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Simple treatment of anharmonic effects on the specific heat

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Abstract. The comparison of the specific heat–temperature dependence data with the values which may be calculated using the measured values as a function of temperature for the normal mode frequencies is a difficult task since the data are gathered at constant pressure, whilst the theory is worked out at constant volume. In this work a formalism is developed which allows the calculation mentioned above to be carried out in a direct and simple manner. This formalism is successfully applied to the case of solid halogens Cl_2 and Br_2 .

1. Introduction

The specific heat is among the most fundamental thermodynamic properties of any physical system. Experimental data (C_p versus T) are generally gathered at constant room pressure, while the theory is worked out at constant configuration, which for the present case, and for simplicity, will be taken as constant volume (C_V versus T), since extension to more general cases may easily be made. The symbols to be used in this work have their standard meaning and closely follow those in the book by Wallace (1972a). To analyse C_p versus T data it is necessary to convert C_p to C_V . The most common procedure is to use the well known thermodynamic relation (Wallace 1972b)

$$C_V = C_p - TV\beta B_T \quad (1)$$

However, β versus T and B_T versus T are rarely available data (and in a non-cubic case they are second-rank tensors). Also, this relation produces C_V where V is $V(T, P)$, while what is actually needed to carry out a meaningful analysis is C_{V_0} , i.e. at a fixed volume.

In this work we shall restrict ourselves to analysing C_p versus T in crystalline insulating solids. The analysis of C_V is carried out in terms of phonons following, generally, the models developed by Debye and Einstein (Wallace 1972c) to account for the acoustic and optic phonon contributions, respectively. The theory is based on the harmonic approximation of the lattice dynamics plus corrections due to the anharmonic cubic and quartic terms in a power series expansion of the crystalline potential. These corrections are extremely difficult to evaluate since it is necessary to know the interatomic forces precisely, which is not the general case. Qualitatively, they add a linear temperature term to C_V at high temperatures. In the rest of this work it will be assumed that these

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cubic and quartic terms are very small perturbations compared with the quadratic term. The main consequences of these anharmonic terms are to produce a shift in the phonon frequencies and a finite phonon lifetime. Therefore, we may write (Wallace 1972d) $\Omega_\chi = \omega_\chi + \Delta_\chi$, where Ω_χ indicates the experimentally measured angular frequency of the χ phonon ($\chi = qs$, q is a reciprocal vector within the first Brillouin zone, and s indicates the phonon branch), ω_χ and Δ_χ are the harmonic frequency and the correction produced by the cubic and quartic anharmonic terms, respectively. To a good approximation, ω_χ depends only on V , while Δ_χ depends only on T (Wallace 1972e), i.e.

$$\Omega_\chi(V, T) = \omega_\chi(V) + \Delta_\chi(T). \quad (2)$$

The total C_V may be written as

$$C_V = C_{VH} + C_{VA} \quad (3)$$

$$C_{VH} = \hbar \omega_\chi (\delta n_\chi / \delta T)_V \quad (4)$$

$$C_{VA} = -T \sum_\chi \hbar \Delta_\chi \left(\frac{\delta^2 n_\chi}{\delta T^2} \right)_V - T \sum_{\chi\chi'} \hbar \theta_{\chi\chi'} \left(\frac{\delta n_\chi}{\delta T} \right)_V \left(\frac{\delta n_{\chi'}}{\delta T} \right)_V \quad (5)$$

where C_{VH} and C_{VA} are the contributions of the harmonic and (cubic and quartic) anharmonic terms to C_V , respectively; $\theta_{\chi\chi'}$ is a complicated expression involving third- and fourth-order derivatives of the crystal potential and the harmonic frequencies of the χ and χ' phonons; n_χ is the Bose population factor of the χ phonon (Wallace 1972f). Let us use a hat ($\hat{\quad}$) to indicate that the harmonic function has been evaluated using Ω_χ instead of ω_χ . Combining equations (3)–(5) we obtain

$$C_V - \hat{C}_{VH} = -T \sum_{\chi\chi'} \hbar \theta_{\chi\chi'} \left(\frac{\delta n_\chi}{\delta T} \right)_V \left(\frac{\delta n_{\chi'}}{\delta T} \right)_V. \quad (6)$$

The right-hand side of this equation may be written as (Wallace 1972g)

$$-T \sum_{\chi\chi'} \hbar \theta_{\chi\chi'} \left(\frac{\delta n_\chi}{\delta T} \right)_V \left(\frac{\delta n_{\chi'}}{\delta T} \right)_V = -TV\beta^2 B_T - T \sum_\chi \hbar \left(\frac{\delta \Omega_\chi}{\delta T} \right)_P \left(\frac{\delta n_\chi}{\delta T} \right)_V \quad (7)$$

and combining equations (1), (6) and (7) we obtain

$$C_P = \hat{C}_{VH} - T \sum_\chi \hbar \left(\frac{\delta \Omega_\chi}{\delta T} \right)_P \left(\frac{\delta n_\chi}{\delta T} \right)_V. \quad (8)$$

Since the anharmonicities are very small, we may change $(\delta n_\chi / \delta T)_V$ to $(\delta \hat{n}_\chi / \delta T)_V$ in equation (8). Thus,

$$C_P = \sum_\chi \hbar \left[\Omega_\chi - T \left(\frac{\delta \Omega_\chi}{\delta T} \right)_P \right] \left(\frac{\delta \hat{n}_\chi}{\delta T} \right)_V. \quad (9)$$

This equation allows direct comparison between theory and experiment, making knowledge of β and B_T , among other quantities, therefore unnecessary. At high temperatures and on the assumption that Ω_χ is constant, the first term in equation (9) exhibits asymptotic behaviour corresponding to the Dulong and Petit law. Also, $C_V(V_0 = V(P_0, T_0))$ may be evaluated, substituting the corresponding value for $\Omega_\chi(V_0, T_0)$. The second term gives, to first order, a linear temperature contribution whose sign depends upon that of $(\delta \Omega_\chi / \delta T)_P$ as is reasonably expected.

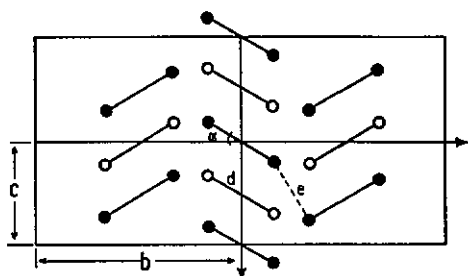


Figure 1. Crystalline structure of the solid halogens as viewed along the a axis. Molecules indicated by open circles are shifted by $\pm a/2$ from those represented by full circles.

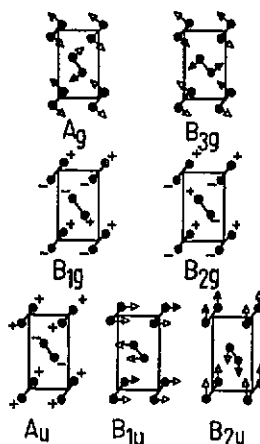


Figure 2. The diagrams show the zone centre eigenvectors of the optic modes together with their symmetry species. Motions perpendicular to the plane of the figure are denoted by + or -, and those in the plane by arrows.

On the assumption that the acoustic and optical modes may exhibit a linear temperature behaviour written in the form

$$\Omega_x = \Omega_{0x}(1 - C_x T) \quad (10)$$

and the contributions to the specific heat may be treated with the models of Debye and Einstein respectively, then equation (9) may be written as

$$C_p = Nk \sum_{j\text{optic}} \frac{1}{1 - C_j T [\exp(x_j) - 1]^2} + \frac{9}{1 - C_D T} \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^2 \exp(x)}{[\exp(x) - 1]^2} dx \quad (11)$$

where $x_j = \hbar\Omega_j/kT$. If all $C_j = 0$ and $C_D = 0$ this expression reduces to the well known formula in standard textbooks (Kittel 1971).

2. Examples

Equation (11) will be applied to the analysis of C_p versus T data in Cl_2 and Br_2 (Giaque and Powell 1939, Hildebrand *et al* 1958) from low temperatures up to their melting points. They are crystallographically isomorphous, the lattice being face centred orthorhombic, of space group $Cmca$ (D_{2h}^{18}) with two diatomic molecules per primitive cell (Collin 1952, 1956). These are laid down in two-dimensional arrays parallel to the bc plane as shown in figure 2. Mode A_u is Raman and IR inactive. In order to apply equation (11), the frequencies and their temperature dependences have to be known for all the modes (hereafter the frequencies will be indicated by ν_x measured in reciprocal centimetres, their relation to Ω_x being $\Omega_x = 2\pi c\nu_x$, with c the speed of light in centimetres per second). Collected data on the frequencies of the librational modes for Cl_2

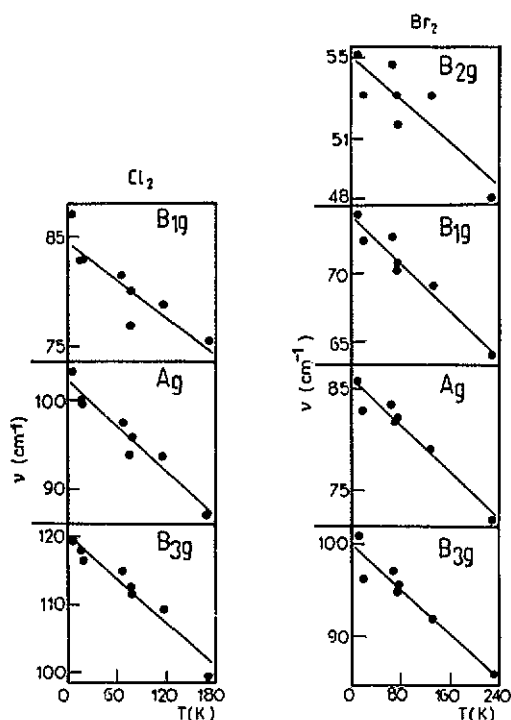


Figure 3. Collected available data (●) for the optical frequencies of the solid Cl_2 and Br_2 . A linear temperature dependence provides a good description of data in all cases. The parameters associated with the various straight lines are given in table 1.

and Br_2 are shown in figure 3 (Cahill and Leroi 1969, Suzuki *et al* 1969a, b, Anderson and Sun 1970, Dumas *et al* 1974, Halac 1983, Halac and Bonadeo 1983; the temperature behaviour may be taken as linear from 4 K up to their melting points, and the corresponding parameters to equation (10), namely $\Omega_{0\chi}$ and C_χ , are given in table 1. This exhausts all the known experimental information on the librational frequencies; therefore, in order to evaluate C_p using equation (11), some assumptions will have to be made on the remaining frequencies. On the basis of the information shown in figure 3 it seems reasonable to assume a linear temperature dependence for the frequencies of the remaining modes including the acoustic modes, since these are of an essentially translatory character. An additional and very convenient observation from the values of $\nu_{0\chi}$ and C_χ with the superscript b shown in table 1, which correspond to the least-squares fit using equation (10) to the various data on mode frequencies depicted in figure 3, is that the values of C_χ may be written as $C_\chi = F\nu_{0\chi}$. In fact, in solid chlorine we obtain $(8.03 \pm 1.8) \times 10^{-6} \text{ cm K}^{-1}$, $(8.08 \pm 0.80) \times 10^{-6} \text{ cm K}^{-1}$ and $(7.64 \pm 0.80) \times 10^{-6} \text{ cm K}^{-1}$, values corresponding to the B_{1g} , A_g and B_{3g} modes, respectively. For solid bromine we obtain $(8.93 \pm 2.5) \times 10^{-6} \text{ cm K}^{-1}$, $(7.70 \pm 0.90) \times 10^{-6} \text{ cm K}^{-1}$, $(7.94 \pm 0.90) \times 10^{-6} \text{ cm K}^{-1}$ and $(6.10 \pm 0.90) \times 10^{-6} \text{ cm K}^{-1}$, as the F -values corresponding to the B_{2g} , B_{1g} , A_g and B_{3g} modes, respectively. Since these modes describe librational motions, the values for F will be indicated as F_l , while those for translatory modes will be indicated by F_t . As is seen, the various F -values for each compound may be considered, to a reasonable degree of approximation, as equal. Therefore, average values for F_l of $(7.29 \pm 0.20) \times 10^{-6} \text{ cm K}^{-1}$ and $(7.74 \pm 0.80) \times 10^{-6} \text{ cm K}^{-1}$ are deduced for solid chlorine and bromine, respectively. A similar approximation will be made for the

Table 1. Values deduced for solid Cl₂ and Br₂. The errors in all cases correspond to the standard deviations deduced from the various least-squares fitting procedures, according to Deming (1964).

Mode	Chlorine		Bromine	
	ν_0 (cm ⁻¹)	C (10 ⁴ K ⁻¹)	ν_0 (cm ⁻¹)	C (10 ⁴ K ⁻¹)
B _{2g}	73.6 ± 0.9 ^a	16.69 ± 0.50 ^a	54.9 ± 0.5 ^b	4.90 ± 1.3 ^b
B _{1g}	84.7 ± 1.1 ^b	6.8 ± 1.4 ^b	74.0 ± 0.6 ^b	5.70 ± 0.6 ^b
A _g	102.1 ± 0.7 ^b	8.25 ± 0.80 ^b	86.2 ± 0.8 ^b	6.84 ± 0.73 ^b
B _{3g}	120.7 ± 1.0 ^b	9.22 ± 0.90 ^b	100.2 ± 1.0 ^b	6.11 ± 0.81 ^b
A _u	32.8 ± 2.0 ^c	3.34 ± 0.28 ^c	32.9 ± 2.0 ^c	3.36 ± 0.34 ^c
B _{2u}	65.3 ± 2.0 ^d	6.64 ± 0.37 ^d	51.1 ± 2.0 ^d	5.23 ± 0.52 ^d
B _{1u}	97.4 ± 2.0 ^d	9.91 ± 0.45 ^d	78.9 ± 2.0 ^d	8.08 ± 0.81 ^d
A _g	530.4 ^d	0 ^d	295 ^d	0 ^d
B _{3g}	542.0 ^d	0 ^d	302 ^d	0 ^d
Acoustic	95.3 ± 0.7 ^c	9.69 ± 0.31 ^c	62.4 ± 0.6 ^c	6.39 ± 0.69 ^c
E_i/k (K)	898 ± 10 ^c		1400 ± 15 ^c	
S_i/k	1.5 ^c		1.5 ^c	
F_i (cm ⁻¹ K) ⁻¹	(7.92 ± 0.20) 10 ^{-6f}		(7.74 ± 0.80) 10 ^{-6f}	
F_i (cm ⁻¹ K) ⁻¹	(10.17 ± 0.25) 10 ^{-6f}		(10.24 ± 0.24) 10 ^{-6c}	

^a Values deduced by Martín (1985).^b Values deduced in this work by least-squares fitting with equation (10) the various sets of data shown in figure 3.^c Values deduced in this work by least-squares fitting to C_p versus T data using equations (11)–(13).^d Values deduced in this work by least-squares fitting of C_p versus T data using equations (11)–(13), with the ν_x given by equation (10) and forcing them to go through the reported values at 77 K (Cahill and Leroi 1969, Suzuki *et al* 1969a, b, Anderson and Sun 1970, Halac 1983, Halac and Bonadeo 1983, Dumas *et al* 1974).^e Assumed values according to Seeger *et al* (1970).^f Average values deduced from those values indicated by^b.

translatory (F_i) modes. An exception, for unknown reasons, to this approximation is that of mode B_{2g} for solid chlorine; however, this mode is somewhat anomalous since it has not been detected by either Raman or IR spectroscopies, and it certainly should have been. Therefore we shall write

$$\nu_x = \nu_{0x}(1 - F\nu_{0x}T). \quad (12)$$

This results in the introduction of a minimum number of parameters to be determined through the fit of C_p versus T using equation (11). The procedures to determine the ν_x for all the modes in each compound are clearly stated in what follows.

2.1. Solid chlorine

The temperature dependence of the librational mode $\nu_{B_{2g}}$ was determined by analysing the temperature dependence of the nuclear quadrupole resonance transition frequency (Martín 1985). As mentioned above, this mode has not been detected either by Raman

or by IR spectroscopies, the probable reason being its strong temperature dependence. The temperature dependences of the $\nu_{B_{1g}}$, ν_{A_g} and $\nu_{B_{3g}}$ modes were determined by fitting the data shown in figure 3 using equation (10). The results are shown in table 1. The translatory modes are described by means of equation (12). The mode frequencies $\nu_{B_{2u}}$ and $\nu_{B_{1u}}$ are forced to go through the only available data gathered at 77 K (13). Therefore the parameters to be determined are ν_{0A_u} and ν_{0D} for the Debye frequency, and F_t . For the internal stretching mode frequencies, although they exhibit isotopic splitting (Cahill and Leroi 1969), average temperature-independent values were used, since because of their large magnitude they make a very small contribution to C_p at solid Cl_2 temperatures. Finally, it was found necessary to add the term

$$\Delta C_p = R \exp(S_f/k) (E_f/kT)^2 \exp(-E_f/kT) \quad (13)$$

to account for vacancy formation (Beaumont *et al* 1961), where S_f and E_f are the entropy and the energy associated with the creation of a vacancy. S_f was taken as $1.5k$ (Seeger *et al* 1970) while E_f was treated as a parameter to be determined. Therefore, the parameters to be determined are ν_{0A_u} , ν_{0D} , F_t and E_f .

2.2. Solid bromine

The four librational frequencies are treated in a similar form to the three librational modes $\nu_{B_{1g}}$, ν_{A_g} and $\nu_{B_{3g}}$ observed for Cl_2 . The three translatory frequencies $\nu_{B_{2u}}$, $\nu_{B_{1u}}$ and ν_{A_u} and the acoustic frequencies are handled analogously to those in Cl_2 . The internal stretching modes do not exhibit isotopic splitting and are also treated as temperature-independent frequencies. Vacancies are dealt with in a similar fashion to that described above for Cl_2 . Therefore, the parameters to be determined are ν_{0A_u} , ν_{0D} , F_t and E_f .

3. Results

The fits were carried out using a non-linear least-squares procedure (Deming 1964), and the parameters determined for the two compounds, as well as the results obtained from these parameters are presented in table 1. Figure 4 shows the results achieved for Cl_2 and Br_2 , respectively. As may be seen, the fits are excellent. This figure depicts the three main contributions to C_p versus T : curve 1 corresponds to the purely harmonic specific heat, i.e. where all the frequencies are temperature independent and take their values at 0 K; adding the effect of anharmonicities (shown in the inset as curve 4), i.e. allowing the temperature dependences indicated above for the various frequencies, curve 2 is obtained; finally, adding the vacancy contribution (shown in the inset as curve 5), curve 3 is obtained. The anharmonic contributions (curve 4 in the insets) exhibit, as expected, an essentially linear temperature behaviour. Curve 5 clearly indicates that there is point defect formation, assigned to vacancies in this case. The values determined for E_f are smaller than those reported (1335 ± 40 K and 1830 ± 50 K for Cl_2 and Br_2 , respectively) by Nakamura and Chihara (1967), and these discrepancies may be due to different choices of the specific heat backgrounds. However, the excellence of the fits and the reasonable values obtained for the various quantities shown in table 1 gives confidence and support to the present analyses and results. The values determined for the ν_{A_u} frequencies are in excellent agreement with those obtained by lattice dynamics calculations (Suzuki *et al* 1969a, b, Halac 1983, Burgos *et al* 1982, Pasternak *et al* 1977,

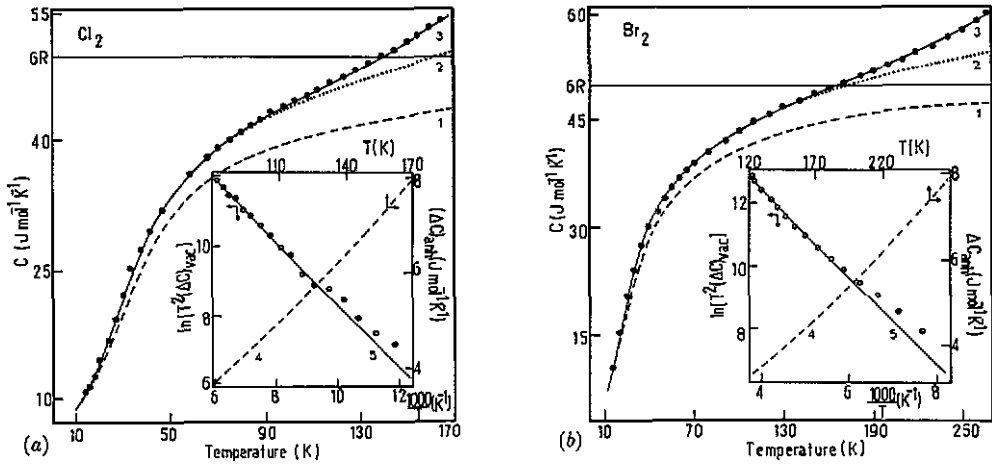


Figure 4. Results for (a) solid Cl_2 and (b) solid Br_2 . The full circles represent C_p versus T data (Giauque and Powell 1939, Hildebrand *et al* 1958). Curve 1 corresponds to the specific heat generated with temperature-independent normal-mode frequencies whose values are taken as those at 0 K, and shows the asymptotic high-temperature $6R$ classical value. Curve 2 corresponds to the specific heat generated with linear temperature-dependent normal-mode frequencies as indicated in text and whose values are given in table 1. Finally, if the creation of vacancies is accounted for in both cases and added to the isolated contribution (ΔC_{anh}) of the anharmonicities to the specific heat, curve 3 is obtained by subtracting curve 1 from curve 2. Curve 4 shows in all cases an essentially linear behaviour, as expected. The open circles for both Cl_2 and Br_2 are obtained by subtracting curve 2 from the full circles ($(\Delta C)_{\text{vac}}$) and this plot shows clearly that we are dealing with thermally activated point defects. Curve 5 is generated by subtracting curve 2 from curve 3. All these plots show that there is an excellent agreement between theory and experiment.

1978). On the other hand, ν_D seems to have in the two cases too high values compared with the fact that dispersion effects on the frequencies in equation (11) have been neglected. Lattice dynamics model calculations show the existence of large dispersion effects (Burgos *et al* 1982, Pasternak *et al* 1977, 1978); however, no experimental data are available to settle the point. The remaining frequencies and their temperature dependences will have to await testing until more experimental information becomes available. However, it must be pointed out that the values obtained in this work are very reasonable. A comment on the values of F_1 and F_t is in order. The values for F_1 , which are deduced from the raw data with a superscript b in table 1, are very similar for Cl_2 and Br_2 . This similarity would suggest that comparable values for F_t should be found for both compounds. In fact, as may also be seen in table 1, the values for F_t are also very similar, therefore giving additional support to the assumptions made, to the approximations involved and to the procedure itself.

The relevant point of this work is that of producing the correct formulae to allow direct dynamical analysis and interpretation of C_p versus T data, allowing straightforward comparison of these data with the measured Ω_x (both of these pieces of information, namely C_p versus T and Ω_x versus T , are easily accessed by experiment), and making it unnecessary to know β and B_T which are not easily obtained experimentally, mainly in the general case where they are tensorial quantities. Another useful property of equations (9) and (11) is that they allow one to evaluate easily the anharmonic contributions to C_p versus T which may be compared with theoretical calculations. Finally,

these equations provide the means to determine a 'background' specific heat in order to evaluate the other physical processes in progress (vacancy formation, phase transition, etc).

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