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Elastic properties of superconducting NbB_{2+x} obtained from first-principles calculations

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Abstract

First-principles calculations have been performed on NbB_{2+x} to obtain its elastic constants using the plane wave pseudopotential method based on density functional theory, within the generalized gradient approximation. We have derived the bulk moduli, shear moduli, Young's moduli, Poisson's ratios and elastic anisotropies for NbB_{2+x} polycrystalline aggregates. The elastic properties obtained here show that the structure becomes less symmetrical as the boron content increases. The higher elastic anisotropies A_K and A_G were associated with the higher superconducting transition temperature T_c reported for this material (Escamilla *et al* 2004 *J. Phys.: Condens. Matter* **16** 5979). Using the Debye temperature, θ_D, and T_c, the electron–phonon coupling constant λ was obtained from the McMillan equation. For the concentrations from $(B/Nb) = 2.20(1)$ to 2.34(1), the values of λ increase from 0.497 to 0.572; this suggests that NbB_{2+x} is a weakly coupled Bardeen–Cooper–Schrieffer type superconductor.

1. Introduction

Since the discovery of superconductivity below 40 K in MgB_2 [1], much experimental [2–5] and theoretical [6–8] research has been carried out on this diboride and isostructural systems. Most of the results suggest that MgB_2 is a conventional superconductor, rather than a high T_c cuprate. The structure contains graphite type B layers that play a very important role for superconductivity. Therefore, the structural characteristic may be important for obtaining a guide for the ever higher T_c in diborides. For example, studying the elastic properties, one can obtain valuable information about the anisotropy of the bonding and structural stability. Among other physical properties, the elastic properties are useful for calculating the acoustic Debye

Table 1. Lattice parameters as a function of boron content (B/Nb) [10].

(B/Nb)	a (Å)	c (Å)	V (Å^3)
2.00(1)	3.110(2)	3.267(2)	27.369
2.10(1)	3.110(2)	3.282(3)	27.488
2.20(2)	3.108(3)	3.296(3)	27.578
2.30(1)	3.105(2)	3.316(3)	27.683
2.32(1)	3.104(2)	3.319(3)	27.695
2.34(1)	3.104(2)	3.319(3)	27.690

temperature, which is associated with the electron–phonon coupling constant in a phonon-mediated superconductor. Any superconductor isostructural with MgB_2 can be important for studying the relationship of the elastic properties with superconductivity. Among various diborides, the NbB_2 is intriguing as it exhibits strong superconducting transition temperature sensitivity to the stoichiometry [9, 10].

In previous studies on crystalline structure and the superconducting properties of NbB_{2+x} it was shown that: (a) the excess boron in the NbB_2 structure is accompanied by the creation of vacancies on the metal (Nb) site, producing important changes in the electronic and superconducting properties, and (b) the increase of boron induces superconductivity [10].

In order to study the influence of elastic properties in NbB_{2+x} on superconductivity, in this work, we report the elastic properties of non-stoichiometric superconducting NbB_{2+x} obtained by first-principles calculations. We have used the well known Voigt and Reuss schemes to calculate the bulk, shear and Young moduli and also the Poisson's ratios and elastic anisotropies of the corresponding polycrystals. The acoustic Debye temperature and the electron–phonon coupling constant are also reported.

2. Theoretical methods

2.1. Crystal structure and elastic constants

Niobium diboride crystallizes in the hexagonal AlB_2 structure with the space group $P6/mmm$. There are three atoms in the unit cell, all of them on the special positions: the niobium atom at the origin and boron atoms at the $(1/3, 2/3, 1/2)$ sites. The structure is thus extremely simple in that it is defined by two lattice parameters, a and c. On the other hand, for this structure there are six elastic stiffness constants, C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66} [11]; five of them are independent since $C_{66} = (C_{11} - C_{12})/2$. In the present calculations, we used the structural and superconducting parameters for NbB_{2+x} reported by Escamilla *et al* [10] (table 1).

The calculations presented in this work were performed employing the Cambridge Serial Total Energy Package (CASTEP) software, with the plane wave pseudopotential code [12, 13]. The correlation functional GGA-PW91 [14] was used in the calculations. A plane wave basis set with energy cut-off 360 eV is applied. For the sampling of the Brillouin zone a Monkhorst–Pack grid [15] of $9 \times 9 \times 8$ k-points was employed. The convergence tolerances were set as follows: 10^{-6} eV/atom for the total energy, 0.002 eV Å^{-1} for the maximum force on atoms, 10^{-4} Å for the maximum atomic displacement, and 0.003 for the maximum strain amplitude.

2.2. Elastic properties of NbB_{2+x} polycrystalline aggregate

A polycrystalline ceramic material can be treated as an aggregate of single crystals at random orientation. There are two extreme cases for external load: Voigt and Reuss

approximations [16, 17]. In the former the uniform strain in a polycrystal is equal to the external strain and the latter indicates the equality of the uniform stress to the external stress. For hexagonal lattices, the Reuss and Voigt shears (G_R and G_V) and the Reuss and Voigt bulk moduli (K_R and K_V) can be defined by

$$G_R = \frac{5}{2}\frac{C_{44}C_{66}[C_{33}(C_{11}+C_{12})-2C_{13}^2]}{3K_VC_{44}C_{66}+(C_{44}+C_{66})[C_{33}(C_{11}+C_{12})-2C_{13}^2]} \tag{1}$$

$$G_V = \frac{1}{30}(C_{11}+C_{12}+2C_{33}-4C_{13}+12C_{44}+12C_{66}) \tag{2}$$

$$K_R = \frac{C_{33}(C_{11}+C_{12})-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}} \tag{3}$$

$$K_V = \tfrac{1}{9}[2(C_{11}+C_{12})+C_{33}+4C_{13}]. \tag{4}$$

The elastic moduli of the polycrystalline material can be approximated by Hill's average [18]. It is $G = \frac{1}{2}(G_R + G_V)$ for shear moduli and $K = \frac{1}{2}(K_R + K_V)$ for bulk moduli. The Young's modulus, E, and Poisson's ratio, σ, are given by

$$E = \frac{9KG}{3K+G} \qquad \text{and} \qquad \sigma = \frac{3K-2G}{2(3K+G)}. \tag{5}$$

In order to measure the elastic anisotropy of polycrystalline samples we calculated the percentage of anisotropy for the bulk and shear. They are defined as [19]

$$A_K = (100)\frac{K_V-K_R}{K_V+K_R} \qquad \text{and} \qquad A_G = (100)\frac{G_V-G_R}{G_V+G_R}. \tag{6}$$

These values can range from zero (isotropic) to 100%, the maximum anisotropy.

2.3. The Debye temperature

As an important fundamental parameter, the Debye temperature (θ_D) is closely related to many physical properties of solids such as the specific heat and melting temperature. One of the standard methods for calculating the Debye temperature is from elastic constant data, since θ_D may be estimated from the average sound velocity (v_m) using the following equation [20]:

$$\theta_D = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m, \tag{7}$$

where h is Plank's constant, k is Boltzmann's constant, N_A is Avogadro's number, ρ is the density, M is the molecular weight and n is the number of atoms in the molecule. The average sound velocity v_m is given by

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]^{-1/3}, \tag{8}$$

v_l and v_t are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equations as follows [21]:

$$v_l = \sqrt{\frac{3K+4G}{3\rho}} \qquad \text{and} \qquad v_t = \sqrt{\frac{G}{\rho}}, \tag{9}$$

where ρ is the density, K is the bulk modulus and G is the shear modulus.

Table 2. Elastic constants (C_{ij}), bulk modulus (K), shear modulus (G), Young modulus (E), Poisson's ratio (ν) and percentage of anisotropy for the bulk (A_K) and shear (A_G) of polycrystalline NbB_{2+x} calculated with the Voigt and Reuss assumptions as a function of boron content (B/Nb).

(B/Nb)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	K (GPa)	G (GPa)	K/G	E (GPa)	ν	A_K	A_G
2.00(1)	590	110	190	474	225	292	212	1.38	512	0.21	0.06	1.69
2.10(1)	584	108	185	465	221	287	210	1.37	506	0.21	0.08	1.67
2.20(2)	580	107	181	455	218	283	207	1.37	500	0.21	0.12	1.68
2.30(1)	574	103	178	427	212	276	202	1.37	487	0.21	0.25	2.13
2.32(1)	574	102	178	423	211	276	201	1.37	486	0.21	0.28	2.23
2.34(1)	574	102	178	423	211	276	201	1.37	486	0.21	0.28	2.23
Diborides												
TiB_2[a]	656	66	98	461	259	253	261	0.97	582	0.12	0.93	1.03
MgB_2[a]	365	98	65	203	58	147	90	1.63	224	0.25	4.71	7.77
TiB_2[b]	650	79	100	443	256	249	255	0.45	570	0.12	1.25	1.10

[a] Reference [27].
[b] Reference [28].

2.4. The electron–phonon coupling

Using θ_D and the experimental T_c, the values of electron–phonon coupling constant (λ), are deduced from the McMillan equation [22]

$$T_c = \frac{\theta_D}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \tag{10}$$

where μ^* ($\approx$0.13 for most materials) is the Coulomb pseudopotential.

3. Results and discussion

Table 2 shows the elastic properties calculated for the polycrystalline aggregate NbB_{2+x} in comparison with those for TiB_2 and MgB_2. Our results show that the values for the elastic constants decrease monotonically with the boron excess. The large (C_{13}/C_{12}) and small (C_{33}/C_{11}) values indicate that atomic bonding along the a-axis is stronger than that along the c-axis, which is consistent with the fact that the crystal structure of NbB_2 is a layered type one with the layers perpendicular to the c-axis.

It is usually assumed that hardness is defined by the elastic moduli: the bulk modulus (K), a measure of resistance to volume change by applied pressure, and the shear modulus (G), a measure of resistance to reversible deformations upon shear stress [23]. Generally, the search for hard materials is simplified to searching for materials with large bulk modulus or shear modulus, because there is a direct relation between bulk modulus, shear modulus and hardness [24]. The high values that we determined for the bulk and shear moduli of NbB_{2+x} are in agreement with the high hardness of the transition metal diborides. However, comparing the bulk modulus of NbB_2 previously reported [25] with our value calculated, we observed that our value is slightly higher that the reported. This difference might be due to our calculation method being based on polycrystalline aggregate, while the previous results were obtained for single crystal.

Figure 1 shows the K and G elastic moduli and unit-cell volume as a function of boron content. We observed that K and G decrease monotonically while the unit-cell volume increases as the boron content increases. The decreases of K and G can be associated with the less densely packed lattice, and the less symmetric and less pronounced directional

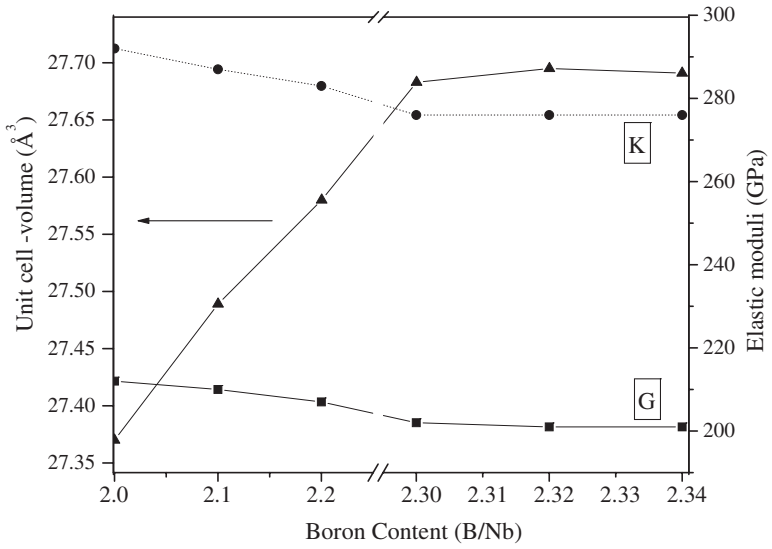

Figure 1. K and G elastic moduli and unit-cell volume as a function of boron content (B/Nb).

bonding of atoms, respectively. This is a strong indication that the NbB_{2+x} may become softer with the increasing of the boron doping. On the other hand, the unit-cell volume increases abruptly in the range composition $2.00(1) \leqslant (B/Nb) \leqslant 2.30(1)$, while that for compositions $(B/Nb) > 2.30(1)$ remains essentially constant. In particular, there is an obvious relationship between the elastic moduli and the unit-cell volume: the softest material (i.e., that with the lowest modulus) has the largest unit-cell volume.

On the other hand, for evaluating material ductility or brittleness Pugh *et al* [26] introduced the K/G ratio: the material is brittle if the ratio is less than the critical value (1.75). In particular, from table 2 it is evident that our NbB_{2+x} samples are brittle, like MgB_2. Moreover, it can be seen from our results that the A_K and A_G increase significantly with the boron content from 0.06 to 0.28 and 1.69 to 2.23, respectively. Similar values are reported for TiB_2 [27, 28].

In summary, the elastic properties obtained here have shown that the structure becomes less symmetrical with boron excess. Moreover, the higher elastic anisotropy A_K and A_G in NbB_{2+x} might be associated with the higher T_c of this material (see figure 2).

Table 3 shows the critical temperature T_c, Debye temperature θ_D and electron–phonon coupling constant λ as functions of boron content. We observed that the increase of boron induces superconductivity from $(B/Nb) \geqslant 2.20(2)$ with a sharp jump in T_c for boron content $(B/Nb) = 2.20(2)$ to 2.30(1). This sharp jump in T_c might be explained by the abrupt increase in the unit-cell volume that is directly proportional to the carrier density and to the in-plane conduction due to an increase in the number of niobium vacancies (see figure 1) [10]. Muon spin rotation/relaxation measurements on NbB_{2+x} samples confirm the increase of the carrier density as boron content increases [29].

Comparing the θ_D values obtained in this work with those reported for MgB_2 [4] and for cuprates HTSC [30], we observed that our values are similar to the former but smaller that the latter. On the other hand, from table 3 we did not observe a clear indication of a proportionality or linear relationship between θ_D and T_c in our samples; apparently θ_D could not be the dominant factor governing T_c.

Finally, using θ_D obtained in this work and T_c reported in [10], the electron–phonon coupling constant λ was calculated from the McMillan equation. For the concentrations from

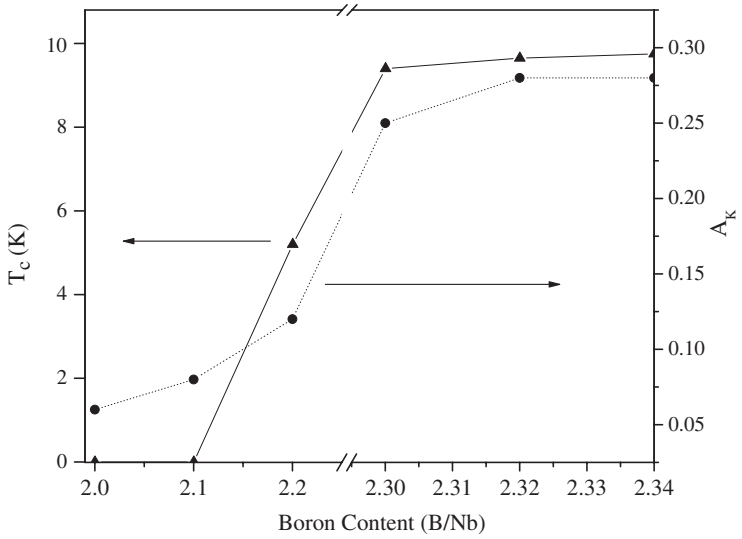

Figure 2. Experimental T_c and anisotropy for the bulk (A_K) calculated as a function of boron content (B/Nb).

Table 3. Debye temperature (θ_D), critical temperature (T_c) [10], and electron–phonon coupling constant (λ) compared with the boron content (B/Nb).

(B/Nb)	T_c (K)	θ_D (K)	λ
2.00(1)	—	869.9	—
2.10(1)	—	875.9	—
2.20(2)	5.20	879.2	0.497
2.30(1)	9.40	878.2	0.567
2.32(1)	9.65	877.9	0.571
2.34(1)	9.75	879.7	0.572

(B/Nb) = 2.20(2) to 2.30(1), the λ values suddenly increase from 0.497 to 0.567 and remain essentially constant from (B/Nb) = 2.30(1) to 2.34(1), like the T_c values. Therefore, the similar behaviors of λ and T_c as functions of the boron content can be associated with changes in the unit-cell volume due to an increase in the number of niobium vacancies. On the other hand, we observed that the electron–phonon coupling constants obtained in this work are smaller that those reported for MgB_2 ($\lambda \approx 1$) [31, 32] but slightly similar than those reported from previous theoretical calculations on NbB_2; for example, Singh [33] obtained 0.43 while another study carried out by Heid *et al* [34] reports a value of 0.67. The differences in previous results might be due to the calculation methods.

From previous theoretical calculations, Shukor [31] has shown that MgB_2 is a moderately strongly coupled BCS type superconductor, using the McMillan expression. Therefore, the small λ ($\approx$0.5) values obtained in this work suggest that NbB_{2+x} samples are weakly coupled superconductors.

4. Conclusions

We have investigated the influence of elastic properties of non-stoichiometric superconducting NbB_{2+x} by means of first-principles plane wave pseudopotential total energy calculations using

the CASTEP code. All the five independent single-crystal elastic constants are determined for samples of composition (B/Nb) = 2.00(1) to 2.34(1). The high values for the bulk moduli are in agreement with the high hardness of the transition metal diborides. The shear moduli decrease with boron excess, indicating less pronounced directional bonding between atoms due to the less symmetric structure. Therefore, the higher anisotropy in this material may be associated with the higher T_c of NbB_{2+x}. On the other hand, using θ_D obtained in this work and T_c reported in [10], the electron–phonon coupling constant λ was calculated from the McMillan equation. We observed that the electron–phonon coupling constant is small, indicating that NbB_{2+x} is a moderately weakly coupled BCS type superconductor. In spite of this, we did not observe a clear indication of a proportionality or linear relationship between θ_D and T_c; therefore apparently the Debye temperature could not be the dominant factor governing T_c.

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