta_D/T) + dT^3 . \qquad (1)$$

The first term represents the usual harmonic contribution, parametrized by an effective single [3] Debye temperature ($\theta_D = 590$ K). Since $T >> \theta_D$, the Debye function is almost saturated and we obtain (with $n = 3$) the classical Neumann–Kopp value of $9R$ ($\simeq 17.88$ cal/mol · K). The second term incorporates the assumed anharmonic contribution, the particular T^3 dependence being *motivated* by earlier considerations [4] based on the theory of anharmonic lattice vibrations (for $T > 2000$ K, $d \simeq 10 \times 10^{-10}$ cal/mol K^4).

Detailed analysis of all subsequently measured enthalpy data (from which $C_p(T)$ is derived) reveals, however, that no definite choice can be made between the T-dependence given by eq. (1), the exponential T-dependence ($\sim T^{-2} \exp(-a/T)$ associated with the original defect mechanism, nor any unique combination of the two.

Later calculations by Catlow [5] (following earlier work by Catlow and Lidiard [6]) showed, however, that the Frenkel defects exploited by Szwarc [1] actually have a *higher* energy of formation than *electronic* defects associated with a disproportionation of the cation sub-lattice, according to:

$$2\,U^{4+} \rightleftharpoons U^{3+} + U^{5+} . \qquad (2)$$

In view of the influence such electronic excitations can have [7] on the high temperature thermophysical properties of solid UO_2, it is clearly of importance to be able to assess the magnitude of their contribution as accurately as possible. To do this in the case of the specific heat clearly necessitates knowledge of the lattice contribution and, in particular, its anharmonic components. It is the aim of the this paper to provide this information with the aid of thermodynamic perturbation theory and existing experimental data obtained from Debye–Waller studies [8]. Our results are also of relevance to considerations of the thermal conductivity UO_2 essential to analyses of the safety and reliability of fast reactors. Although we are able to give a general expression for the anharmonic lattice specific heat, its evaluation is restricted to $T <$ 1773 K, the highest temperature at which the necessary neutron scattering experiments have yet been performed. Accordingly the relative contributions to the observed anomaly in $C_p(T)$ of the electrons and lattice remain in doubt for the important, higher-temperature, regime.

2. Experimental data

The dominant contributor to anharmonic lattice vibrations in solid UO_2 is the anion sub-lattice. Since the sites are non-centrosymmetric (of $\bar{4}3m$ symmetric), the terms of odd order in atomic displacements are not suppressed as they are for the cations. It has proved possible [8] to account for the observed T-dependence of the Debye–Waller factors of UO_2 satisfactorily using an effective single *anion* potential $V_0(\boldsymbol{r})$ of the form:

$$V_0(\boldsymbol{r}) = V_h(\boldsymbol{r}) + v(\boldsymbol{r}) \,, \tag{3}$$

where the harmonic V_h and anharmonic v components have, respectively, the forms

$$\begin{aligned} V_h &\equiv \tfrac{1}{2}\alpha_0(x^2 + y^2 + z^2) \,, \\ v &\equiv \beta_0 xyz \,. \end{aligned} \tag{4}$$

Values of the parameters α_0 and β_0 have been obtained by Dawson et al. [8] from an analysis of the T-dependence of the Bragg scattering found by Willis [9] using neutrons. Subsequent experiments by Rouse et al. [10] showed these values to remain stable down to 300 K. Recently Willis and Hazell [11] have reanalysed the data. They conclude that, in the range 293 to 1373 K, the data are described well by eq. (4) with

$$\begin{aligned} \alpha_0 &= 4.2 \text{ eV/Å}^2 \,, \\ \beta_0 &= 7.3 \text{ eV/Å}^3 \,. \end{aligned} \tag{5}$$

However, it is important to realise that the harmonic and anharmonic components do not correspond to exactly the same ionic motions. In α_0, both acoustic and optic modes contribute, i.e. there are terms from modes in which both U and O move in phase as well as from those in which they move out of phase. In β_0, however, only the relative U–O motions are relevant. If we wish to represent the oxygen motion relative to uranium (as in the anharmonic term) by by a suitable Einstein oscillator, the acoustic components (which involve in-phase motion of anions and cations) should not be included. This can be seen by calculations assuming a harmonic Einstein oscillator of phonon energy $\hbar\omega_E$. We may deduce these values:

$\hbar\omega_E = 21$ meV	using α_0 of eq. (5);
$\hbar\omega_E = 70.5$ meV	from the fit of ref. [9] to Debye and Einstein components;
$\hbar\omega_E = 82.7$ meV	from the highest energy of the phonon dispersion curves [12].

In our subsequent analysis we shall use both the value in (5) and a value

$$\alpha_0^{\text{eff}} = \alpha_0\sqrt{(82.7/21)} = 1.98\alpha_0 \,, \tag{6}$$

which would correspond to the highest phonon energy. The two values should bracket any reasonable choice of harmonic term.

3. Calculations of the specific heat

The contribution to the specific heat deriving from $v \neq 0$ is most simply obtained using the thermodynamic perturbation theory of Peierls [13], in which the well-known difficulties associated with the actual non-perturbative nature of v (it is proportional to the total number of particles) are circumvented by working with the Helmholtz free energy, F. In terms of F, the specific heat $C_V(T)$ is given by:

$$C_V(T) = -T(\partial^2 F/\partial T^2)_V \,, \tag{7}$$

whilst the result for F can be written:

$$F = F_h + \langle v \rangle_h - \frac{1}{2k_B T}\left[\langle v^2 \rangle_h - \langle v \rangle_h^2\right] \,, \tag{8}$$

where $\langle\ \rangle_h$ denotes averaging over the distribution $\exp(-\beta V_h)$. Accordingly, from eq. (4), $\langle v \rangle_h \equiv 0$ and $\langle v^2 \rangle_h = (\beta_0^2/\alpha_0^3)(kT)^3$, whence we obtain (per anion) from eqs. (7) and (8)

$$C_V(T) = C_V^h(T) + (\beta_0^2/\alpha_0^3)\, k_B^2 T \,,$$

which gives, *per mole*,

$$C_V(T) = 9R + (2(\beta_0^2/\alpha_0^3)\, k_B R)\, T \,. \tag{9}$$

The first term on the right of (9) is simply the classical Neumann–Kopp value appropriate to triatomic UO_2 in the high temperature limit asumed in the perturbation theory, whilst the second is the required *anharmonic* contribution. With the parameter values given by eq. (5) it evaluates to

$$C_V^{anh}(T) \simeq 2.46 \times 10^{-4} T \text{ cal/mol} \cdot \text{K} ; \qquad (10)$$

with the altered harmonic value (6) we find

$$C_V^{anh}(T) \simeq 0.318 \times 10^{-4} T \text{ cal/mol} \cdot \text{K} .$$

4. Discussion

Deriving as it does from a convergent perturbation theory, $C_V^{anh}(T)$ given by eq. (9) is, in fact, the dominant contribution from anharnomicity, its linearity in T contrasting with the T^3 contribution conjectured by Hoch [3]. In comparing with Hoch, however, it must be remembered that his T^3 contribution is actually in $C_p(T)$ and not $C_V(T)$, the connection between which is given by the (exact) thermodynamic identity:

$$C_p(T) - C_V(T) = \beta^2(T)\, V(T)/K(T) , \qquad (11)$$

where the symbols have their usual meaning. Accordingly, the appropriate way to analyse the 'observed' $C_p(T)$ data is to first convert it to $C_V(T)$ using eq. (11) (using the T-dependent valued of β, V and K which have been tabulated for $300 \leqslant T \leqslant 2300$ K by Momin and Karkhanavala [14]) and then to decompose the $C_V(T)$ into its various hypothesized components, e.g.

$$C_V(T) = C_V^{lattice}(T) + C_V^{electronic}(T) ,$$

where

$$C_V^{lattice}(T) = C_V^{h}(T) + C_V^{anh}(T) .$$

Then, e.g.

$$C_V^{el}(T) = [C_p^{obs}(T) - C_V^{h}(T)] - \left[\frac{\beta^2(T)\, V(T)}{K(T)} + \begin{Bmatrix} 2.46 \\ \text{or} \\ 0.32 \end{Bmatrix} \times 10^{-4}\right] T . \qquad (12)$$

The net T-dependence displayed by the β, V, K data of ref. [14] can be represented by

$$\beta^2 V/K = (0.36 \times 10^{-3} + 0.81 \times 10^{-6} T) \text{ cal/mol} \cdot \text{K}^2 , \qquad (13)$$

from which the relative magnitudes of the last two items on the right of eq. (12) can be estimated. Thus, for example at $T = 1000$ K, the anharmonic contribution is only 21% (α_0 from (5)) or 3% (α_0^{eff} from (6)) of the $C_p - C_V$ correction term, and less than 2% of the total $C_V(T)$!

As mentioned repeatedly above, however, the validity of our anharmonic estimate (eq. (9)) is restricted to $T < 1273$ K. Since this is much lower than the temperature of the onset of the anomaly and of intrinsic semiconductivity it is, accordingly, not yet possible to quantitatively assess the relative magnitudes of the contributions to the anomaly of electrons and lattice. In fact, an *increase* in anharmonicity might be anticipated upon entering the regime of intrinsic semiconductivity in consequence of the phonon softening accompanying the increase in carrier density; in support of this the extra 5% decrease in vibrational frequencies found [13] in UO_2 over that in insulating ThO_2 might be noted.

5. Other comments on the anharmonic term

In any quantum model, the energy levels of an oscillator with a potential given by eqs. (4) and (5) are discrete. They are equally spaced when β_0 is zero, the spacing being $\hbar\omega_E$. The anharmonic terms disturb the spacing, for the levels are shifted. If the anharmonic terms are weak, the splittings can be written [15]

$$\hbar\omega = \hbar\omega_E \left(1 - \tfrac{1}{24}\lambda \frac{\hbar^2 \beta_0^2}{M\alpha_0^2}\right) , \qquad (14)$$

where λ is an integer depending on which levels are involved. It should be stressed that $\hbar^2\beta_0^2/24M\alpha_0^2$ is of order unity here: it is 3.2 if one uses α_0 corresponding to $\hbar\omega_E = 0.021$ eV, and 0.8 if one uses α_0 corresponding to $\hbar\omega_E = 0.083$ eV. In either case, the anharmonicity clearly constitutes a substantial perturbation on the precise energies of excited states. The specific heat involves the different combination of parameters β_0^2/α_0^3; the large corrections embodied in eq. (14) simply emphasise the uncertainties at very high temperatures.

In the fluorites, the specific heat shows a λ-type anomaly (see, e.g., the review in chapter 3 of ref. [16]). This involves defect production or other major

Table 1

Values of β_0^2/α_0^3; we quote both values of β_0^2/α_0^3 from neutron or X-ray data and also $\beta_0^2/(\alpha_0^{\mathrm{eff}})^3$, correcting the harmonic term to correspond to the longitudinal optic frequency; energies are in electron volts and lengths in angstroms

Crystal	Anion $\lvert\beta_0\rvert$	β_0^2/α_0^3	$\beta_0^2/(\alpha_0^{\mathrm{eff}})^3$
CaF_2	4.0 [a]	0.537	0.048
	2.8 [b]	0.263	0.023
BaF_2	1.6 [c]	0.625	0.055
UO_2	7.3 [d]	0.719	0.093

[a] Neutron data: B. Dawson, A.C. Hurley and V.W. Maslen, Proc. Roy. Soc. (London) A298 (1967) 289.

[b] X-ray data: H.B. Strock and B.W. Batterman, Phys. Rev. B5 (1972) 2337.

[c] 900 K data: M.J. Cooper, K.D. Rouse and B.T.M. Willis, Acta Cryst. A24 (1968) 484.

[d] Data as in the main text.

deviations from the harmonic approximation, and is not covered by our theory. We note that, even in these cases, the anion anharmonicity (deduced from data listed in chapter 2 of ref. [16]) gives a negligible contribution to the specific heat. The values of β_0^2/α_0^3 are listed in table 1.

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