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ANALYSIS OF THE SPECIFIC HEAT IN SOLID AR AND KR[*]

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ABSTRACT

The temperature dependence of the specific heat at constant pressure (C_p vs T) is analyzed in solid Ar and Kr applying a method developed by the author. The values and temperature behaviours deduced for the anharmonic contributions to C_p vs T, the Debye temperature (T_D vs T) and for the activation energy (E_f) and formation entropy (S_f) required to create a vacancy will be compared with previous analyses, obtaining additional support to the used method of analysis.

The aim of this work is to analyze the reported C_p vs T in solid Ar and Kr (1,2) by recourse to a method developed to include the anharmonic effects (3), in order to evaluate: a) the difference between C_p and C_v (specific heat at constant volume V) as a function of temperature; b) T_D vs T; and c) E_f and S_f. All these quantities are determined and compared with the results obtained in Ref. 2, and the agreement is found to be very reasonable, therefore bringing additional support to the formalism developed in Ref. 3. It may be mentioned that in Ref. 2 C_v is obtained from C_p by means of the standard expression $C_p - C_v = \alpha^2 T/\rho \chi_T$ (4), where α is the volumetric thermal expansion coefficient, ρ the density and χ_T is the isothermal compressibility.

Ar and Kr are isomorphous, crystallizing in a face-centred cubic lattice, with one atom per primitive cell, therefore the only vibrational modes are the acoustic ones. Thus, the appropiate expression to evaluate C_p vs T is (3)

$$C_p = \frac{9RX^{-3}}{(1 - CT)} \int_0^X \frac{u^4 e^u du}{(e^u - 1)^2} + R \exp(S_f/k) (E_f/kT)^2 \exp(-E_f/kT) \qquad (1)$$

where $X=T_D/T$; $T_D=T_{oD}(1 - CT)$. The last term is due to lattice vacancy formation. The parameters obtained, by fitting with a non-linear least-squares procedure (5), are:

Ar: $T_D = 86.23(1 - 3.036\ 10^{-3}\ T)$ K --- $E_f/k = (581 \pm 40)$ K
$R \exp(S_f/k) = (123 \pm 40)$ J mol^{-1} K^{-1}

Kr: $T_D = 66.37(1 - 2.277\ 10^{-3}\ T)$ K --- $E_f/k = (761 \pm 43)$ K
$R \exp(S_f/k) = (92.5 \pm 24)$ J mol^{-1} K^{-1}

Fig. 1 shows a comparison of the actual data (1,2) and the values pro-

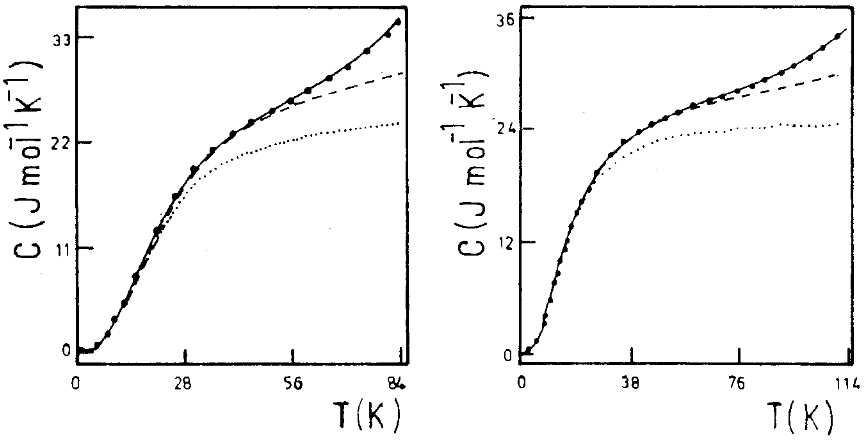

Fig. 1 : The left and right figures correspond to Ar and Kr respectively. Full circles indicate actual data, and the full lines are the fits obtained in this work. As may be seen the agreement is, in both cases, excellent. The dashed lines are obtained from the full lines by substructing the contribution due to vacancy formation. The dotted lines are obtained from the dashed lines by substracting the anharmonic contributions.

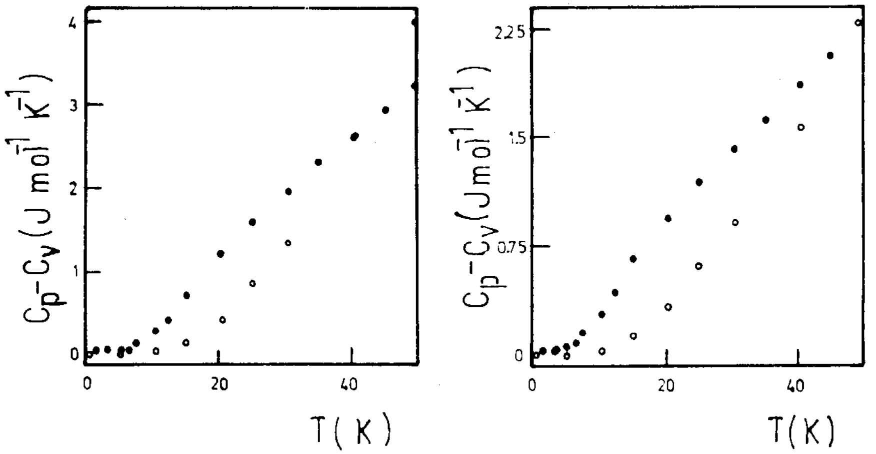

Fig. 2: Comparison of (C_p - C_V) vs T as evaluated in Ref. 2 (circles) and in this work (full circles), for Ar and Kr, respectively left and right figures.

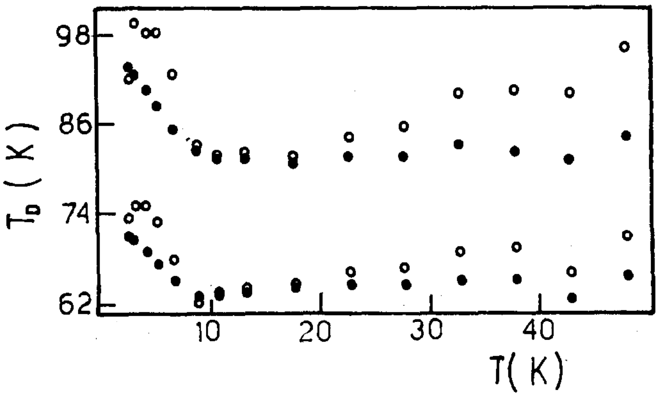

Fig. 3: The upper and lower pair of curves correspond to Ar and Kr Debye's temperatures respectively. Open circles represent $T_D(V(T=0), T)$ vs T, while full circles indicate $T_D(V(T),T)$ vs T.

duced by the above given parameters substituted into Eq. 1. As may be seen both fits are excellent. The values for E_f and S_f agree well, within experimental uncertainties, with those determine in Ref. 2. The Debye temperatures do not agree so well with those previously determined (2), but that is due to the particular temperature dependence we have assumed for T_D vs T. If T_D is taken as T_{oD} for all T, we may evaluate $C_V(V(T=0),T)$, where C_V is the specific heat at constant volume, and in this form we determine $(C_p - C_V)$ vs T which is shown in Fig. 2 along with the values determined in Ref. (2). It may be mentioned that in Ref. 2 what is actually determined is $C_V(V(T),T)$, and this may be the reason for the discrepancies shown in Fig. 2. In order to improve the determination of T_D vs T we may assume that T_D does not change too much between two adjacent temperatures; in this form Eq. 1 produces a system of two equations, one at each T, with two unknowns: T_{oD} and C. The results obtained using the smoothed data given in Refs. 1 and 2 are shown in Fig. 3. It may be mentioned that at low T ($T < 10$ K) large values for C are determined, indicating the existence of important anharmonicities. The increase in T_D at higher temperatures also reveals the presence of growing anharmonicities, in agreement with the conclusions in Ref. 2.

This work shows how easily activation energies, volume and anharmonic effects may be obtained by using the procedure described in Ref. 3, not requiring, when optical modes are absent, of any additional information to fully analyze C_p vs T (6).

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