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SPECIFIC HEAT STUDY OF SOLID CHLORINE AND BROMINE*

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ABSTRACT

The specific heat at constant pressure as a function of temperature (C_p vs T) in solid Cl_2 and Br_2 is analyzed by recourse to a method develop in a companion paper. Values for the lattice frequencies, their temperature dependences and the Debye temperature (T_D) have been determined for both halogens. Activation energies corresponding to lattice vacancy formation were determined in both cases.

INTRODUCTION

Although C_p vs T has been measured in solid Cl_2 and Br_2 (1,2), a dynamical analysis like that proposed by Martín (3) has not been carried out in any of these halogens. They are isomorphous, crystallizing in a face centred orthorombic lattice, spatial group Cmca (D_{2h}^{18}), with two molecules per primitive unit cell (4,5), therefore there are twelve normal modes of vibration: nine optic and three acoustic. The optic modes may be divided into four librational, three translational and two internal stretching. The zone center eigenvectors for the optic modes are shown in Fig. 1 along with their symmetry species. Mode Au is both Raman and Infra-Red inactive. Collected data on the frequencies of the librational modes are shown in Fig. 2 (6-12). As may be seen a linear temperature dependence seems reasonable, and the parameters corresponding to the straight lines, written in the form $W_x=W_{ox}(1-C_xT)$, are given in Table 1 (the notation used throughout this paper is that used in Ref. 3). Mode B2g in Cl_2 has not been detected by Raman and Infra-Red spectroscopies, and the result shown in Fig. 2 has been deduced by analyzing the temperature dependence of the chlorine Nuclear Quadrupole Resonance transition frequency (13). This analysis also made possible the assignment of the various librational frequencies to their symmetry species, in agreement with Ref. 9.

In order to evaluate C_p vs T as indicated in Ref. 3 it is necessary to know the temperature dependence of the frequencies for all the modes. On the basis of the results shown in Fig. 2 it seems reasonable to adopt a linear temperature dependence for all the remaining mode frequencies including the acoustic modes since these are essentially translatory. The next question is what particular linear dependence is to be chosen for the modes not included in Fig. 2. Since experimental information is lacking,

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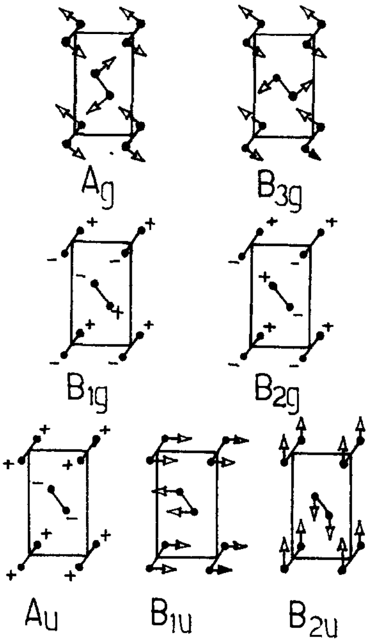


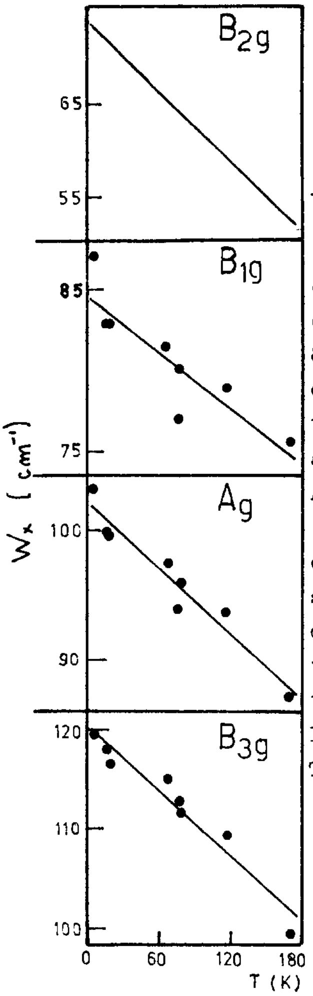
Fig. 1: Zone center eigenvectors for optic modes along with their symmetry species. Arrows indicate in-plane motion while + and - indicate out-of-plane motions.

and in order to introduce as few parameters to be adjusted as possible, we make a choice based on the following observation on the temperature dependence of the librational mode frequencies in Cl_2 and Br_2: from Fig. 2 and the values on Table 1 we find reasonable to write $W_x = W_{ox}(1 - F\ W_{ox}\ T)$, where F has different values for the librational and translational modes and for each of the halogens under investigation in this work. The internal stretching mode frequencies are considered temperature independent. The frequencies of the modes B2u and B1u have been given the above form forcing the straight line to go through the experimental values at liquid nitrogen temperatures (6); the acoustic and Au modes were given the above form. Therefore, the parameters to be fitted are F, W_{oAu} and T_D, where T_D is the Debye temperature.

At high temperatures an additional contribution was found necessary to be taken into account, which is attributed to vacancy formation. The term to be added to Eq. 4 in Ref. 3 is (14):

$$\Delta C_p = R \exp(S_f/k)\ (E_f/kT)^2 \exp(-E_f/kT) \qquad (1)$$

where S_f and E_f are the entropy and energy associated to the creation of



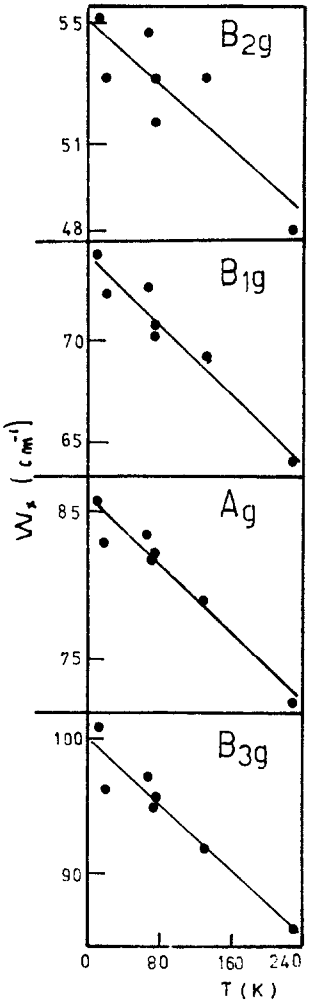


Fig. 2: Full circles correspond to frequency data of the various librational modes obtained from Refs. 8-14. The left column of figures correspond to Cl_2, while those at the right to Br_2. As may be seen, a linear temperature dependence provides a reasonable description of data. The parameters associated with the various straight lines are given in Table 1.

a vacancy. S_f was given a value of 1.5 k (15) (k and R are Boltzmann and gas constant, respectively). This additional contribution renders one more parameter to be adjusted in the fitting to C_p vs T, i.e. E_f.

RESULTS AND DISCUSSION

Fitting, as indicated above, by means of a non-linear least-squares procedure (16) the values for the parameters F, W_{0Au}, T_D and E_f shown in Table 1 are obtained. Fig. 3 shows the results achieved, and as may be seen the fits are excellent. Curve 1 corresponds to the specific heat assuming the mode frequencies are temperature independent, their values taken as those at 0 K; curve 2 is obtained adding to curve 1 the contribution

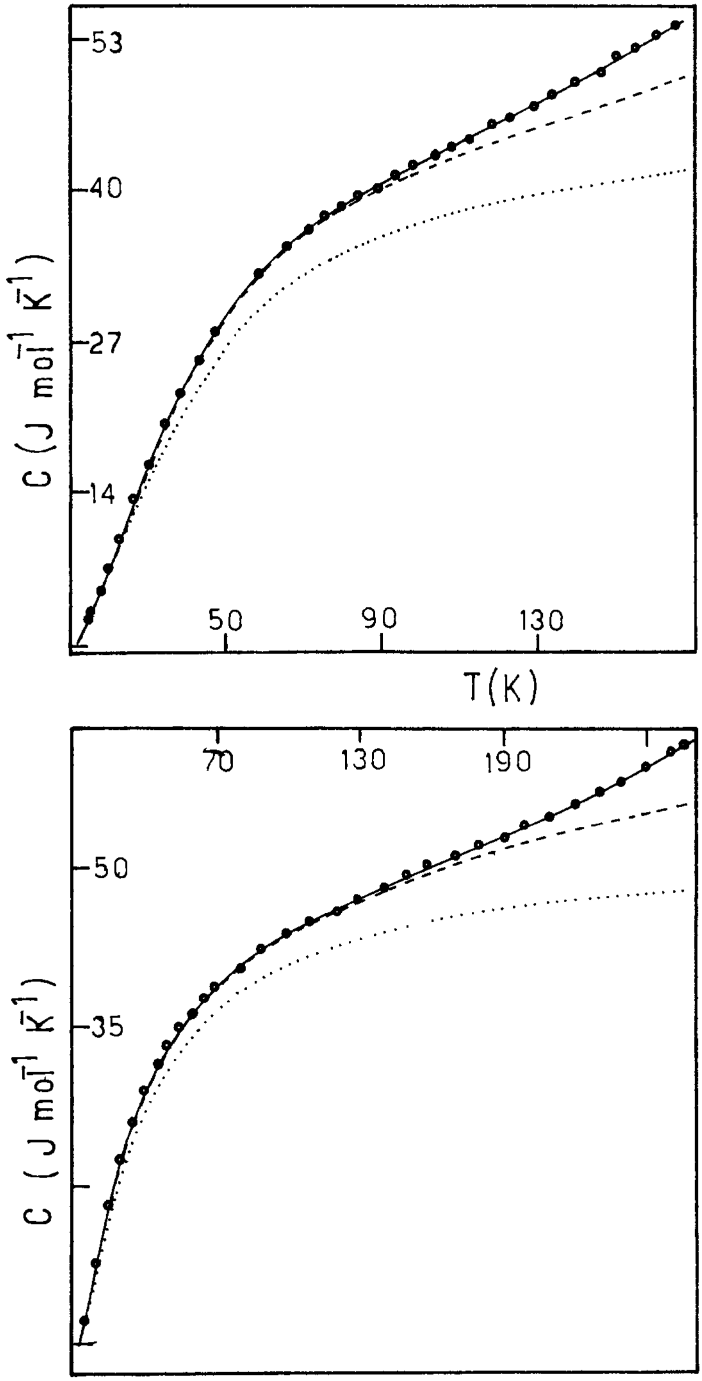


Fig. 3: The circles in the upper and lower figures represent the C_p vs T data in solid Cl_2 and Br_2 respectively, up to the melting point. The dotted line corresponds to the specific heat produced by temperature independent lattice frequencies. The dashed line is obtained by adding to the dotted the contributions due to the anharmonicities. Adding to this line the contribution due to vacancy formation, the full line is obtained. As may be seen, the agreement with C_p vs T data is, in both cases, excellent.

TABLE 1

Values Deduced for Solid Chlorine and Bromine

	Chlorine		Bromine	
Mode	W_0 (cm^{-1})	C (10^4 K^{-1})	W_0 (cm^{-1})	C (10^4 K^{-1})
B2g	73.6 ± 0.9	16.69 ± 0.50	54.9 ± 0.8	4.9 ± 1.3
B1g	84.7 ± 1.1	6.8 ± 1.4	74.0 ± 0.6	5.7 ± 0.68
Ag	102.1 ± 0.7	8.26 ± 0.80	86.2 ± 0.8	6.84 ± 0.73
B3g	120.7 ± 1.0	9.22 ± 0.90	100.3 ± 0.9	6.11 ± 0.81
Au	32.8 ± 2.0	3.34 ± 0.28	32.9 ± 2.0	3.36 ± 0.34
B2u	65.3 ± 2.0	6.64 ± 0.37	51.1 ± 2.0	5.24 ± 0.52
B1u	97.4 ± 2.0	9.91 ± 0.45	78.9 ± 2.0	8.08 ± 0.81
Ag	530.4 ± 0.5	0	295.0 ± 0.5	0
B3g	542.0 ± 0.5	0	302.0 ± 0.5	0
T_D	95.3 ± 0.7	9.69 ± 0.31	62.4 ± 0.6	6.39 ± 0.69
E_f/k	(898 ± 10) K		(1400 ± 15) K	
S_f/k	1.5		1.5	

due to the temperature change of the mode frequencies, and by adding to curve 2 the contribution from vacancy formation we obtain curve 3, which goes through the experimental values. To a good degree of approximation it may be seen that the anharmonic contribution exhibits a linear behavior with temperature, as expected (17). The obtained vacancy formation energies are somewhat smaller than those previously reported (18), and these discrepancies may be due to different choices of specific heat backgrounds. However, the excellence of the fits and the reasonable values obtained for the various quantities shown in Table 1 bring confidence and support to the present analysis (19).

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