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# First-principles studies of solid halogens under pressure: scaling rules for properties among I<sub>2</sub>, Br<sub>2</sub> and Cl<sub>2</sub>

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## Abstract

We have theoretically studied the properties of solid iodine, bromine and chlorine under pressure, by employing the full-potential linear muffin-tin orbital method within the local density approximation (LDA). Furthermore, in this paper we study bromine by the use of the generalized gradient approximation (GGA) and compare the results with those obtained using LDA. We examine the pressure dependence of the frequencies of Raman-active A<sub>g</sub> modes using the frozen-phonon method. We also examine the scaling rules and find that they hold for these band-theoretical results.

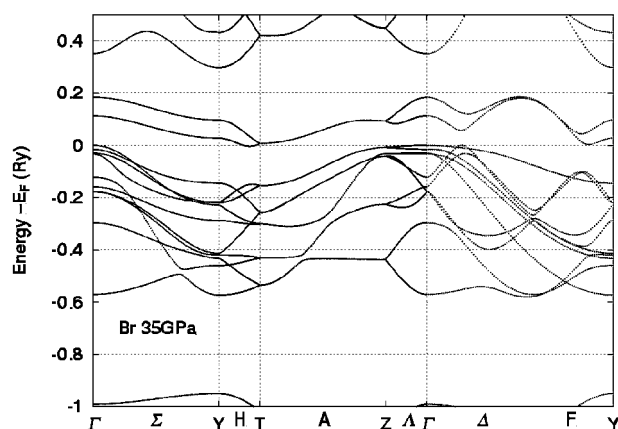
## 1. Introduction

In 1984, Düsing *et al* [1] found a scaling rule among the pressure dependences of iodine, bromine and chlorine, by performing x-ray diffraction experiments. In 1995, Fujihisa *et al* [2] examined the scaling rule in detail, on the basis of their new observations.

Under pressure, iodine, bromine and chlorine form diatomic molecular crystals. The lattice structure is base-centred orthorhombic, the space group being D<sub>2h</sub><sup>18</sup> (*Cmca*).

Fujihisa *et al* [2] also reported that the surface of bromine began to reflect light at around 60 GPa, and considered this to be an indication of metallization. This metallization pressure agrees with their scaling rule as well.

However, very recently, San Miguel *et al* [3] reported that the metallization pressure of bromine is  $25 \pm 5$  GPa, by analysing the x-ray absorption spectrum. On the other hand, according to the direct measurement by Shimizu *et al* [3], the electric resistance of bromine decreases gradually without singularity up to the molecular dissociation pressure.



**Figure 1.** The band structure and density of states of molecular solid bromine at 35 GPa, within the LDA.

We are interested in the softening of phonon frequencies, as well. In 1982, Shimomura *et al* [4] studied Raman scattering spectra of iodine and found softening of the librational mode of Raman-active  $A_g$  mode, but not of the vibrational mode.

In 1998, Yamaguchi and Miyagi [5] reported a theoretical study of solid iodine under pressure using the full-potential linear muffin-tin orbital (FP-LMTO) [6] and frozen-phonon methods. They found similar behaviour of phonon frequencies in iodine to that seen in experiment, and considered the softening of the librational mode to originate from metallization.

In this paper, we evaluate the pressures of metallization of these halogens. We also examine the pressure dependences of Raman-active  $A_g$  modes and discuss the softening of the computed frequencies in three halogens. And we examine whether or not the empirical scaling rule, originally proposed by Düsing *et al* [1] and Fujihisa *et al* [2], holds for band-theoretical results.

Furthermore, we study bromine by the use of the generalized gradient approximation (GGA) and compare the results with those obtained using the local density approximation (LDA).

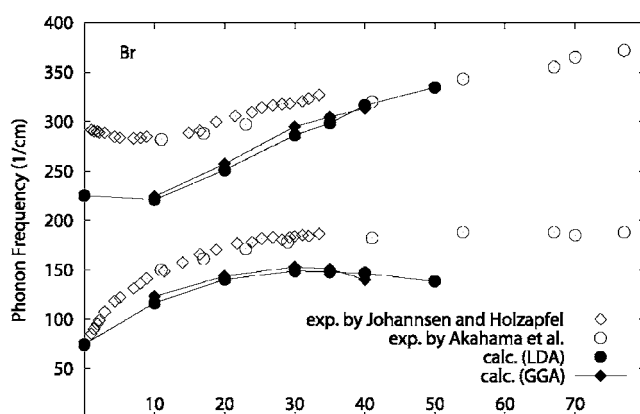
## 2. Calculation

We used the FP-LMTO method developed by Savrasov [6] within the LDA to calculate the electronic states and total energy of solid molecular iodine, bromine and chlorine. For bromine, we also calculate the electronic states by using the GGA for comparison.

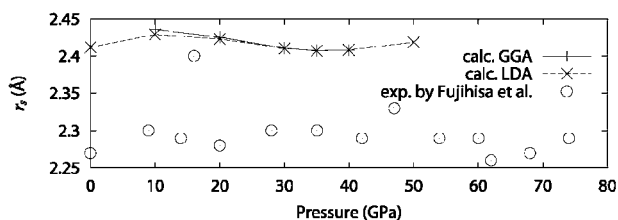
The muffin-tin-sphere radii were fixed at each pressure, at about 49% of the molecular lengths.

We used the frozen-phonon method to obtain the molecular configuration and phonon frequencies. In the computations, the lattice parameters  $a$ ,  $b$  and  $c$  of solid iodine and bromine for each pressure were taken from the x-ray experimental results of Fujihisa *et al* [2, 10]. The lattice parameters of solid chlorine for 60, 80 and 100 GPa were obtained by extrapolation from their data up to 40 GPa. We also made calculations for two Raman-active  $A_g$  modes.

The band structures of solid molecular bromine in the equilibrium structure at 35 GPa are presented in figure 1. In the calculation, metallization by band overlap occurs at about 35 GPa,



**Figure 2.** Pressure dependences of phonon frequencies of Raman-active  $A_g$  modes of molecular solid bromine. Filled symbols denote calculated results. Open symbols denote experimental results [7–9].



**Figure 3.** The molecular bond lengths of bromine. Crosses denote calculated results. Open circles denote experimental results [2].

which is in the molecular state. There is no distinguishable difference between LDA and GGA results. For chlorine, the metallization occurs at about 100 GPa, in the molecular state.

Pressure dependences of the calculated frequencies  $\omega$  of the Raman-active  $A_g$  modes are shown in figure 2. For all three halogens, these are similar to the experimental results. But we detect slight softening of the low-frequency mode, which corresponds to the librational mode, in bromine after metallization. When we use the GGA, the softening is more conspicuous.

The equilibrium molecular bond lengths are slightly larger in all halogens. In the GGA calculation, the lengths become longer, moreover (figure 3).

### 3. Metallization and softening

The metallizations result from indirect band overlap. The metallization pressures are 10, 35 and 100 GPa, for iodine, bromine and chlorine, respectively.

In comparison, the experimental value is 16 GPa for iodine [11]. For bromine, Fujihisa *et al* [2] reported the value of 60 GPa. And for chlorine it is expected to be 165 GPa from the extrapolation and scaling rule of Fujihisa *et al* [2].

It is well known that in the LDA band closure occurs at pressures lower than in experiments. For bromine, the GGA seems to make no distinguishable correction to the metallization pressure from the LDA.

We find a slight softening in the pressure dependence of the low-frequency mode (librational mode) for Raman-active  $A_g$  modes of bromine, after metallization. This result

is consistent with former theoretical examinations of iodine, by Yamaguchi *et al*, in which the softening is considered to originate from metallization.

However, this result is different from the experimental results [7, 9]. We consider that the tendency towards gradual molecular dissociation is overestimated in our calculation, because of the overestimate of the molecular bond length caused by the LDA. For bromine, the GGA seems to increase this tendency.

#### 4. Scaling rule

Fujihisa *et al* [2] defined the scaled volume as  $\tilde{v} = abc/8r_s^3$ , where  $a$ ,  $b$  and  $c$  are the lattice parameters and  $r_s$  is the molecular bond length.

Here, we examine scaling rule among the present results for iodine, bromine and chlorine. The scaled volumes are determined from molecular bond lengths calculated at normal pressure.

The calculated metallization pressures, 10 GPa for iodine, 35 GPa for bromine and 100 GPa for chlorine, correspond to  $\tilde{v} = 1.3$ – $1.4$ . In this case the scaling rule still holds for the three halogens, as expected by Fujihisa *et al* [2], empirically.

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