Compressibility of Lattice Parameters of Several Layered Compounds *

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The lattice parameters of AlB2, MgB2, and TiB2 under pressures are determined with a high-energy synchrotron source in a diamond anvil cell. The experimental results indicate that these three compounds have different mechanical behaviour under pressures, TiB2 is the hardest and MgB2 is the softest among the three materials. The phenomena are explained in terms of bonding strength in the crystal. Our results may be helpful for understating the decrease of the superconducting transition temperature of MgB2 under pressures.

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Since the remarkable discovery of superconductivity in MgB2 which is considered as a Bardeen–Cooper–Schrieffer (BCS) phonon-mediated superconductor with critical temperature $T_c$ above the commonly accepted limits for phonon-assisted superconductivity,1–3 many investigations, such as the chemical substitution,[4] have been carried out. It is interesting that, for substitution of Al on the Mg site, i.e. in the case of Mg1-xAlxB2, the value of $T_c$ decreases smoothly with increasing $x$, accompanied with a slight decrease of length in the c direction. When x increases up to a certain value, there is an abrupt transition to a nonsuperconducting isostructural compound so that the parameter c has a decrease of about 0.1 Å. Using the full potential-linearized augmented plane wave method and the generalized gradient approximation, Mora et al.[5] reported that the $\sigma$ band, which is associated with the large superconducting gap, is very anisotropic at the Fermi surface, while the $\pi$ bands have very little anisotropic character. Researchers also investigated the electrical properties and the crystal structure of MgB2 under pressure. It was found that superconducting transition temperature $T_c$ of MgB2 decreases with the increasing pressure, while the crystal structure does not change, and only the lattice parameters a and c are almost iso-compressed.[6–8] It seems that the influence of pressure on $T_c$ is the same as the substitution of Al on the Mg site. Since pressure can change crystal parameters, it may also change the band character, band conductivity and band anisotropy, and then superconductivity of materials.

In this letter, we compare the change of lattice parameters of TiB2, MgB2 and AlB2 with pressure. This is useful not only for overall understanding of the properties of the AlB2-type structure under pressure, but also for deeper study of the mechanism of decrease of $T_c$ of MgB2 under pressures.

We use the energy dispersive x-ray diffraction with a high-energy synchrotron source, at the Institute of High Energy Physics, Chinese Academy of Sciences, to study the isothermal compression curves of AlB2, MgB2 and TiB2. Details of the experimental equipment were described by Wang et al. in Ref.[10]. In our experiment, an intrinsic Ge detector was used. The data collecting time for a diffraction spectrum was typically 10 min. Diamond tips of 500 μm diameter was used. A 250-μm-thick stainless-steel sheet was first preindentted and then a 300-μm gasket hole was drilled. The sample was mixed with certain Pt powder to obtain a good diffraction peak ratio between the sample and the calibration. The Pt was used as a pressure calibration based on the equation of state described in Refs. [11–13]. A mixture of methanol ethanol water=16:4:1 was used as the pressure transmitting medium to keep good hydrostatic conditions. A computer programme[14] was used to proceed the experiment data.

Over the entire pressure range studied, no obvious phase transition was observed in the compounds. Figure 1 shows the dependences of lattice parameter a of the three compounds on pressure. The lattice parameters decrease monotonically and almost linearly with the increasing pressure.

Figure 2 depicts the behaviour of the lattice parameter c of the three compounds with pressure. For the MgB2 compound, the lattice parameter c decreases monotonically and almost linearly with the in-

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creasing pressure up to 35 GPa. For AlB$_2$ and TiB$_2$, the $c$ values decrease monotonically. Figure 3 shows that the change of $a/a_0$ of TiB$_2$ with pressure is the smallest among the three materials. This means that TiB$_2$ is the hardest among the three diborides. For other two materials, the changes of $a/a_0$ are slightly different. Figure 4 indicates that $c/c_0$ of TiB$_2$ changes with pressure more slowly than that of the others. For the MgB$_2$ compound, the change of $c/c_0$ is slightly faster than AlB$_2$. Figure 5 shows that the $c/a$ ratio of MgB$_2$ decreases linearly up to 35 GPa, with a slope of $-1.3 \times 10^{-3}$ GPa$^{-1}$. The compression is more isotropic than that expected for a layered system. However, although the $c/a$ ratio of AlB$_2$ to TiB$_2$ decreases monotonically with the increasing pressure, the slopes are not linear. This is due to the fact that the changes of lattice parameters $c$ with pressure are not linear. This may be related to the non-hydrostatic condition under higher pressure when the pressure transmitting medium becomes solid. Figure 6 shows the $V/V_0$ behaviour of the three materials.

![Fig. 3. Behaviour of $a/a_0$ versus pressure.](image3.png)

![Fig. 4. Behaviour of $c/c_0$ versus pressure.](image4.png)

The obtained values are $B_0 = 185$ GPa for AlB$_2$, 150 GPa for MgB$_2$, and 295 GPa for TiB$_2$. Those values are in agreement with other reports. The bulk modulus reflects the incompressibility of a material. The larger the bulk modulus, the less the compressibility. It is clear that TiB$_2$ is the hardest among the three materials, and AlB$_2$ is in the middle.

Singh calculated the plasma frequencies of MgB$_2$ and AlB$_2$ and some other AlB$_2$-type materi-
als, and found that the plasma frequencies of vibration along the a direction are nearly the same for all the four diborides, which is the reason why the compressibility along the a axis for MgB$_2$ and AlB$_2$ are almost the same. However, the plasma frequencies of vibration along the c direction are related with the c/a ratio of the compounds. The smaller the c/a ratio, the more the coupling enhancement in the c direction, then the less the compressibility. Figures 2 and 4 show that the c axis of AlB$_2$ is compressed less than MgB$_2$, because it has a small value of c. Our previous results of ultrasonic study also indicated that the average phonon frequency of MgB$_2$ increases with the increasing pressure,[17] i.e. the decrease of the lattice parameter leads to enhancing coupling.

![Fig. 5. Ratio of c/a as a function of pressure.](image)

![Fig. 6. V/V$_0$ versus pressure.](image)

MgB$_2$ shows that a rather isotropic compressibility is indicated by the small changes of the c/a ratio. This means that the intra- and inter-layer bonding are in similar strength. Investigation of Bester and Fähnle[19] presented that the total covalent bond energy is larger in the absolute value for AlB$_2$ than for MgB$_2$. This is why the bulk elastic module of AlB$_2$ is larger than that of MgB$_2$. The work points out that, as is expected, the B–B intralayer covalent bond energy is the largest. Interestingly, it is larger in the absolute value for the MgB$_2$ compound although the B–B distance is larger than that in the Al compound. This may be due to the fact that the anti-bonding position is not filled. However, for the Al compound, since it has one more electron, the anti-bonding position is filled, therefore the B–B intralayer covalent bond energy for AlB$_2$ is smaller than MgB$_2$. This is the reason that the a axes of AlB$_2$ and MgB$_2$ are almost equally compressed. Bester and Fähnle[19] also indicated that contrary to the general belief, there is also a considerable covalent bond energy between the layers and even in the M layers. Therefore MgB$_2$ and AlB$_2$ are of rather isotropic compressibility. The B–M covalent bond energy increases when element M is selected from Mg to Al, which is consistent with the smaller c/a ratio of the Al compound and less compress of c of AlB$_2$. The B–M distance is in fact smaller for M =Al than for M =Mg.

The covalent bond energies for the most important atom pairs are further analysed by considering the dominant angular-resolved contributions. In all the cases, the p–p coupling contributions are strongest and the s–s contributions are weakest. Bester and Fähnle[19] assumed that because the d-orbitals of M in the compound are unoccupied, the d-orbitals make a non-negligible contribution to the bonding between the B and M layers, which was denoted as a ‘metallic contribution’. This metallic contribution is stronger for AlB$_2$ than for MgB$_2$. Nevertheless, the covalent contribution is also dominant for the bonding between the layers, mediated by the metal atoms. Therefore, the mechanical behaviour of the layer compounds under pressures is almost isotropic. The band character, band structure, charge distribution, and charge density at the Fermi surface of the materials are related to the crystal parameters. Therefore, changes of the crystal parameters under pressures may change the characters of the bands, then change the properties of electricity of the materials.

For the TiB$_2$ compound, although the band character, band structure, charge distribution, and charge density at the Fermi surface are complicated because it is a transition metal compound that has more electrons and empty d orbitals, the above discussions are still suitable. Spoor et al.[20] studied the elastic constants and the crystal anisotropy of TiB$_2$. They indicated that the elastic properties of TiB$_2$ are considerably isotropic under the ambient condition. In our work, the experiment also indicates that they are almost completely isotropic under pressures.

In conclusion, we have performed an experimental study of the high pressure behaviour of AlB$_2$-type compounds. The results indicate that the three
compounds of TiB$_2$, MgB$_2$ and AlB$_2$ have different mechanical behaviour under pressures, which are explained by the bonding strengths in the crystal.

**References**


