Structural stability and electrical properties of AlB_2-type MnB_2 under high pressure*

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The structural stability and electrical properties of AlB_2-type MnB_2 were studied based on high pressure angle-dispersive x-ray diffraction, *in situ* electrical resistivity measured in a diamond anvil cell (DAC) and first-principles calculations under high pressure. The x-ray diffraction results show that the structure of AlB_2-type MnB_2 remains stable up to 42.6 GPa. From the equation of state of MnB_2, we obtained a bulk modulus value of 169.9±3.7 GPa with a fixed pressure derivative of 4, which indicates that AlB_2-type MnB_2 is a hard and incompressible material. The electrical resistance undergoes a transition at about 19.3 GPa, which can be explained by a transition of manganese 3d electrons from localization to delocalization under high pressure.

Keywords: transition metal compounds, high pressure effects, structural stability, electrical properties

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1. Introduction

Phase transitions are important subjects in physics, chemistry, bioscience, etc., and they are always accompanied by many interesting phenomena.[1–4] The isostructural phase transition is a vital phase transition with a volume collapse; the material remains in the same space group, which has been observed in many transition metal and rare-earth metal compounds. For instance, a 9.8% volume collapse was observed in the cubic $PbCrO_3$ perovskite at 1.6 GPa, which was related to the mixing of $PbCrO_3$–$CrPbO_3$ combination.[5] A first-order isostructural Mott transition was observed in MnO with a 6.6% volume collapse at about 105 GPa.[6] Hexagonal $ThAl_2$ changes 2% in volume at 5.5 GPa.[7] Isostructural phase transitions are always ascribed to the electronic structure phase transition in the SmS system,[8] or a spin related phase transition in the orthorhombic perovskites of $PrFeO_3$, $EuFeO_3$ and $LuFeO_3$.[9] To our knowledge, although the isostructural phase transitions are not rare and have been discussed a great deal, till now multiple isostructural phase transitions in a single system have not been reported.

Many transition metal diborides have been studied because of their special combinations of mechanical, chemical, thermal and electrical properties; they are considered stiff materials.[10] For instance, rhenium diboride (ReB_2) is the hardest material that exhibits a metallic behavior;[11] its structure is stable due to its high hardness under high pressure. Seeking to understand the high hardness and large bulk modulus of transition metal diborides, many reports have been devoted to the high-pressure behavior in a diamond anvil cell (DAC) of AlB_2-type (space group $P6/mmm$) transition metal diborides, such as VB_2 and ZrB_2 (both up to 50 GPa),[12] TiB_2 (up to 65 GPa),[13] and HfB_2 (up to 30 GPa).[14] However, no structural phase transitions were observed in those experiments. The elastic and electronic properties of NbB_2 at high pressure were calculated with the first-principles plane-wave pseudopotential density functional theory; they did not find the structural phase transformation.[15] Although the ReB_2-type MnB_2 (space group $P6_3/mmc$) was predicted to be more energetically favorable than the AlB_2-type one, no experimental results have shown its existence so far.[16,17]

In this paper, we study the high-pressure behavior of AlB_2-type MnB_2 both experimentally and theoretically. We find that the electrical resistance undergoes a transition at about 19.3 GPa, which can be explained by a transition of manganese 3d electrons from localization to delocalization that is induced by the high pressure, which may help to understand the compression behavior, the electron transport behavior and the spin reactions of AlB_2-type transition metal compounds.

The rest of the paper is arranged as follows. In Section 2, we provide the experimental and theoretical methods in detail. In Section 3, we show our results with some discussion. Finally in Section 4, we give the conclusion of this research.

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2. Experimental and theoretical methods

AlB_2-type MnB_2 was prepared by high pressure high temperature (HPHT) synthesis with a SPD6×600T cubic anvil apparatus. The raw materials were manganese powder (Alpha Co.; average particle size 1–5 μm, purity 99.9%) and amorphous boron powder (Alpha Co.; average particle size 1–5 μm, purity 99.5%). The manganese powder and amorphous boron powder in a stoichiometric ratio were carefully mixed in an agate mortar with some alcohol for better mixing. Then the mixture was pressed into a pellet, 10 mm in diameter and 3 mm in height. The details of the HPHT synthesis process have been presented elsewhere.[18,19]

The high pressure angle-dispersive x-ray diffraction (ADXRD) experiment was carried out with a 300 μm culet Mao–Bell type diamond anvil cell (DAC) at Beamline X17C of the National Synchrotron Light Source (NIST), Brookhaven National Laboratory. The x-ray had a wavelength of $\lambda = 0.406417$ Å and a focus of 25 μm × 25 μm. In this work, silicone grease was used as the pressure-transmitting medium to restrain quasi-hydrolyzation. The synthesized MnB_2 powder was loaded into a 100 μm hole in a T301 stainless steel gasket, which was prepressed to 46 μm thick. A CeO_2 standard from NIST was used to calibrate the sample–detector distance and the geometric parameters. A piece of ruby was loaded into the sample hole to calibrate the pressure based on the shift of its R_1 photoluminescence line.[20] The XRD patterns were analyzed with the FIT2D program.[21]

We measured the *in situ* high pressure electrical resistivity in a DAC at room temperature under high pressure. In this measurement, the culet of the diamond was 400 μm in diameter. The gasket was a piece of T301 stainless steel with a 110 μm hole, prepressed to 56 μm in thickness. Molybdenum was used as the electrode material; the insulated material was an aluminum oxide layer. The details can be found in Ref. [22].

We carried out first-principles calculations of AlB_2-type MnB_2 with the Vienna *ab initio* simulation package (VASP).[23–26] The interaction between ions and electrons was described by the ultra-soft Vanderbilt pseudopotentials and the projector augmented wave (PAW) pseudopotentials.[27–29] Exchange and correlation effects were described by the scheme of Perdew–Wang 91 (PW91) and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerh.[30,31] We chose a cutoff energy of 800 eV and a *k*-point grid of 0.015 $Å^{-1}$ after performing accurate convergence tests, which ensured error bars for the total energy per atom of no more than 1 meV.

3. Results and discussion

The sample of MnB_2 was synthesized in a stoichiometric ratio at 5.5 GPa, 1350 °C and held for 10 min.[14] The structure of the prepared MnB_2 was indexed to a *P6/mmm* structure with lattice parameters $a = b = 3.010(1)$ Å and $c = 3.038(1)$ Å,[19] which are quite consistent with the previously reported values ($a = b = 3.009$ Å, $c = 3.039$ Å).[32] The *in situ* high-pressure ADXRD data are presented in Fig. 1. Except for the (110) peak of iron, the (001), (100), (101) and (110) peaks of MnB_2 are clearly seen in the high pressure XRD patterns. With increasing pressure, no new diffraction peaks appeared and all the peaks could be well indexed to the $P6/mmm$ space group. Therefore, we conclude that the structural symmetry remains unchanged in the whole pressure range studied.

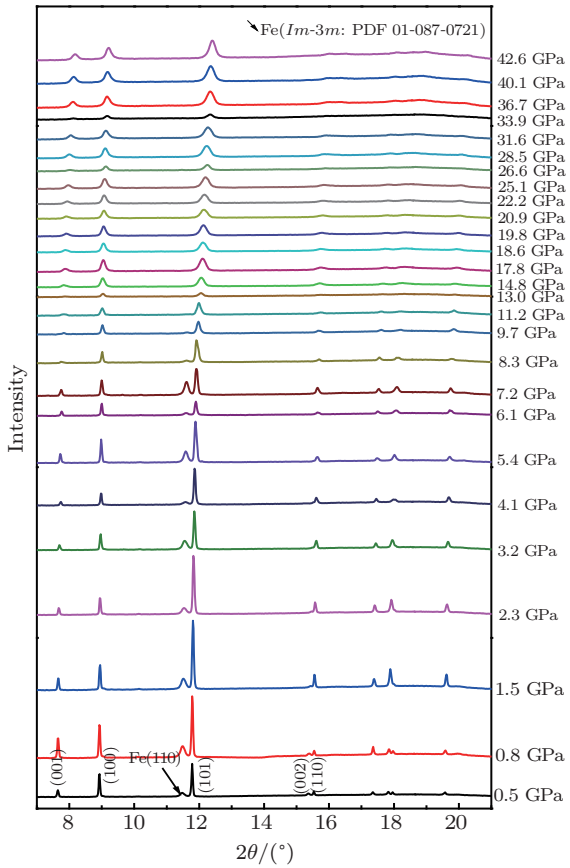


Fig. 1. (color online) High pressure angle diffraction x-ray diffraction data of prepared MnB_2 sample.

We studied the physical properties of MnB_2 under pressure experimentally. The lattice parameters are shown in Fig. 2. We find that both the *a* axis and the *c* axis change discontinuously at 11.2 GPa and 19.8 GPa. The AlB_2-type MnB_2 is a stacking of intercalated graphite-like boron sheets and hexagonal layers of manganese atoms. Therefore, the lower compression of the *a* axis can be ascribed to the strong interactions of the B–B covalent bond in the graphite-like sheets and the higher compression of the *c* axis can be ascribed to the weak bond between the manganese and boron atoms at high pressure.

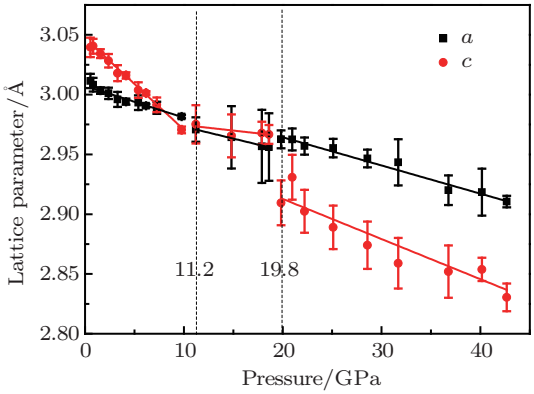


Fig. 2. (color online) Lattice parameters of MnB_2 from experimental measurements as functions of pressure.

We show the volume dependence of MnB_2 under pressure in Fig. 3. The P–V data of AlB_2-type MnB_2 are fitted to the usual Birch–Murnaghan (BM) equation of state (EOS)[33]

$$P = 3/2B_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + 3/4(B_0' - 4) \times [(V_0/V)^{2/3} - 1]\}, \quad (1)$$

where B_0 is the isothermal bulk modulus, B_0' is the first pressure derivative of the bulk modulus and V is the volume. We obtain the bulk modulus $B_0 = 169.9 \pm 3.7$ GPa with a fixed $B_0' = 4.0$. The B_0 is close to the theoretical bulk modulus B_0 (210 GPa).[34] It is worth noting that the bulk modulus of MnB_2 obtained in our work is lower than those of TiB_2 (236.3 ± 23.4 GPa) and HfB_2 (232 ± 13 GPa), which indicates that MnB_2 may be not as hard as TiB_2 (33 GPa) and HfB_2 (30.8 GPa).[13,14] However, it is reasonable to consider the AlB_2-type MnB_2 as a hard material due to its large bulk modulus.

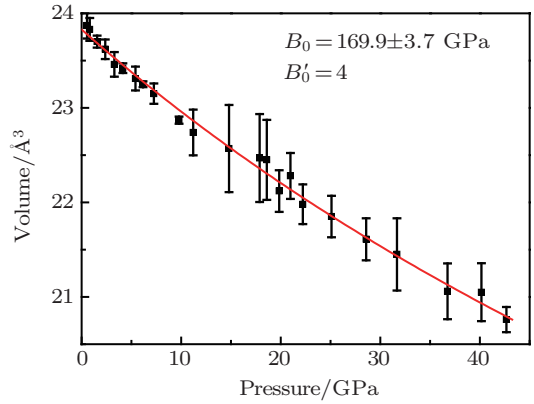


Fig. 3. (color online) Pressure–volume data of MnB_2.

The most direct evidence reflecting the electron transport property is the change of electrical resistivity as a function of pressure. We successfully measured the electrical resistivity of MnB_2 *in situ* at high pressure, which we show in Fig. 4, where one can clearly see that the resistance of MnB_2 decreases during compression. We can see that there are clearly two regions: region I (0–19.3 GPa) and region II (19.3–35.2 GPa). With compression, the electrical resistivity varies from the order of magnitude of 10^{-3} Ω·cm at 0.1 GPa to 10^{-6} Ω·cm at 30.3 GPa, with a three-order difference.

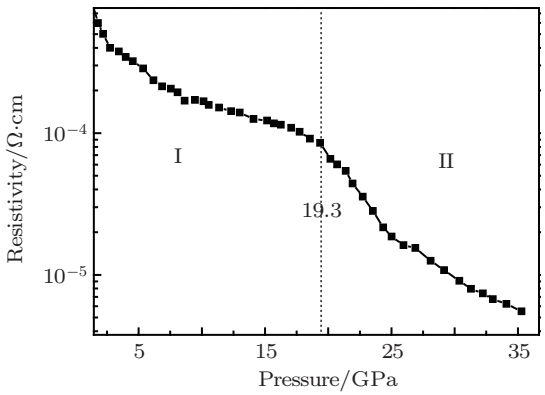


Fig. 4. *In situ* high pressure measurements of the electrical resistivity of our prepared MnB_2 sample.

Manganese has a special position in the periodic table, in the cross-over region between delocalization and localization.[35] All elements in this region and their compounds show complex and interesting behaviors; it is reported that MnB_2 is paramagnetic at room temperature.[36] All our calculations were performed on ferromagnetic MnB_2 at 0 K. The resistance transition at 19.3 GPa of MnB_2 is in good agreement with compounds of this region, such as Ce, MnO, SmS, $ThAl_2$ and PdN_2.[6–8,37,38] A shrinkage of volume from ferromagnetic to non-magnetic phase in Fe_3C was also observed at 55 GPa without any structural changes.[39]

The physical properties of MnB_2 are calculated under pressure and shown in Fig. 5. According to the density of state (DOS) in Fig. 5(a), MnB_2 is metallic at ambient pressure. The calculated enthalpy at 0 K reveals that the ferromagnetic phase has a lower enthalpy, as shown in Fig. 5(d), which suggests that our ferromagnetic phase models are reasonable. We show the DOS of MnB_2 in Figs. 5(a)–5(c). The d DOS shows that the d orbital splits and broadens during compression (Fig. 5(a)). The conductive electrons mostly localize around the Fermi level, so a change in the density of electrons localized around the Fermi level can lead to the change of resistivity. The density of electrons at the Fermi level, shown in Fig. 5(b), changes only a bit from 3 GPa to 19 GPa; however, it becomes larger and larger at pressures higher than 19 GPa, which indicates that the quantity of 3d conductive electrons increases under pressure. Therefore, the 3d electrons become delocalized at 19.3 GPa. This may be the main reason for the sharper drop of resistivity at 19.3 GPa. We show the Fermi level DOS ($n_{\text{spin down}} - n_{\text{spin up}}$) in Fig. 5(c). The value at the Fermi level is zero at 28 GPa, where the total spin disappears. More experimental evidence is needed to prove this.

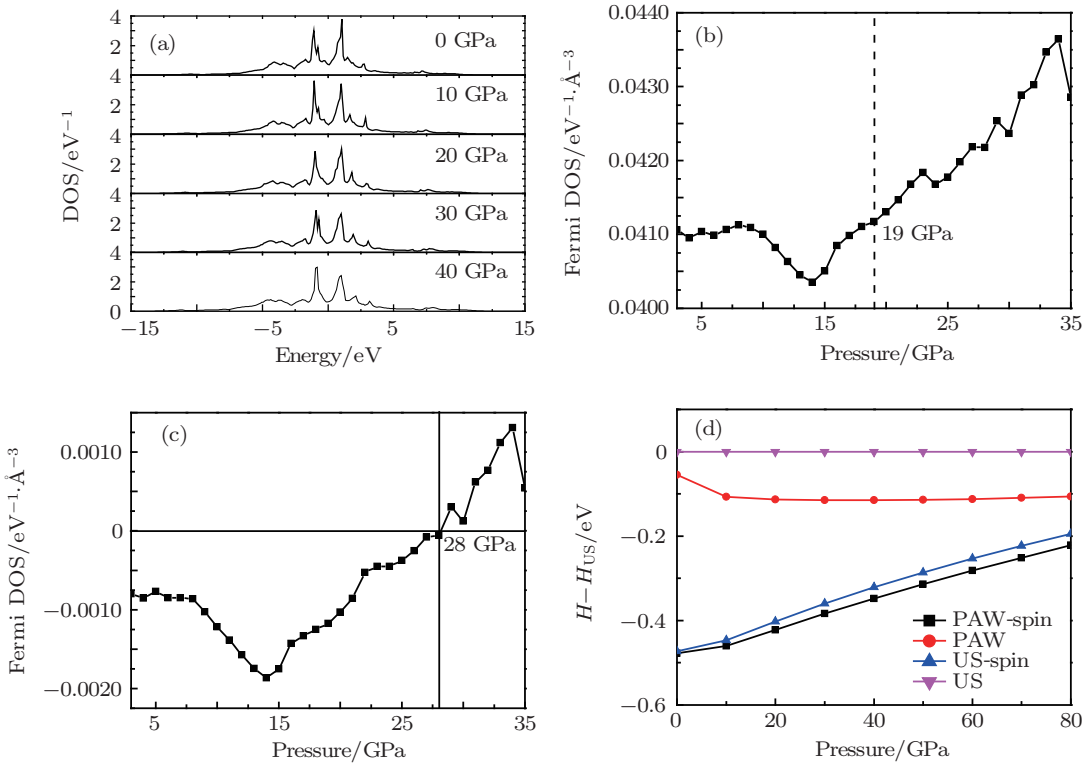


Fig. 5. (color online) The physical properties of MnB_2 under pressure obtained theoretically: (a) d-orbital DOS, (b) Fermi DOS, (c) Fermi DOS (spin down − spin up), (d) calculated static enthalpies difference of the AlB_2-type MnB_2 with different magnetism as a function of pressure. The pink and red lines represent the results from the ultrasoft pseudopotential (US), which are defined as the zero point, and from the projector augmented-wave (PAW) pseudopotential, respectively; the blue and black lines indicate the calculations based on the US with a ferromagnetic lattice and based on the PAW with a ferromagnetic lattice, respectively.

4. Conclusion

We carried out *in situ* high pressure ADXRD experiments on AlB_2-type MnB_2 with a space group $P6/mmm$ up to 42.6 GPa. No crystal structural transitions occurred in the pressure range of 0–42.6 GPa, only the unit cell shrinks with the compression. We also studied the electrical properties of AlB_2-type MnB_2. The electrical resistivity decreased continuously with pressure; a subtle change of the rate of decrease was detected around 19.3 GPa. According to our first-principles calculation, the transition at about 19.3 GPa can be attributed to a sudden increase of the density of electrons at the Fermi level, which is induced by manganese 3d electrons' transition from localization to delocalization. From the equation of state of MnB_2, we obtained a bulk modulus value of 169.9±3.7 GPa along with its pressure derivative 4, indicating that AlB_2-type MnB_2 is a hard material.

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