EQUATION OF STATE OF SOLID CHLORINE AND BROMINE

E.-Fr. Düsing, W. Grosshans, W. Holzapfel

► To cite this version:

E.-Fr. Düsing, W. Grosshans, W. Holzapfel. EQUATION OF STATE OF SOLID CHLORINE AND BROMINE. Journal de Physique Colloques, 1984, 45 (C8), pp.C8-203-C8-206. 10.1051/jphyscol:1984837 . jpa-00224337

HAL Id: jpa-00224337

<https://hal.science/jpa-00224337>

Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

EQUATION OF STATE OF SOLID CHLORINE AND BROMINE

E.-Fr. Düsing, W.A. Grosshans and W.B. Holzapfel

Fachbereich Physik, Universität-GH-Paderborn, D-4790 Paderborn, F.R.G.

Résumé - Le chlore et le brome ont été étudiés par rayons X en dispersion d'énergie à des pressions jusqu'à 45 GPa à 300 K. Leurs pressions de dissociation moléculaire sont estimées en comparant nos mesures avec les résultats déjà publiés.

Abstract - Chlorine and bromine have been studied by energy dispersive X-ray diffraction under pressure up to 45 GPa at room temperature. A comparison of these data with the earlier results for iodine is used for an estimate of the molecular dissociation pressures P_t for bromine and chlorine.

INTRODUCTION

Chlorine, bromine and iodine crystallize at room temperature and about 4 GPa in the same orthorhombic structure (D_{2h}^{18} - Cmca) and are normally considered as simple molecular crystals (1).

Earlier investigations of iodine under pressure report two transitions up to 30 GPa: I) a continuous transition into a metallic state (2-6) around 18 GPa and II) a first order structural transition at 20 GPa with molecular dissociation to a monoatomic form (7,8). A similar behaviour can be expected also for bromine and chlorine and the present study intends to give first estimates for the respective transition pressures in these substances.

EXPERIMENTAL

Chlorine and bromine were investigated up to 45 GPa in a gasketed diamond anvil cell by energy dispersive X-ray diffraction with synchrotron radiation. The experimental techniques have been described in detail elsewhere (9). The solid samples of chlorine and bromine were filled into the gasket at liquid nitrogen temperatures (10). The use of nitrogen as pressure transmitting medium leads to nearly hydrostatic conditions over the whole pressure range (9). The pressure was measured by the Ruby R_1 -fluorescence method with the calibration constant of 365 pm/GPa (11).

RESULTS

Neither chlorine nor bromine show phase transitions in the pressure range up to 45 GPa at room temperature. The compression of chlorine and bromine is represented in fig. 1 together with previous data (8) for iodine, whereby the unit cell volume V for each element is scaled by the bond length L of the free molecules to arrive at scaled volumina $\bar{V} = V/L^3$, which allow for a better comparison in corresponding states.

If one fits these room temperature equation of state data with the two parameter Birch equation (12) using the known scaled volume at ambient condition V_{RT}^0 , one obtains for the bulk moduli at ambient condition B_{RT}^0 and for their pressure dependences B^0 , the values which are given in the second and third column of table 1.

Fig. 1: Room temperature equations of state for solid chlorine, bromine and iodine. The broken lines represent the liquid phase. The dashed-dotted line indicates the volume for the molecular dissociation in iodine.

	Two parameter fit		One parameter fit with $B^{01} = 5.2$	
	B^{01}	B_{RT}^0 / GPa	B_{RT}^0 / GPa	B_0^0 / GPa
Cl	4.3(9)	14.2(24)	11.7(9)	13.1(9)
Br	5.6(8)	12.2(20)	13.3(7)	14.3(7)
I	5.2(7)	13.6(11)	13.6(2)	14.5(3)

Table 1: Comparison of bulk moduli.

The large statistical errors of these values in table 1 result from a strong correlation of B^0 and B^{01} in a Birch fit. These correlations are illustrated in fig. 2, which represents the loci of constant standard deviations as "error ellipsoids". This figure shows more clearly than tab. 1 that the expected systematics of B^0 and B^{01} may be just masked by their strong correlations. It appears therefore more reasonable to compare the B_{RT}^0 -values, which are obtained by a one parameter fit using a constant average B^{01} value for B^{01} , as indicated by the vertical line in fig. 2. The value $B^{01} = 5.2$ leads then to the data in the fourth column of table 1. Since the melting temperatures of chlorine and bromine are below room temperature at ambient pressure, one may want to compare the bulk moduli of these elements at zero pressure and temperature: B_0^0 . These values are derived from the values of B_{RT}^0 by corrections for the thermal pressure and are compiled in the last column of tab. 1, which shows apparently the same systematic variation of the B_0^0 as for B_{RT}^0 , however, still with large uncertainties.

Since the approach to the monoatomic phase is characterized first of all by a continuous decrease of the asymmetry in the bonding within the b-c-plane of the orthorhombic lattice (8), one can define an asymmetry parameter $\Delta = [(b/2L)^2 + (C/4L)^2]^{1/2} - 1$, which tends to zero when all the bonds in the b-c-plane of the

Fig. 2: Contours of constant standard deviation for the bulk moduli

Fig. 3: Variation of the asymmetry parameter Δ for chlorine, bromine and iodine with respect to the scaled volumina $\bar{V}$.

orthorhombic lattice would approach the value L of the free molecules. Fig. 3 shows in fact that this parameter decreases strongly in iodine under pressure down to a critical value $\Delta_t = 0.11$ at the first order phase transition to the monoatomic phase. For a reasonable comparison with bromine and chlorine, fig. 3 represents the variation of these asymmetry parameters with respect to the scaled volumina $\bar{V}$. Apparently fig. 3 shows a common variation for all three substances and one may therefore speculate that also bromine transform at the same value $\Delta_t = 0.11$ into monoatomic phases. This assumption gives as first estimates for these transition pressures $P_t = 58(6)$ GPa for bromine and $P_t = 140(30)$ GPa for chlorine in good agreement with recent Raman studies on these substances (13).

This work was performed with synchrotron radiation at HASYLAB, DESY and supported in part by the Bundesministerium für Forschung und Technologie.

REFERENCES:

- 1) J. Donohue, *The Structures of the Elements* (John Wiley & Sons, New York, 1974) p. 396
- 2) A.S. Balchan and H.G. Drickamer, *J. Chem. Phys.* **34**, 1948 (1961)
- 3) B.M. Riggleman and H.G. Drickamer, *J. Chem. Phys.* **37**, 446 (1962)
- 4) B.M. Riggleman and H.G. Drickamer, *J. Chem. Phys.* **38**, 2721 (1963)
- 5) R.W. Lynch and H.G. Drickamer, *J. Chem. Phys.* **45**, 1020 (1966)
- 6) O. Shimomura, K. Takemura, Y. Fujii, S. Minomura, M. Mori, Y. Noda and Y. Yamada, *Phys. Rev. B* **18**, 715 (1978)
- 7) K. Takemura, Y. Fujii, S. Minomura and O. Shimomura, *Solid State Comm.* **30**, 137 (1979)
- 8) K. Takemura, S. Minomura, O. Shimomura, Y. Fujii and J.D. Axe, *Phys. Rev. B* **26**, 998 (1982)

- 9) W.A. Grosshans, E.-F. Dusing and W.B. Holzapfel, High Temp., High Press. (in press)
- 10) P.G. Johannsen, W. Helle and W.B. Holzapfel, this conference
- 11) G.J. Piermarini, S. Block, J.D. Barnett and R.A. Forman, J. Appl. Phys. 46, 2774 (1975)
- 12) F. Birch, Phys. Rev. 71, 809 (1947)
- 13) P.G. Johannsen, E.-F. Dusing and W.B. Holzapfel, in Int. Symp. on Solid State Physics under Pressure, ed. S. Minomura (Terra Scientific Publishing Corporation, Tokyo), Izu-Nagaoka (1984), in press