Ab initio calculations for high-pressure phases of Ar(H$_2$)$_2$

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Abstract
High-pressure structures of Ar(H$_2$)$_2$ are studied with possible molecular dissociation and metallization using density functional theory in the local density approximation (LDA) and generalized gradient approximation (GGA) for the exchange–correlation energy. We have estimated the transition pressure from the low-pressure MgZn$_2$-type structure to the high-pressure AlB$_2$-type structure to be around 240 GPa. The band gap of the MgZn$_2$-type structure does not close, while the band gap of the AlB$_2$ closes at 420 GPa, which is much higher than the pressure of the band gap closure in pure hydrogen obtained by the same GGA. The lattice vibrations in those structures are also studied. The frequencies of the vibronic motions show good agreement with experiments. The molecular dissociation of the hydrogen in Ar(H$_2$)$_2$ occurs at higher pressures than in pure hydrogen.

1. Introduction

Realization of metallic hydrogen in the laboratory has long been the ultimate goal for high-pressure experimentalists. One of the processes of the metallization of hydrogen is the overlapping of the electronic bands, and the other is molecular dissociation. Both processes are thought to occur at very high pressure. For pure hydrogen, recent theoretical estimation of the metallization pressure is around 400 GPa [1].

In some of the hydrogen compounds, however, metallization or molecular dissociation is expected to occur at much lower pressures because of the shorter inter-molecular distances in those compounds. One of those compounds is Ar(H$_2$)$_2$, where an experiment [2] reported the disappearance of the Raman-active vibron peak, suggesting molecular dissociation. That report raised much interest in possible metallization in that compound. Metallization in Ar(H$_2$)$_2$ is expected to occur through the molecular dissociation of hydrogen and at lower pressures than in pure solid hydrogen. The compound Ar(H$_2$)$_2$ is realized above 4.3 GPa [2]. In 1999, Ulivi *et al* [3] made another Raman and infrared (IR) study on Ar(H$_2$)$_2$ up to 50 GPa, and reported that the
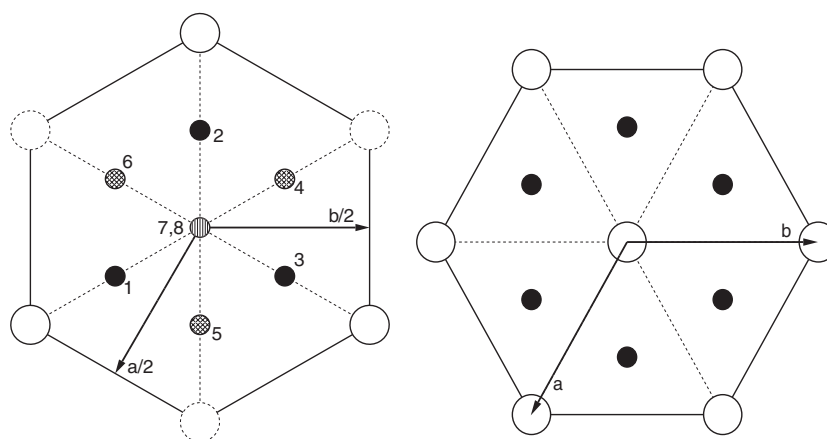
Figure 1. Ar(H$_2$)$_2$ in the MgZn$_2$-(left) and AlB$_2$-(right) type structures. Large circles show the Ar atoms and smaller circles show the position of the molecular centres of H$_2$. Circles with broken lines and shaded circles show the positions at different heights.

properties of hydrogen molecules are well maintained in the compound up to higher pressure. A more recent experiment [4] observed the pressure dependences of the vibrational modes up to 200 GPa, and reported no jumps in the vibron frequencies associated with structural phase transitions.

In the theoretical studies, Bernard *et al* [5] made an *ab initio* molecular dynamics (MD) study of Ar(H$_2$)$_2$ at high pressures based on the local density approximation (LDA) by the use of the Car–Parrinello method. They reported that the structural transition from the MgZn$_2$-type structure to the AlB$_2$-type structure and band gap closure occur simultaneously at the transition pressure. They used the extended unit cell and single *k*-point sampling at the Γ-point. In this paper we report *ab initio* calculations for Ar(H$_2$)$_2$ with much denser *k*-points sampled over the Brillouin zone and we study the possibility of molecular dissociation and metallization. We also report calculations of the pressure dependence of vibron frequencies and compare with recent experimental results.

2. Optimization of the structures

The structure of NeHe$_2$ is known to be a MgZn$_2$-type Laves structure [6]. The electron density profile of the hydrogen molecule is very similar to that of the helium atom when we look at the distance of inter-molecular separation in the solid hydrogen [7]. Then the replacement of the He atoms by the H$_2$ molecules and Ne by other rare-gas atoms is expected, and Ar(H$_2$)$_2$ in the same structure as that of NeHe$_2$ was confirmed by the experiment [2].

The space group of the MgZn$_2$ structure is D$_{6h}^4$($P6_3/mmc$) (no.194). It is shown in figure 1. The Ar atoms occupy the 4f-sites of the D$_{6h}^4$ space group, four H$_2$ molecules occupy the 6h-sites, and the remaining two H$_2$ molecules occupy the 2a-sites. At room temperature and low pressure the hydrogen molecules are rotating almost freely and only the position of the molecular centres can be determined, and they are shown in the figure. This structure remains up to 50 GPa, but above 50 GPa the structure is not clear. More complicated structures than the Laves structure may be considered, but we do not study those complicated structures in this paper.

For the structure of the high-pressure phase, Bernard *et al* proposed the AlB$_2$-type structure from their *ab initio* molecular dynamics study. The space group of the AlB$_2$-type structure of

$Ar(H_2)_2$ is $D_{6h}^1 (P6/mmm)$ (no.191), as shown in figure 1. The Ar atom occupies the $1a$-site of the D_{6h}^1 space group and two hydrogen molecules occupy the 2d-sites.

A molecular dynamics (MD) study by Bernard *et al* was performed using a super-cell containing four times the number of atoms in the primitive cell of the $MgZn_2$ structure and the single k-point at Γ, which is equivalent to the four k-points sampling over the Brillouin zone in the case of the primitive unit cell. We performed calculations for the $Ar(H_2)_2$ in the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange correlation energy functional using the primitive unit cell of the $MgZn_2$-type structure with $6 \times 6 \times 6$ mesh points for the k-point sampling. We checked the validity of the results by increasing the mesh points to $8 \times 8 \times 8$. For the LDA exchange–correlation energy functional we used the Perdew–Wang expression and the GGA Perdew–Burke–Ernzerhof expression [8]. We set the cut-off energy of the plane-wave basis, E_{cut}, at 25 Hartree, and used the Troullier–Martins-type pseudo-potentials for Ar and H. We confirmed the convergence of the total energy with respect to E_{cut} and the k-point mesh.

We allowed full relaxation of c/a and all positions of the atoms at constant volume, and obtained the optimized structure at each density.

2.1. Structural optimization starting near the $MgZn_2$-type structure and the equation of states

In the low-pressure region we performed optimization of the structure, starting from atomic positions near the $MgZn_2$ structure. In the resultant optimized structures, the Ar atoms and the molecular centres of H_2 at the 2a-sites moved to align on the same planes, i.e. the hydrogen molecules at the 2a-sites are on the same plane as the Ar atoms, and the H_2 molecules at the 6h-sites are intercalated between the Ar planes. The molecular axes of the hydrogen molecules were not ordered completely in the optimized structures at all the pressures that we studied. The polar angles, θ, of the molecular axes of H_2 on the 6h-sites are inclined from the c-axis by about 70° and the azimuthal angles are aligned to form nearly three-fold symmetry. The θ of the 2a-sites' H_2 are about 30°, but the azimuthal angles were not fixed. The bond length of the hydrogen molecules decreased as the pressure increased. At the volume for ambient pressure, the bond length calculated by the GGA is 1.4 a_0, which is almost the same as that for the isolated molecule. This reduces to 1.34 a_0 at 110 GPa. In all optimization runs starting near the $MgZn_2$-type structure, the structure converged to the above structure.

To check the accuracy of our calculation, we compare the equation of states (EOS) calculated by the GGA and the LDA with the experiments (taken from figure 2 in [5]), where the EOS is calculated for the above optimized structures. The GGA result shows better agreement with the experimental EOS than the LDA result at pressures below 150 GPa. No experimental EOS data have been reported above 150 GPa. The EOS calculated by the GGA and the LDA is shown with the experimental values in figure 2.

2.2. Structural optimization starting near the AlB_2-type structure

In the high-pressure region we tried optimization of the structure starting near the AlB_2-type structure with random orientation of the hydrogen molecules. To make an accurate comparison of the energy between the $MgZn_2$-type and AlB_2-type structures, we performed these calculations using the super-cell which contains the same number of atoms as the primitive cell of the $MgZn_2$-type structure and using a $6 \times 6 \times 6$ k-point mesh with the same E_{cut} as in $MgZn_2$. At high pressures the optimized structures are those in which the orientation of the molecular bonds of hydrogen molecules are aligned in the direction parallel to the c-axis. In this case also, the GGA bond length decreased from 1.32 a_0 at 133 GPa to 1.29 a_0 at
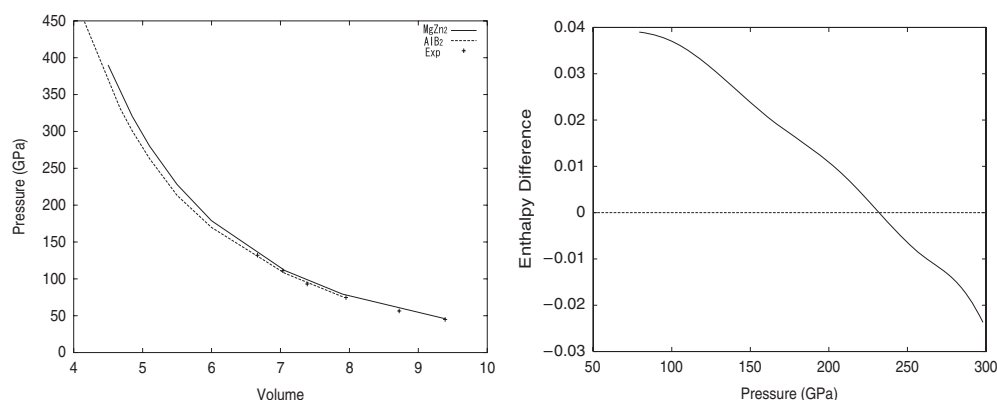
Figure 2. (Left) Equation of states calculated by the GGA. Experimental data points are taken from figure 2 in [5]. The volume is in units of A^3 per atom. (Right) Enthalpy of the optimized AlB_2-type structure plotted with reference to that of the optimized $MgZn_2$-type structure. Calculations are performed by the GGA.

396 GPa with increasing pressure. The LDA bond length is longer than the GGA's by about 0.03 a_0 at ∼300 GPa. The AlB_2 structures are stable and all optimizations starting from this type of structure do not go to other types of structures up to about 600 GPa.

### 2.3. The transition between low-pressure and high-pressure structures

Both types of structures were stable in the vicinity of the starting configurations, and at high pressures the total energy of the optimized structure starting from the AlB_2-type structure becomes lower than that from a $MgZn_2$-type structure. To estimate the transition pressure between these two types of optimized structures, we compared the enthalpies in figure 2, where we show the GGA results of the enthalpy difference. The enthalpy of the AlB_2-type structure becomes lower than that of the $MgZn_2$-type structure above about 240 GPa. This transition pressure is nearly equal to that predicted by Bernard *et al* (260 GPa).

3. Band structure and the metallization of $Ar(H_2)_2$

For the optimized structures we calculated the band structures. In the optimized $MgZn_2$-type structure, the band gap of the electronic energy bands is open at all pressures to about 300 GPa, which means that $Ar(H_2)_2$ does not metallize in the $MgZn_2$ phase.

We also calculated the band structures of the optimized AlB_2-type structures in which the hydrogen molecules orient along the c-axis. In figure 3 we show the band structures. The top of the valence band exists at the A-point in the Brillouin zone of the hexagonal lattice, and the bottom of the conduction band is at the L-point. At 451 GPa, the closed band gap is shown.

Before we go on to study the band gap closure, we discuss the effects of the bond length of the hydrogen molecules on the band gaps. In pure hydrogen the bond length has a big influence on the band gaps, because a longer bond length means a larger size for the hydrogen molecules [10]. According to our calculations on the $MgZn_2$-type structure at the experimental values of the volume observed at 4.3 GPa [3], the LDA gives the bond length, 1.45 a_0, of the hydrogen molecule, while the similar GGA calculation gives 1.4 a_0. The LDA value is longer than the bond length of pure solid hydrogen at ambient pressure by about 0.05 a_0, which is
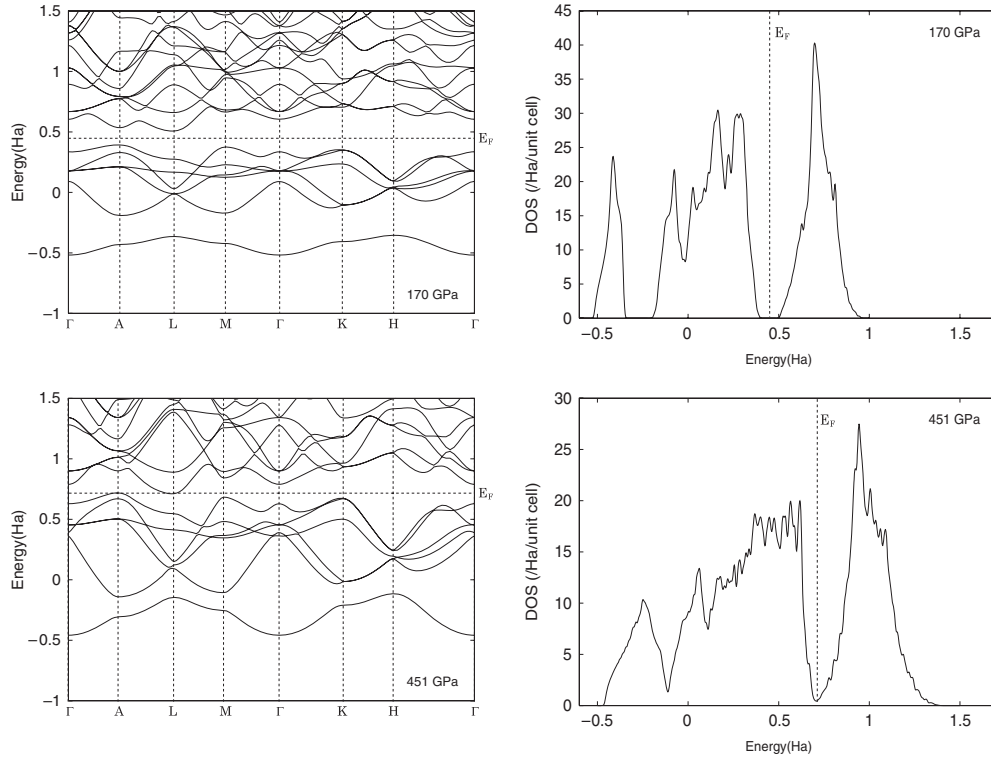
Figure 3. Band structure and the electronic DOS of the optimized AlB_2 structure at 170 and 451 GPa. At 451 GPa the closed band gap is shown.

well known [8, 9]. At high pressures the difference in the bond lengths between LDA and GGA reduces a little, but it still affects the band gaps. In fact, the bond length in the optimized AlB_2-type structure calculated by the GGA at 394 GPa is 1.29 a_0 and the value of c/a is 0.943. The band gap is still open there (the nearest-neighbour inter-molecular distance between hydrogen molecules is 2.74 a_0). We made the same calculation using the LDA, assuming the same volume. The optimized bond length is 1.32 a_0, the LDA pressure shows 374 GPa, and the value of c/a is 0.935. The LDA band gap is closed there (the nearest-neighbour inter-molecular distance is 2.75 a_0). To elucidate the effect of the bond length on the band gaps, we recalculated the band gap with fixed atomic positions at those obtained above by the LDA, changing the approximation from LDA to GGA. The GGA band gap is closed for this case. Here we note that the LDA inter-molecular distance is a little bit larger than the GGA inter-molecular distance.

In figure 4, we show the pressure dependence of the GGA band gap in the optimized AlB_2-type structure. The band gap closes at about 420 GPa. The same calculation by the LDA gives band gap closure at about 330 GPa for the optimized AlB_2 structure. Our LDA value of 330 GPa is higher than Bernard *et al*'s LDA value of 260 GPa. We think this difference comes from the number of the *k*-point sampling and the E_{cut}.

A further increase in the metallization pressure to 420 GPa by the GGA calculations is thought to come mainly from the decrease in the bond length to around 1.28 a_0, as discussed above. In pure solid hydrogen, the band gaps calculated by the GGA close at ∼200 GPa [10]. The nearest-neighbour inter-molecular distance in the AlB_2 structure is 2.74 a_0 at ∼390 GPa,

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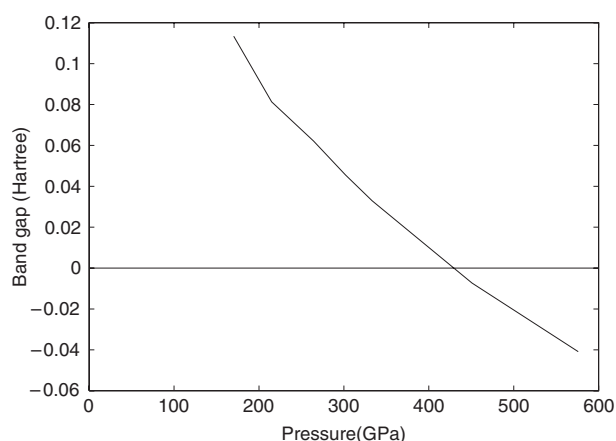
Figure 4. Pressure dependence of the band gap in the optimized AlB_2-type structure. Calculations are made by the GGA.

while that of pure molecular hydrogen in the close-packed structure is 3.24 a_0 at $\sim$200 GPa and the bond length is 1.41 a_0. These results mean that the argon prevents the metallization of the hydrogen or overlapping of the wave functions at least in the AlB_2 structure where hydrogen molecules align with its molecular bonds parallel with each other.

Since the GGA and LDA usually underestimate the band gaps, the metallization may occur at much higher pressure than the 420 GPa in $Ar(H_2)_2$, which means that the metallization pressure in the $Ar(H_2)_2$ is substantially higher than that in pure compressed hydrogen.
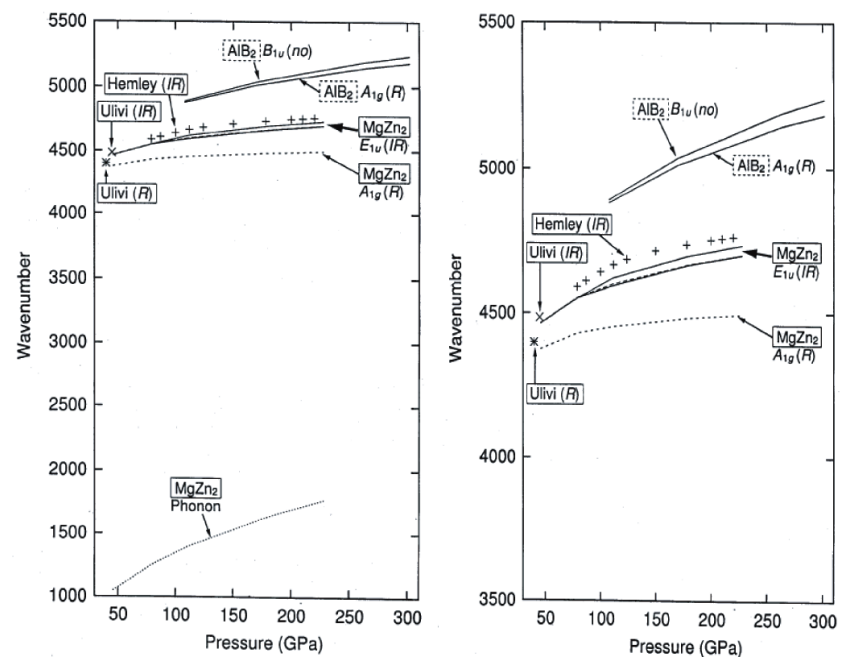
4. Pressure dependences of the vibrational frequencies

To know the structure and its stability, the vibrational modes and their frequencies are very important. Ulivi *et al* [3] measured the Raman- and IR-vibron frequencies up to 40 GPa, and Hemley *et al* [4] reported IR-vibron frequencies at pressures between 80 and 230 GPa. We made the calculation for the vibrational frequencies at the Γ-point using linear response theory. The $MgZn_2$-type structure has 20 atoms in the unit cell and has 60 vibrational modes, while the AlB_2-type structure has five atoms and 15 modes. In the crystal, the vibrational modes which belong to the same symmetry couple with each other and we cannot precisely say which one is phonon, libron, or vibron. But, as figure 5 shows, the vibrational mode which consists mainly of vibronic motion has a very high frequency and can be distinguished from the others. In figure 5, we compare the positions of the vibrational frequencies for the optimized $MgZn_2$-type structure (space group C_s^4) and those of the $MgZn_2$-type structure in which all H_2 molecular axes are aligned along the c-axis (space group D_{4h}^4). The latter structure is not an optimal one with respect to the atomic positions and has imaginary frequencies which are shown in the negative frequency region. In the D_{6h}^4 diagram, the two peaks near 4400 cm^{-1} come from the vibrons of the two H_2 molecules on the 2a-sites, and the other six modes near 4800 cm^{-1} come from the molecules on the 6h-sites. In the optimized structure, the symmetry reduces to C_s^4 because of the different orientations of the H_2 molecules, but the lower two vibron peaks and the upper six peaks are well separated from the other vibrational modes. All modes are Raman active as well as IR active, which is due to the symmetry of the C_s^4.

To compare our vibron frequencies with the experiments, we selected the vibron modes of the optimized structure C_s^4. We assumed the lowest vibron frequency and the third, fourth,
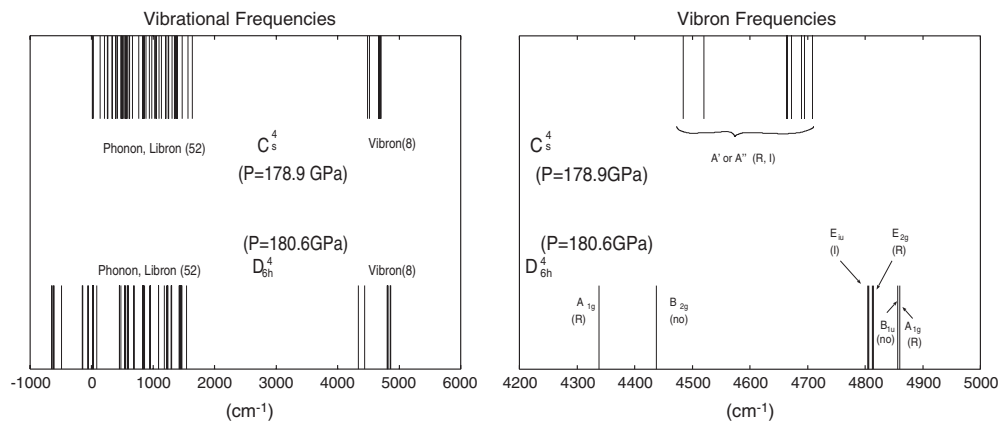
Figure 5. Calculated vibrational frequencies for the optimized MgZn$_2$-type structure. The space group of the structure is C$_s^4$, which is due to the inclinations of molecular axes of the H$_2$. When the molecular axes are aligned along the *c*-axis, the space group becomes D$_{6h}^4$. This structure is not an optimal one and has imaginary frequencies which are shown in the negative frequency region. The frequencies in the D$_{6h}^4$ are shown and compared to guess the modes of the C$_s^4$. The number in parentheses shows the number of the peaks. (Right) The magnification of the vibronic mode region. The group theoretical assignment of the modes are shown and the letters R and IR in parentheses show the Raman- and infrared-active modes, respectively.

Figure 6. The pressure dependence of the vibrational frequencies in the optimized MgZn$_2$-type and the optimized AlB$_2$-type structures. The experimental values from Ulivi *et al* [3] and Hemley *et al* [4] are also shown. The mode assignments are made by guessing in accordance with those of D$_{6h}^4$.

and seventh lowest ones as those corresponding to the experimentally observed frequencies and plotted, in figure 6, those frequencies as a function of pressure with the experimental

values [3, 4]. Our values are lower by about 1%, but the agreement with the experimental values are very good for the MgZn$_2$-type structures. No special anomaly which was pointed out by the experiment [2] is observed around 170 GPa.

In the same figure we plot the vibron frequencies for the optimized AlB$_2$-type structure, for which we have no experimental data to compare with. In the AlB$_2$-type structure the vibron frequencies are higher by about 300–400 cm^{-1} than in the MgZn$_2$-type structure. In both structures the vibron frequencies remain high up to much higher pressures. This means that molecular dissociation does not occur in this structure. When experimental values of the vibron frequencies above 200 GPa are obtained, they may be useful to identify the theoretically predicted AlB$_2$ structure as the structure in the high-pressure phase of Ar(H$_2$)$_2$.

5. Conclusions

We studied the high-pressure properties of the rare-gas hydrogen compound, Ar(H$_2$)$_2$, based on *ab initio* calculations in the GGA and LDA. The low-pressure structure is MgZn$_2$ type, and the EOS and the vibron frequencies are in good agreement with the experimental values. At 240 GPa, the MgZn$_2$-type structure transforms to the AlB$_2$-type structure in which molecular axes of the H$_2$ align along the *c*-axis. The GGA band gap closes at 420 GPa, which is much higher than that of pure hydrogen. The molecules persist above 500 GPa in the AlB$_2$ structure and there is no sign of the molecular dissociation around 170 GPa.

Acknowledgment

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