First-principles study of the modulated structure of solid Iodine in the phase-V

Kiichiro Mukose, Hitose Nagara, and Hiroshi Miyagi,
Grad. School of Engineering Science. Osaka Univ., Toyonaka, Osaka 560-8531, Japan,
mukose@hbar.mp.es.osaka-u.ac.jp, nagara@mp.es.osaka-u.ac.jp
miyagi@mp.es.osaka-u.ac.jp

Abstract

The new modulated structure (phase-V) of Iodine discovered by Takemura et al. in the pressure range from 23GPa to 30GPa is studied through phonon properties by the use of first-principles calculations with the pseudo-potential and plane wave basis. Our phonon calculations show that the FCO Iodine is unstable with respect to atomic displacements with a particular wave-vector in the pressure region of the phase-V. The pressure dependence of the unstable wavelength is in conformity with the experiments. When we optimize the structure using extended unit cell of a size four times bigger along a-axis of the original FCO cell, we get the modulated structure in which the amplitude of the modulation agrees well with the experimentally observed one. We find that similar instabilities appear in solid bromine under high pressure.

I INTRODUCTION

In Iodine, a number of structural phase transitions including metallization and the molecular dissociation have been observed at high pressures. First it becomes a metal at 16GPa (Sakai,1982, p1811) where it is in molecular phase. This molecular phase, phase-I, with space group D_{2h}^{18}-Cmca transforms to an atomic phase, phase-II, at 21GPa in which the lattice structure is body-centered orthorhombic (BCO) with space group D_{2h}^{25}-Immm(Takemura,1980, p1881). Then at 43 GPa, another structural phase transition to the phase, phase-III, which has the body-centered-tetragonal structure (BCT) and, with further increase in pressure, at 55 Gpa the phase transition into FCC phase, phase-IV, have been observed. (Fujii, 1987, p796) Very recently a new incommensurately modulated structure has been observed between 23 and 30 Gpa.(Takemura, 2003, p971) This new phase is called phase-V.

The structure of the phase-V has been identified as an incommensurately modulated one which is obtained from the face-centered orthorhombic (FCO) lattice by a modulation. The modulation wave-vector is along a-axis with displacements along the b-axis which is perpendicular to the wave-vector. The wavelength increases when the pressure is increased. No evidence of an incommensurate-commensurate transition is observed at k_x=0.25 (in units of 2 \frac{\pi}{a})

We study this modulated structure through phonon properties using first principles band theoretical methods taking the FCO structure as a reference one.

II COMPUTATIONAL DETAILS

We performed the first-principles calculations using pseudo-potential and plane wave basis, where we used the generalized gradient approximation(GGA) for the exchange-correlation(EC) energy. We used Perdew-Burke-Ernzerhof(Perdew, 1996, p3865) expression for the EC energy functional and the Troullier-Martins(TM) type pseudo-potential.(Troullier, 1991, p1993) For the TM type pseudo-potential of Iodine, we observed a ghost band when we use the Kleinman-Bylander representation.(Fuchs, 1999, p67) We treated the l=1 as a local potential to eliminate the ghost band. We set the energy cut-off of the plane wave at about 50Hartree. In most of the calculations we performed k-point sampling over the Brillouin zone using 16x16x16
We used the packaged code ABINIT for the implementation of the calculations. (Gonze, 2002, p478) The equation of states obtained by these scheme and parameters shows good agreement with experiment in phase-I.

Fig.1  The phonon dispersion curves as functions of $k_x$ (in units of $2\pi/a$) at various pressures. On the vertical axis, frequencies in units of cm$^{-1}$ are shown where imaginary frequencies are plotted as negative values. The imaginary frequencies at the $\bar{I}$ - point are less than 0.4 cm$^{-1}$, which show almost complete translational invariance of the lattice.
III RESULTS OF OUR CALCULATION

Before we start the phonon calculation, we performed the optimization of the FCO structure. As the pressure is increased, we observed that the lattice parameters $a$ and $b$ became equal. This shows that the FCO transforms to the BCO structure, at a pressure below the BCO-BCT (phase-II-phase-III) transition pressure.

With the optimized FCO structure we have performed the phonon calculation and got the dispersion along the $k_x$-direction to study the lattice modulation in the structure. The results are shown in Fig.1 at several values of the pressures.

Before analyzing the instability in the atomic phase, let us first look at the dispersion curves at 15.5GPa for which Iodine is in the phase-I. The unstable mode at $k_x=0.25$ continues from that at higher pressure. Besides it another unstable mode at $k_x=0.5$ exists with larger magnitude of imaginary frequency and a hump between this wave-vector and $k_x=0.25$. The displacement of this mode is along the $b$-axis and corresponds to the formation of the molecules in the FCO in conformity with the Cmca structure of the phase-I.

To study the formation of the Cmca structure, we performed full optimization of the lattice constants and the atomic coordinate using extended unit cell with doubled size along the $a$-axis and starting from the FCO. In Fig.2, we show the structure in the phase-I with definition of the atomic coordinates. In Fig.3 pressure dependencies of the lattice constants and in Fig.4 parameters defining the atomic positions are shown for the fully optimized structure. The optimized lattice constants and the atomic coordinates agree very well with the experiments. (Fujihisa, 1996, p335) In the same figures we plot the values of the same quantities optimized at higher pressures where we used the same size of the unit cell. The value of $(y, z)$ remains nearly constant at $(b/4, c/8)$ in the pressure region between 20 and 41GPa. The instability corresponding to the $k_x=0.25$ is expected to be suppressed by the molecular formation. In the present optimization using double size of the unit cell, however, the instability is suppressed owing to the size of the unit cell.

Fig.2 Crystal structure of Iodine in the phase-I which has the space group $D_{2h}^{18}$-Cmca. The rectangle denotes a unit cell. The direction of the lattice vectors $a$, $b$, and $c$ are shown. The molecular axes are on the $bc$-plane. The molecules shown by solid lines are on the plane and those by broken lines are on adjacent plane(s) which is above (or below) the plane with separation $a/2$. 
Fig. 3 Pressure dependencies of the optimized lattice constants $a$, $b$, and $c$ of Iodine in the phase-I. Open circles denote experimental results. (Fujihisa, 1996, p335).

Fig. 4 Pressure dependencies of the optimized atomic coordinates ($y$, $z$) of Iodine in the phase-I. Open circles denote experimental results. (Fujihisa, 1996, p335)
Then let us analyze the instability at pressures above 20.4GPa. There exists one unstable mode at $k_x=0.25$ and the wave-vector of this unstable mode moves toward the $\bar{\Gamma}$-point with increasing pressure as is shown in Fig.1 and the instability disappears below 31.8GPa.

The instability of the phonon mode show only the behavior of the energy surface with infinitesimal displacement of the atomic positions. To know what structure grows from this instability, we made an optimization of the structure. We have chosen the unit cell with dimension $(4a,b,c)$ where $(a,b,c)= (4.283,4.218,5.765)$ in units of $\AA$ is that of the primitive cell of the FCO at 20.4GPa. The optimization was done first allowing the displacement in accordance with the transverse modulation of the $k_x=0.25$ mode which is the unstable mode at 20.4GPa. After finding the optimum displacement, we made full optimization of the structure. Final structure thus obtained is shown in Fig.5. The parameters of the optimal structure are $y_3=0.0350b$, $y_2=0.0247b$, and $x_2=8.34 \times 10^{-6}a$. The atomic distances in this optimal structure are 2.935, 2.976, 3.037, and 3.081A, which are compared with the experiment. (Takemura, 2003, p971) The experiment reports the distribution of the distance over the range 2.86-3.11 at 24.6GPa where the modulation vector is $k_x=0.257$. The agreement with the experiment is very good. The present methods can perform this kind of optimization of the modulated structure only at wave-vectors commensurate with the original structure, but we can expect similar good agreement at wave-vectors very close to those incommensurate with the original structure.

![Fig.5 The optimized structure of the modulated FCO which has a modulation wave-vector $k_x=1/4$. The atoms shown by solid lines are on the plane and those by broken lines are on adjacent plane(s) above (or below) the plane with separation c/2. The atomic displacements are on the ab-plane. The parameters ($x_2$, $y_2$) and $y_3$ define the following 8 positions of the atoms in this unit cell: 1:(0,0,0), 2:(a/2+x_2, b/2+y_2,0), 3:(2a/2, y_3,0), 4:(3a/2-x_2, b/2+y_2,0), 5:(4a/2,0,0), 6:(5a/2+x_2, b/2-y_2,0), 7:(6a/2, -y_3,0), 8:(7a/2-x_2, b/2-y_2,0).](image)

IV CONCLUSION

We studied the modulated structure of Iodine using the first principles calculations. From the phonon study of the FCO structure, we found instabilities corresponding to the modulation wave-vector. The pressure dependence of the wave-vector corresponding to the unstable mode agree well with the experiment. The structure which is obtained starting from the displacements corresponding to the unstable mode agrees well with the experiments. We performed same kind of calculations for Bromine and have got similar results.
References

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