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Electronic structures and mechanical properties of iron borides from first principles

Yanpeng Gou [a], Zhao Fu [a], Yongcheng Liang [a,*], Zheng Zhong [b], Shiming Wang [a]

[a] College of Engineering Science and Technology, Shanghai Ocean University, Shanghai 201306, China
[b] School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, China

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ABSTRACT

The structural properties, mechanical behaviors and electronic structures of FeB_4 and FeB_2 have been studied systematically by first-principles calculations considering the strong correlation effect. Our results show that FeB_4 is incompressible and hard, but the recently reported superhard feature [Phys. Rev. Lett. 111 (2013) 157002] is not supported by the present calculations. Interestingly, we find that FeB_2 rivals FeB_4 in hardness. By analyzing their crystal geometries, band structures and density of states, we elucidate the underlying origins of the related physical properties.

1. Introduction

Iron borides have attracted much attention, not only because of the potential to serve as a hardening agent in steels [1] or as hard protective coatings [2,3], but also because of the possibility of finding brand new stable Fe–B phases with appealing properties. Strikingly, Kolmogorov et al. [4] used advanced compound prediction methods to identify two previously unknown structures FeB_4 (space group *Pnnm*) and FeB_2 (space group *Pnma*). Moreover, the former was predicted to have the necessary features to exhibit phonon mediated superconductivity with a T_c of 15–20 K while the latter was shown to be the first metal diboride semiconductor. By examining their thermodynamic factors that could promote the formation, FeB_4 and FeB_2 were stabilized further under pressure [5]. Subsequently, Gou et al. [6] successfully synthesized the novel FeB_4 at pressure above 8 GPa and high temperatures. They not only confirmed FeB_4 to exhibit bulk superconductivity below 2.9 K, but also reported that it should belong to the group of superhard materials ($H_v > 40$ GPa), thus bridging the gap between the superhardness and superconductivity community.

Generally, superhard materials such as diamond and cubic boron nitride (*c*BN) are insulators or semiconductors with covalent bonds. Hardness depends strongly on plastic deformation, which brings about electron-pair bonds being broken and remade in a covalent crystal. Breaking an electron-pair bond means that two electrons become energetically excited from the valence band to the conduction band, so the intrinsic hardness of a single crystal is often related to its electronic structure, particularly to the band gap [7]. However, the measured nanoindentation hardness of FeB_4 was reported to be 62 GPa and its microhardness measurement with a load of 20 N gave the value of Vickers hardness ranging from 43 to 70 GPa [6]. All values in this range are exceptionally high, not only exceeding that of other hard metal-based compounds including OsB_2 (16.8–23.5 GPa), ReB_2 (26.6–48 GPa), and WB_3 (28.1–43.3 GPa), but also that of rivaling *c*BN (45–50 GPa) [8–15]. It therefore is a bit surprising that a superconducting metallic system is so hard. Because of the technical difficulties, no adequately sized single crystals of FeB_4 may be obtained, and thus its mechanical properties need to be confirmed theoretically.

In order to fully clarify mechanical properties of FeB_4, the theoretical calculations that can provide further details are highly desirable. So far, only two theoretical reports on the mechanical properties of FeB_4 were available [16,17], but their predicted hardness values (24.2 GPa, 25.1 GPa) are much lower than the measured data (43–70 GPa). As we know, Fe is one of the 3*d* transition metals with strong correlations. Although their calculations provide useful information for the understanding of mechanical characters of FeB_4, they neglect the strong correlations. Thus, the effect of strong correlations on mechanical properties of FeB_4 is unknown. Furthermore, less attention has been paid to the band structure of FeB_4, which is critical to understanding the related physical properties. On the other hand, FeB_2 is currently raising great expectations for superhard materials since it combines the semiconducting feature, high stability and

* Corresponding author. Tel.: +86 21 61900820; fax: +86 21 61900805.
E-mail address: ycliang@shou.edu.cn (Y. Liang).

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compact structure with the prediction of a very large bulk modulus (311 GPa) [5], but its mechanical properties and electronic structures are not fully explored. In the present work, we first perform systematic first-principles calculations to study mechanical properties of FeB_4 and FeB_2. Our calculations indicate that FeB_4 is incompressible and hard, but do not support the experimentally measured superhardness [6]. It is found that the hardness of FeB_2 matches that of FeB_4. Then, the structural and electronic origins of the related physical properties of FeB_4 and FeB_2 are elucidated.

Calculations on FeB_4 and FeB_2 were performed using the projector augmented wave (PAW) method and the Vienna *ab initio* simulation package (VASP) [18]. We have conducted very careful tests for the convergence of calculated results with respect to the *k*-points number and the cutoff energy. A large cutoff energy of 500 eV was adopted and the dense Monkhorst–Pack *k*-points meshes were generated with the $12\times10\times14$ and $10\times12\times14$ grids for FeB_4 and FeB_2, respectively. We allowed spin polarization and did not find the existence of local magnetic moments on Fe atoms of FeB_4 and FeB_2. To compare the effect of strong correlations on their mechanical properties and electronic structures, we have used two approximations, the generalized gradient approximation (GGA) [19] and the GGA together with Hubbard model (GGA+*U*) [20] with effective Hubbard *U* (after subtraction of the exchange parameter *J*) of 4 eV.

Structural optimizations and total-energy calculations for FeB_4 and FeB_2 have been performed. The equilibrium volume (V_0), bulk modulus (B_0) and its pressure derivative (B_0') are obtained by the least-square fit of calculated volume-energy sets to the Birch–Murnaghan equation of states [21]. The complete set of elastic constants and other mechanical properties (shear modulus, Young's modulus, and Poisson's ratio) are evaluated through our developed methods, which have been demonstrated to be very good in providing accurate and reliable predictions of mechanical properties of various systems [22–24]. The obtained results are summarized in Table 1. First, let us look at EOSs of FeB_4 and FeB_2. The lattice constants and bulk moduli with the GGA+*U* calculations are slightly smaller than those with GGA within an error of 2%. For FeB_4, the bulk moduli for the cases with GGA and GGA+*U* are 268 GPa and 263 GPa, respectively. Both values accord with the experimental value (252 GPa) [6], but are smaller than those of WB_3 (295 GPa) [13] and ReB_2 (356 GPa) [10]. Interestingly, the bulk modulus of FeB_2 (311-314 GPa) is larger than that of FeB_4 and WB_3, even rivals that of ReB_2. To further compare the incompressibility of FeB_4, FeB_2, WB_3 and ReB_2 under pressure, their volume compressions as a function of pressure are presented in Fig. 1(a). We can explicitly see the order of incompressibility from low to high: $FeB_4 < WB_3 < FeB_2 < ReB_2$, although they are all incompressible materials. Then, we discuss the elastic constants of FeB_4 and FeB_2. It is noticed that the maximum difference between our GGA and GGA+*U* calculations totals to up to 18.6%, thus the effect of strong correlations on the mechanical properties should be considered. Large values of FeB_4 ($C_{11}=429$ GPa, $C_{22}=790$ GPa, $C_{33}=487$ GPa) and FeB_2 ($C_{11}=599$ GPa, $C_{22}=730$ GPa, $C_{33}=579$ GPa) demonstrate that both phases possess high linear incompressibility. However, there is substantial anisotropy in the compressibility of FeB_4 and FeB_2. Their anisotropic behaviors can be observed from their axial compressions as function of pressure, as shown in Fig. 1(b). It is obvious that the *c* axis of FeB_4 is the most incompressible while the *a* axis of FeB_4 is the most compressible. At the same time, the shear properties of FeB_4 ($C_{44}=220$ GPa, $C_{55}=171$ GPa, $C_{66}=235$ GPa) and FeB_2 ($C_{44}=275$ GPa, $C_{55}=199$ GPa, $C_{66}=230$ GPa) also exhibit much anisotropy, although they have high shear stiffness.

For FeB_4, its shear and Young's moduli ($G=207$ GPa, $E=495$ GPa) are much larger than those of Fe_2B ($G=143$ GPa, $E=355$ GPa) and FeB ($G=157$ GPa, $E=399$ GPa) [5], but are much smaller than those of WB_3 ($G=252$ GPa, $E=588$ GPa) [13] and ReB_2 ($G=293$ GPa, $E=691$ GPa) [10], respectively. On the contrary, the Poisson's ratio of FeB_4 (0.20) is smaller than that of Fe_2B (0.24) and FeB (0.27) [5], but is larger than that of WB_3 (0.168) [13] and ReB_2 (0.181) [10]. These results suggest that FeB_4 is superior to Fe_2B and FeB from the aspect of mechanical properties, but is inferior to WB_3 and ReB_2. According to the recently proposed hardness model [25], we have further estimated the Vickers hardness H_v of FeB_4 to be 25.5 GPa from the GGA calculation. This value is close to the previous predictions (24.2 GPa, and 25.1 GPa) [16,17] but largely deviates from the experimentally reported value (43–70 GPa) [6]. Considering the strong correlation effect, our GGA+*U* calculations have presented a large hardness value of 31.2 GPa, which is still much smaller than the measured one. Therefore, FeB_4 is an incompressible and hard material but not a superhard one, at odds with the conclusion of Gou et al. [6].

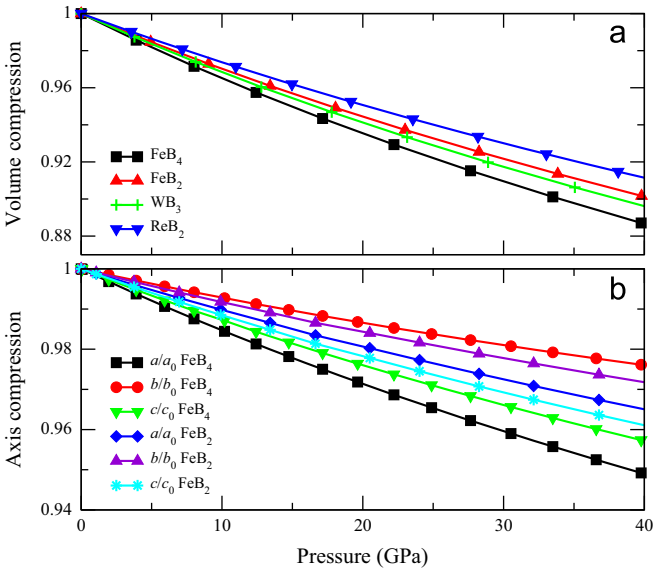

Fig. 1. (Color online) (a) Calculated volume compression V/V_0 and (b) axis compression a/a_0, b/b_0, c/c_0 of FeB_4 and FeB_2 as a function of pressure.

Table 1
Calculated equilibrium lattice parameters a_0 (Å), b_0 (Å), c_0 (Å), bulk modulus B_0 (GPa), its pressure derivative B_0', elastic constants C_{ij} (GPa), shear modulus G (GPa), Young's modulus E (GPa) and Poisson's ratio ν for FeB_4 and FeB_2.

	a_0	b_0	c_0	B_0	B_0'	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	G	E	ν
FeB_4																	
GGA	4.517	5.285	3.007	268	4.02	409	768	451	161	161	152	216	154	222	189	462	0.22
GGA+*U*	4.500	5.265	2.998	263	3.91	429	790	487	131	137	130	220	171	235	207	495	0.20
FeB_2																	
GGA	4.815	4.805	3.738	314	4.14	592	723	574	185	160	136	271	198	221	230	555	0.21
GGA+*U*	4.772	4.775	3.698	311	4.10	599	730	579	179	154	129	275	199	230	235	564	0.19