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CORRECTIONS TO THE SPECIFIC HEAT EXPRESSION IN ORDER TO INCLUDE ANHARMONIC EFFECTS*

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ABSTRACT

The aim of this work is to develop a formalism allowing a direct and simple analysis of the temperature dependence of the specific heat at constant pressure (C_p vs T), which is the quantity rendered by experiment. This formalism permits to determine some of the crystal normal mode frequencies and their temperature dependence (W_x vs T; $x \equiv \vec{q}s$; $\vec{q}$ and s indicate a phonon wave vector in the first Brillouin Zone and its polarization, respectively), anharmonic contributions to C_p vs T, activation energies, temperature dependence of the Debye temperature (T_D vs T), etc.

In this work we will closely follow the notation and relevant results obtained by Wallace (1). The thermodynamic functions (free energy, entropy, specific heat, etc.) may be written in terms of the harmonic (w_x) and anharmonic (Δ_x) contributions to $W_x = w_x + \Delta_x$. These W_x, which are the normal mode frequencies measured by means of spectroscopic techniques (inelastic neutron scattering, Raman and Infra-Red Scatterings, etc.), correspond to those of the renormalized phonons. The point is that, if we try to evaluate thermodynamic functions employing the harmonic formulas with the W_x substituting the w_x, the anharmonic contribution will not, in general, be correctly evaluated (1).

There are two ways to solve the problem. The first is to experimentally separate the harmonic and the anharmonic contributions to W_x. The second is to work out correct formulas, i.e. formulas in which only the experimentally measured W_x are used, which properly evaluate the thermodynamic functions. Since, in general, only the W_x are determined we will stick to the second alternative, and also, from now on we will restrict ourselves to the analysis of C_p vs T.

It has been shown that in an expansion of the crystal potential energy, in a power series of the displacements of the atoms measured from their equilibrium positions, the cubic and quartic terms contribute to the same order giving complicated expressions, which are given in full in Ref. 1, to evaluate Δ_x. It is also shown in Ref. 1 that, to leading order, Δ_x are volume independent, and therefore they will be considered to depend on T, since the w_x depend only on volume (V) we may write

$$W_x(V,T) = w_x(V) + \Delta_x(T) \qquad (1)$$

Proceedings of ICTA 85, Bratislava

Following Ref. 1 it can be shown that

$$C_p = \sum_x \hbar \left[W_x - T \left(\frac{\partial W_x}{\partial T} \right)_p \right] \left(\frac{\partial n_x}{\partial T} \right)_V \tag{2}$$

where $\hbar$ is Planck's constant divided by 6.283185, and n_x is the x-phonon Bose population factor. The following comments on Eq. 2 are in order:

1) It may be generalized to anysotropic cases.

2) The first term contains the harmonic specific heat, which reaches a constant value given by the Dulong and Petit law (1) at high T; while the second term gives, in first order, a linear temperature contribution whose sign depends upon that of $(\partial W_x/\partial T)_p$, as expected (1).

3) It may be considered valid as far as the anharmonicities are only a small perturbation, which is the general case.

4) It allows a direct and inmediate comparison of C_p vs T theory and experiment, requiring as additional information $W_x(T,P)$, which are easily determine by spectroscopic means.

5) It makes unnecessary the knowledge of the thermal expansion and bulk modulus tensors as functions of temperature. This quantities are needed in order to correct the experimental information (C_p) which is obtained at constant pressure to that which would be obtained had the strain been kept constant (C_V or equivalent), therefore allowing a meaningful comparison of theory and experiment. It may also be mentioned that the vast mayority of specific heat data is gathered at constant room pressure.

6) Assuming that: a) the acoustic and optical modes may be treated with Debye's and Einstein's models; b) the W_x exhibit a linear temperature dependence, reflecting the strains effect due to temperature changes, written in the form

$$W_x = W_{ox} (1 - C_x T) \tag{3}$$

where W_{ox} is W_x at T=0 K and C_x is a, generally positive, constant; and c) the optic modes exhibit negligible dispersion, then Eq. 1 may be written as

$$C_p(T) = R \left\{ \sum_{j\,\text{optic}} \left[\frac{1}{(1 - C_j T)} \frac{X_j^2 \exp(X_j)}{(\exp(X_j) - 1)^2} \right] + \frac{9\,(T/T_D)^3}{(1 - C_D T)} \int_0^{T_D/T} \frac{x^4\, e^x\, dx}{(e^x - 1)^2} \right\} \tag{4}$$

where R is the gas constant; the sum extends over all of the optical branches; $X_j=\hbar W_j/kT$ (k being Boltzmann's constant). This expression for C_p vs T reduces to that well known (1) by simply considering W_x to be temperature independent.

REFERENCES

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1 D. C. Wallace, "Thermodynamics of Crystals", Wiley, New York, 1972.
2 C. A. Martín, companion papers in this journal.