# Superconductivity in boron under pressure: A full-potential linear muffin-tin orbitals study

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Using the full-potential linear muffin-tin orbitals (FP-LMTO) method we examine the pressure dependence of superconductivity in the two metallic phases of boron (B), body-centered-tetragonal (bct) and fcc. Linear response calculations are carried out to examine the phonon frequencies and electron-phonon coupling for various lattice parameters, and superconducting transition temperatures are obtained from the isotropic Eliashberg equation. The fcc phase is found to be stable only at very high pressure (volume per atom $<21.3$ bohrs$^3$), estimated to be in excess of 360 GPa. The bct phase (volume per atom $>21.3$ bohrs$^3$) is stable at lower pressures in the range 210–360 GPa. In both bct and fcc phases the superconducting transition temperature $T_c$ is found to decrease with increasing pressure, due to the stiffening of phonons with an accompanying decrease in electron-phonon coupling. This is in contrast to a recent report, where $T_c$ is found to increase with pressure. Even more drastic is the difference between the measured $T_c$, in the range 4–11 K, and the calculated values for both bct and fcc phases, in the range 60–100 K. The calculation reveals that the transition from the fcc to bct phase, as a result of increasing volume or decreasing pressure, is caused by the softening of the *X*-point transverse phonons. This phonon softening also causes large electron-phonon coupling for high volumes in the fcc phase, resulting in coupling constants in excess of 2.5 and $T_c$ nearing 100 K. Although it is possible that the method used somewhat overestimates the electron-phonon coupling, its success in studying several other systems, including $MgB_2$, clearly suggests that the experimental work should be reinvestigated. We discuss possible causes as to why the experiment might have revealed $T_c$'s much lower than what is suggested by the present study. The main assertion of this paper is that the possibility of high $T_c$, in excess of 50 K, in high pressure pure metallic phases of B cannot be ruled out, thus pointing to (substantiating) the need for further experimental investigations of the superconducting properties of high pressure pure phases of B.

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## I. INTRODUCTION

Although metallization of boron (B) under pressure was predicted on the basis of electronic structure calculations some time ago,[1] experimental verification of this result has so far been lacking. On the basis of the calculations,[1] nonmetallic icosahedral B is expected to undergo a structural transition, first to a body-centered-tetragonal (bct) phase at ~210 GPa and then to a face-centered-cubic (fcc) phase at ~360 GPa. Recently high pressure experiments by Eremets *et al.*[2] have found B to be not only a metal, but also a superconductor at high pressure, with superconducting transition temperature $T_c$ increasing with increasing pressure. Superconductivity appears at around 160 GPa, and $T_c$ increases from 4 K at 160 GPa to 11.2 K at 250 GPa. The appearance of superconductivity in B under pressure is not surprising, because the existence of different phases is usually an indication of strong electron-phonon coupling, which is (most often) also responsible for superconductivity. In this work we study the superconductivity in bct and fcc phases of B using *ab initio* theoretical calculations. We use the linear response scheme implemented by Savrasov[3,4] to study the phonon properties and electron-phonon coupling. The electronic structure is calculated by using the full-potential linear muffin-tin orbital (FP-LMTO) method.[5] Recently such calculations have been performed for $MgB_2$ (Ref. 6) and several other systems,[7,8] including some B-containing compounds,[9,10] and have been found highly successful in capturing the essence of electron-phonon superconductivity in these compounds.

A theoretical study of superconductivity in the fcc phase of B was reported by Papaconstantopoulos and Mehl[11] shortly after Eremets *et al.*[2] reported their experimental results. However, the lattice parameters for the fcc phase used by the authors correspond to volumes per atom for which a lower energy structure is bct, as had been revealed by an earlier calculation of Mailhiot *et al.*[1] Papaconstantopoulos and Mehl[11] calculate the electron-phonon coupling or the Hopfield parameter using the rigid muffin-tin approximation, arguing that the fcc phase might be metastable for such lattice parameters. This speculation is based on their calculation of elastic constants showing $C_{11}-C_{12}>0$; $C_{12}>0$, i.e., the

 

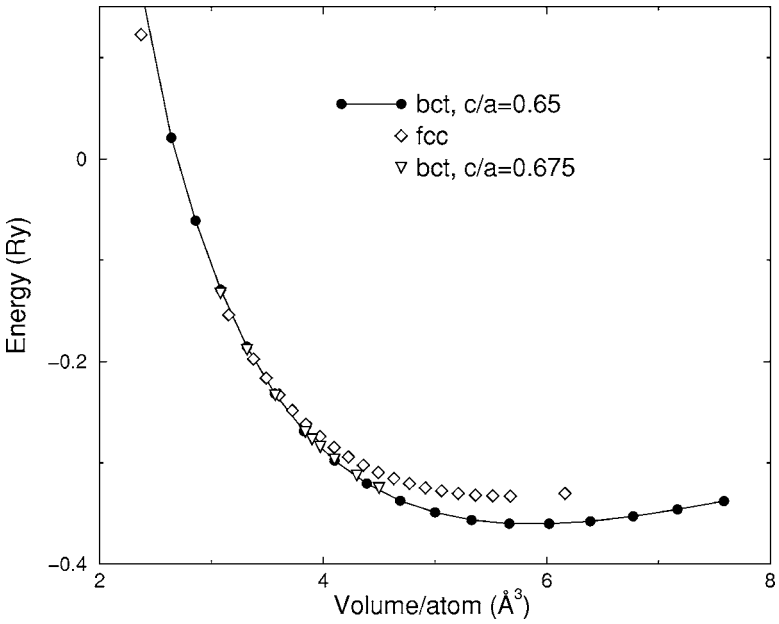


FIG. 1. Energy vs volume (per atom) curves for the fcc and bct phases of B. A constant energy of 49.0 Ry has been added to the energies per atom for convenience in plotting.

Born criteria[12] for the stability of the cubic phase are not violated. However, our linear response calculations yield imaginary phonon frequencies for lattice parameters in excess of 4.4 a.u. in the fcc phase. Thus, although the existence of a metastable fcc phase for lattice parameters 4.6–6.0 a.u. used by Papaconstantopoulos and Mehl[11] cannot be ruled out, the chances are that the equilibrium phase at such lattice parameters is not fcc. Our calculations for the equilibrium fcc phase (lattice parameter less than 4.4 a.u.) shows a volume dependence of the superconducting transition temperature that is the opposite of what is observed experimentally, i.e., $T_c$ decreases with increasing pressure. The study by Papaconstantopoulos and Mehl[11] only involves the fcc phase with large lattice parameters, for which the structure is unstable or, at best, metastable. The present work studies both the fcc and bct phases, each within its appropriate range of lattice parameters. Our linear response calculations also indicate the onset of a bct phase via preference for a change in the $c/a$ ratio as the volume per atom is increased. Detailed discussion of the relevance of our results to the experimental work and that of Papaconstantopoulos and Mehl[11] is provided in appropriate sections.

The organization of this paper is as follows. In Sec. II we discuss the calculated stability of the bct and fcc phases of B as a function of volume per atom. In Secs. III and IV we discuss the calculated electronic bands, phonon spectra, and electron-phonon coupling for the fcc and bct phases, respectively. In Sec. V we discuss the volume dependence of the superconducting transition temperature, summarize and compare our results with the experimental data, and discuss possible sources of difference between the two.

## II. STABILITY OF fcc AND bct PHASES

The volume vs energy curves for fcc and bct phases of B, obtained via FP-LMTO calculations, are shown in Fig. 1. A constant energy of 49.0 Ry has been added to the energies per atom for convenience in plotting. These results are very similar to those given by the LMTO-ASA (atomic sphere approximation) method, and are in close agreement with the earlier plane-wave pseudopotential calculations of Mailhiot *et al.*[1] Pseudopotential calculations of total energy of the bct structure by Mailhiot *et al.*[1] as a function of $c/a$ had indicated a global minimum around $c/a \sim 0.6$. Via an elaborate study of the total energies for various monoclinic and tetragonal distortions of the fcc unit cell as well as the bct total energies for various $c/a$ values, these authors concluded that the bct minimum occurs around $c/a \sim 0.65$. We have not carried out extensive calculations to locate the exact value of $c/a$, but our FP-LMTO calculations on a crude mesh of $c/a$ for fixed volumes do indicate a value in the range 0.6–0.7. Our linear response calculations for $c/a=0.65$, however, produced complex phonon frequencies at the symmetry point $N$ and nearby wave vectors. Increasing $c/a$ to 0.675 resulted in real frequencies at all symmetry and intermediate points. Thus the linear response results in this paper are presented for this value of $c/a$. It is evident from Fig. 1 that the actual energy values for $c/a=0.65$ and 0.675 for the same volume in the bct phase are very close, and their energy-volume curve intersects the fcc energy-volume curve at almost the same point. Thus the conclusions regarding the stability of the bct phase against fcc are not influenced critically by the choice of $c/a$ in the range 0.65–0.675. The volume per atom at which the fcc and the bct energy-volume curves intersect is 21.3 bohrs$^3$ or 3.156 Å$^3$, as found by Mailhiot *et al.*[1]

## III. THE fcc PHASE

### A. Energy bands

In Fig. 2 we show the FP-LMTO energy bands in fcc B as a function of the lattice parameter "a". Calculations were carried out with a double-$\kappa$ *spd* LMTO basis set for describing the valence bands. The charge densities and potentials were represented by spherical harmonics with $l \leqslant 6$ inside the

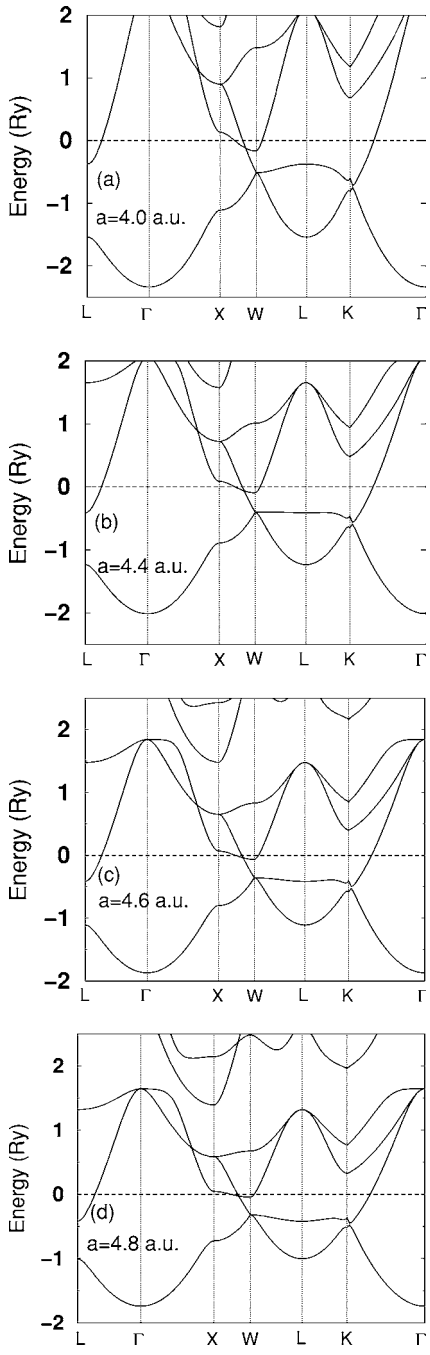


FIG. 2. The FP-LMTO energy bands in fcc B for four different lattice parameters. The flat energy band between the symmetry points $X$ and $W$, which provides strong electron-phonon coupling, also renders the structure unstable at larger volumes. The zero of energy has been set at the Fermi level.

nonoverlapping (touching) muffin-tin spheres and by plane waves with energies $\leqslant$495 Ry in the interstitial region. Brillouin zone integrations were carried out with the tetrahedron method[13] using a 24,24,24 division of the Brillouin zone, corresponding to 413 wave vectors in the irreducible part. The extraordinarily large bandwidths in Fig. 2 are due to the extreme pressures of the systems. The fcc phase is stable for $a$=4.4 a.u. and less, and unstable for $a$=4.6 a.u. and higher values. The smallest volume per atom at which the bct phase is stable is around 3.55 Å$^3$, according to the volume-energy curves shown above. This volume corresponds to a fcc lattice parameter of 4.576 a.u. One of the two energy bands crossing the Fermi level between the two symmetry points $X$ and $W$ becomes very flat at larger volumes. The character of the flat energy band between $X$ and $W$ is primarily "$s$" and "$p$", at $W$ it is purely of $p$ and at $X$ it is purely of $s$ character. Papaconstantopoulos and Mehl[11] have speculated that this flat band is responsible for superconductivity of the fcc phase in B, pointing out that a similar flat band at the Fermi level appears in $MgB_2$. The Fermi surface plot of Papaconstantopoulos and Mehl[11] shows hole pockets near $X$ and electron pockets near $W$, as would also be expected according to the present calculations. Although we have not verified this explicitly, it is very likely that the flat band between $X$ and $W$ points contributes significantly to the electron-phonon coupling in fcc B. As this band becomes flatter for larger lattice parameters, the electron-phonon coupling increases. However, this large electron-phonon coupling also makes the fcc phase unstable at larger volumes via softening of $X$-point transverse phonons, and brings about the fcc$\rightarrow$bct transition, as discussed below. The steep band crossing the Fermi level between $X$ and $W$ is of $p$ character.

### B. Phonons and electron-phonon coupling

In Fig. 3 we show the variation of the calculated phonon spectra with the lattice parameter for fcc B. The phonon frequencies were calculated for 29 wave vectors in the irreducible part of the Brillouin zone (BZ), resulting from a 8,8,8 division of the BZ. This division of the BZ yields only a small number (3–4) of wave vectors along the high symmetry directions. The solid lines in Fig. 3 should be taken only as a guide to the eye, rather than actual phonon branches with correct branch crossings. With increasing volume, the phonon frequencies soften throughout the Brillouin zone, as expected. However, the softening of the two transverse phonon branches near the $X$ point is most pronounced. The $X$-point transverse phonons are related to the 180° out of phase vibration of the two atoms in a bct unit cell ($c/a$ =1.414 for fcc lattice). Softening of these phonons with increasing volume indicates growing instability of the fcc structure with respect to the $c/a$ ratio, and acts as a precursor to the fcc$\rightarrow$bct phase transition. This phonon softening has two important effects, it increases the phonon density of states at low frequencies beyond the usual parabolic density of states (DOS) given by the Debye (continuum) model and increases the electron-phonon coupling in the low frequency region (partly due to increased phonon DOS and partly due to increased the electron-phonon matrix element). These effects are clearly seen in Fig. 4, where the calculated Eliashberg spectral function [upper panel, Fig. 4(a)] and the phonon density of states [lower panel, Fig. 4(b)] are displayed for three different lattice parameters. The sharp peaks in both the density of states and the Eliashberg spectral function at the high end of the spectrum are due to the lack of dispersion in the longitudinal phonon band close to the $X$ point in the $\Gamma$-$X$ direction. The lack of dispersion is enhanced as the atoms move farther apart with the lattice parameter changing

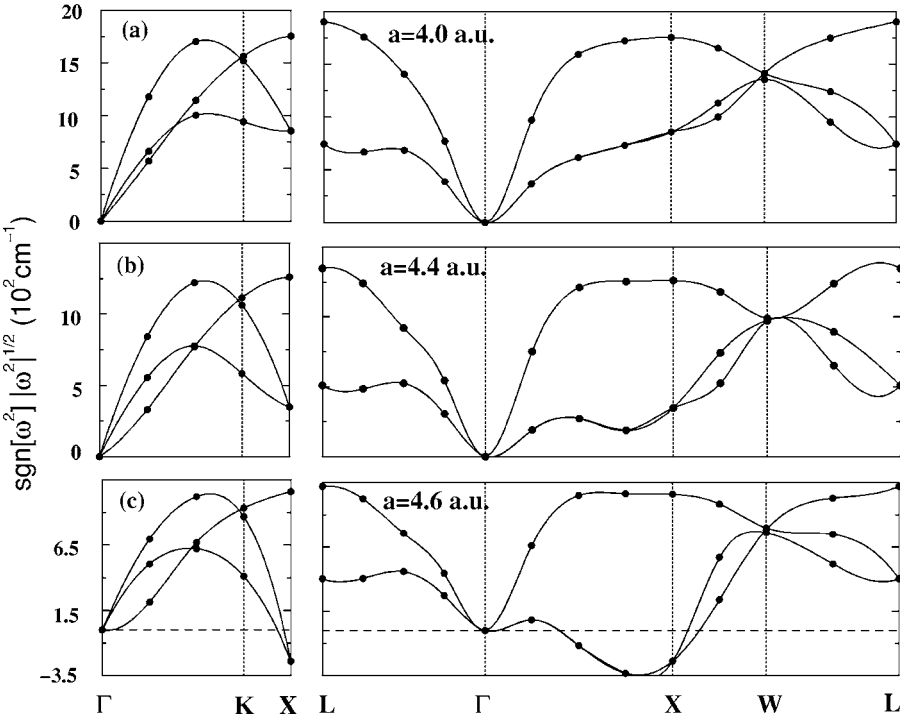


FIG. 3. Calculated phonon spectra for fcc B for the lattice parameters (a) $a=4.0$ a.u., (b) $a=4.4$ a.u., and (c) $a=4.6$ a.u. The dots represent the calculated phonon frequencies, with solid lines providing only a guide to the eye. The softening of the transverse phonons at the symmetry point $X$ occurs as the system expands to a volume above 3.4 Å$^3$/atom, in accordance with the earlier results of Mailhiot *et al.* (Ref. 1).

from 4.0 to 4.2 a.u., giving a higher density of states and consequently higher electron-phonon coupling. No such enhancement is observed as the lattice parameter increases from 4.2 to 4.4 a.u. For the lattice parameter 4.4 a.u. a sharp peak in the Eliashberg spectral function appears around 900 cm$^{-1}$, most probably due to the strong coupling of the electrons to phonons close to the $W$ point. However, this coupling is seen to grow weaker at smaller lattice parameters.

In short, the transition from the fcc to bct phase with increasing volume (lowering of pressure) is driven by softening of transverse $X$-point phonons, driving the system to a $c/a$ ratio different from (in this case, lower than) the fcc value of 1.414. The system in this pressure and/or volume region shows strong electron-phonon coupling, suggesting the possibility of a superconducting phase with a relatively high transition temperature $T_c$.

## IV. THE bct PHASE

### A. Energy bands

In Fig. 5 we show the FP-LMTO bands structure of bct B for $a=4.35$ a.u. for two different $c/a$ ratios, 0.675 and 0.65. Another band structure for $c/a=0.675$, but $a=4.0$ a.u. is also shown for comparison. Calculations were carried out with a double-$\kappa$ spd LMTO basis set for describing the valence bands. The charge densities and potentials were represented by spherical harmonics with $l \leqslant 6$ inside the nonoverlapping (touching) muffin-tin spheres and by plane waves with energies $\leqslant 400$ Ry in the interstitial region. Brillouin zone integrations were carried out with the tetrahedron method[13] using a 30,30,30 division of the Brillouin zone, corresponding to 1992 wave vectors in the irreducible part.

As in the fcc case, the bandwidths are abnormally large due to extreme high pressures of the systems. The change in

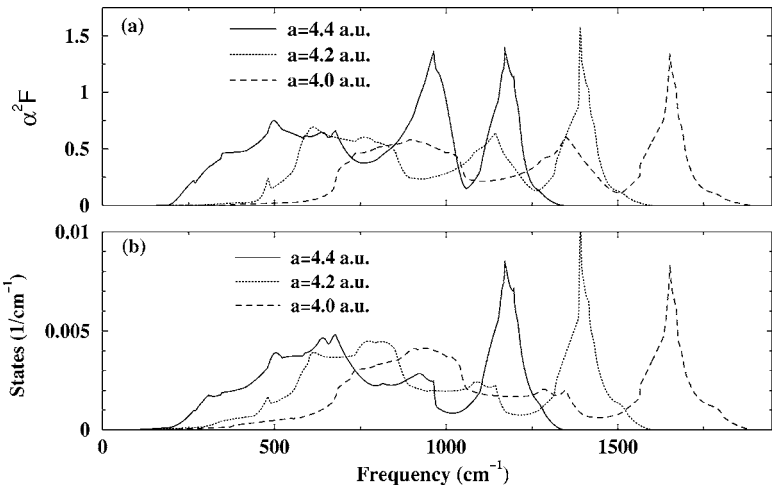


FIG. 4. The Eliashberg spectral function (a) and phonon density of states (b) for fcc B, for three different lattice parameters.

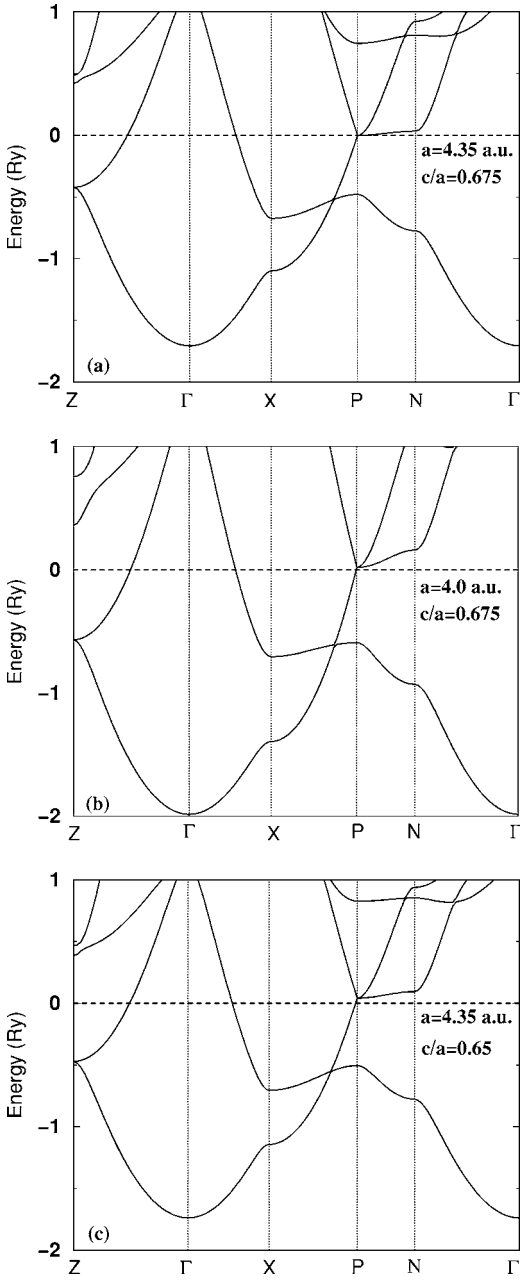


FIG. 5. FP-LMTO band structure of bct B for lattice parameter $a$=4.35 a.u., $c/a$=0.675 (a), $a$=4.0 a.u., $c/a$=0.675 (b), and $a$ =4.35 a.u., $c/a$=0.65 (c). The zero of energy has been set at the Fermi level.

the band structure is understandable as a result of decreasing volume as shown in Figs. 5(a) and 5(b). In panel (c) of Fig. 5 we show the bands for a $c/a$ ratio of 0.65 and $a$ =4.35 a.u., for which one of the transverse $N$ point phonons has imaginary frequency. There is no discernible feature in the band structure that would indicate the softening of these phonons. For the small $c/a$ ratio the B chains along the $c$ directions become unstable against transverse vibrations. This is also found to occur for the $c/a$ ratio of 0.675 for lattice parameters in excess of $a$=4.35 a.u. At such large volumes B presumably enters the nonmetallic icosahedral phase. The bands at the Fermi level are mostly of $p_x$ and $p_y$ character.

### B. Phonons and electron-phonon coupling

In Fig. 6 the phonon spectra of bct B for two different lattice parameters and with the $c/a$ ratio of 0.675 are shown. The linear response calculations for the phonon properties were carried out for 30 points in the IBZ resulting from a 6,6,6 division of the BZ. The solid lines in Fig. 6 have been drawn through the calculated frequencies to provide a guide to the eye and should not be interpreted as the actual phonon branches.

With increasing values of the lattice parameter phonons at other symmetry points become soft as well. Thus our linear response calculations yield real phonon frequencies only for a small range of volume for the chosen $c/a$ ratio of 0.675. For $c/a$=0.65 the $N$-point transverse phonons are found to be imaginary for all lattice parameters corresponding to volumes where the bct phase should be stable according to the energy-volume curve in Fig. 1. Of all the phonons the ones at the $N$ point are found to be most sensitive to the $c/a$ ratio. In principle, the $c/a$ ratio should be determined for each volume and the lattice parameter. It is likely that the optimum $c/a$ value changes with volume per atom. The $c/a$ value should have some effect on the calculated $T_c$. As discussed earlier (Sec. II) we believe the $c/a$ ratio should stay in the range 0.6–0.7, most probably 0.65 and higher. Hence, it is reasonable that $T_c$ values obtained for optimum values of $c/a$ should not be far from the results presented in this work.

In Fig. 7 the phonon density of states and the Eliashberg spectral functions for three different lattice parameters are shown. Unlike in the fcc phase the bulk of the electron-phonon coupling is via lower frequency phonons, as most of the spectral weight in Fig. 7(b) comes from the lower half of the allowed frequency range. As in the fcc case, the Eliashberg spectral function and the phonon density of states follow each other closely. There is no disproportionately large contribution from a particular mode.

## V. SUPERCONDUCTING TRANSITION TEMPERATURES AND SUMMARY OF RESULTS

Superconducting transition temperatures $T_c$ were calculated by solving the linearized isotropic Eliashberg equation at $T_c$ (see, e.g., Ref. 14);

$$Z(i\omega_n) = 1 + \frac{\pi T_c}{\omega_n}\sum_{n'} W_+(n-n')\mathrm{sgn}(\omega_{n'}),$$

$$Z(i\omega_n)\Delta(i\omega_n) = \pi T_c \sum_{n'}^{|\omega_n|\ll\omega_c} W_-(n-n')\frac{\Delta(i\omega_{n'})}{|\omega_{n'}|}, \qquad (1)$$

where $\omega_n=\pi T_c(2n+1)$ is a Matsubara frequency, $\Delta(i\omega_n)$ is an order parameter, and $Z(i\omega_n)$ is a renormalization factor. In the present work spin fluctuation and impurity scattering effects are neglected. Hence, interactions $W_+$ and $W_-$ contain a phonon contribution $\lambda$, and the Coulomb pseudopotential $\mu^*$ only,

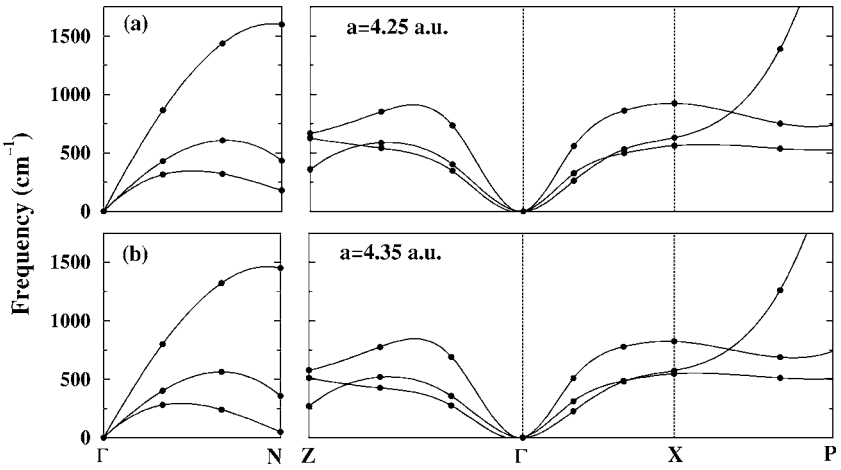


FIG. 6. Calculated phonon spectra for bct B for the lattice parameters (a) $a=4.25$ a.u. and (b) $a=4.35$ a.u. for the $c/a$ ratio of 0.675. The dots represent the calculated frequencies, while the solid lines have been drawn through them to guide the eye. For lattice parameters higher than 4.35 a.u. the structure becomes unstable with the $N$-point transverse phonons becoming soft first.

$$W_+(n-n') = \lambda(n-n')$$

and

$$W_-(n-n') = \lambda(n-n') - \mu^*.$$

The phonon contribution is given by

$$\lambda(n-n') = 2\int_0^\infty \frac{d\omega\ \omega\alpha^2(\omega)F(\omega)}{(\omega_n-\omega_{n'})^2+\omega^2}, \tag{2}$$

where $\alpha^2(\omega)F(\omega)$ is the Eliashberg spectral function. $\lambda(0)=\lambda$ is the electron-phonon coupling parameter, the values of which are given in Table I.

The Coulomb pseudopotential $\mu^*$ that appears in the Eliashberg equation above will be written as $\mu^*(\omega_c)$. $\omega_c$ denotes a cut-off frequency, chosen to be much larger (usually ten times) than the maximum phonon frequency. We estimate $\mu^*(\omega_c)$ using the relation[14]

$$\mu^*(\omega_c) = \frac{\mu(E_F)}{1+\mu(E_F)\ln(E_F/\omega_c)}. \tag{3}$$

We start by assuming $\mu(E_F)=1.0$. This value is consistent with that for $MgB_2$, where the measured $T_c \sim 40$ K can be reproduced with the linear response results of phonon frequencies and Eliashberg functions with $\mu \sim 0.85$. Thus from the calculated Fermi energies $E_F$ we obtain $\mu^*$ for all volumes, with the cut-off frequency $\omega_c$ assumed to be ten times the maximum phonon frequency. A different value of $\mu(E_F)$, e.g., 0.8 or 0.7, would result in a minor change in the calculated $T_c$ and would have no effect on the nature of variation of $T_c$ with volume or pressure.

The results of our calculation are summarized in Table I, where, for comparison, results for $MgB_2$ and two typical low $T_c$ superconductors, fcc Pb and bcc Nb, obtained via the same method are also presented. Both for fcc and bct B the Hopfield parameter $\eta$ increases with decreasing volume per atom. This trend is also supported by the rigid muffin-tin approximation results of Papaconstantopoulos and Mehl.[11] The Hopfield parameters in these high pressure phases of B are 2–4 times larger than in $MgB_2$ and about 10–15 times larger than in typical low $T_c$ metals because of the vastly reduced distances between the atoms. In fcc B, $\eta$ is larger than in the bct phase, since the fcc phase is the equilibrium phase at higher pressures or lower volumes. Phonon frequencies $\omega$ in the high pressure bct and fcc phases of B are much higher than in $MgB_2$ or a typical metal. As a result the increase in the electron-phonon coupling parameter $\lambda$, which is

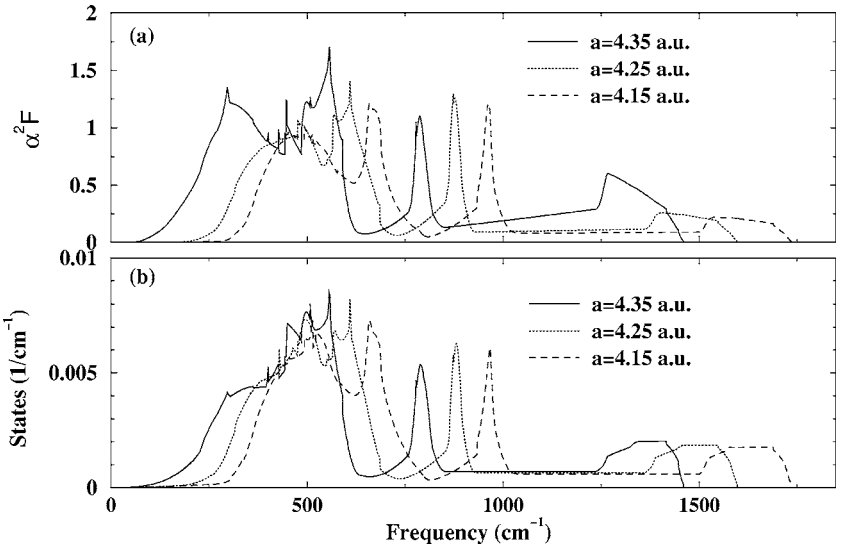


FIG. 7. Eliashberg spectral function (a) and phonon density of states (b) for bct B, for three different lattice parameters, and $c/a=0.675$.

TABLE I. Variation of superconducting transition temperature $T_c$ with volume in the bct and fcc phases of B. $V$=volume per atom, $\omega$ stands for phonon frequency, and $\langle\cdots\rangle$s denote averages, $\bar{\omega}=\sqrt{\langle\omega^2\rangle}$. $\omega_m$ is the maximum phonon frequency, $\eta$ is the Hopfield parameter, and $A$ denotes the area under the Eliashberg spectral function $\alpha^2F$ versus phonon frequency curve. For comparison, results for hexagonal $MgB_2$ and two typical low $T_c$ superconductors, fcc Pb and bcc Nb, are also presented. $a_0$ denotes the bohr radius. Results for $MgB_2$ are taken from Ref. 6.

| bct B | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $V(a_0^3)$ | $\omega_m$(meV) | $\bar{\omega}$(meV) | $\langle\omega\rangle$(meV) | $\mu^*(\omega_c)$ | $\eta$(Ry/$a_0^2$) | $\lambda$ | $A$ (meV) | $T_c$(K) |
| 20.80 | 254 | 153 | 97 | 0.297 | 0.624 | 1.025 | 50.06 | 56.33 |
| 24.12 | 215 | 123 | 77 | 0.289 | 0.552 | 1.396 | 55.01 | 78.44 |
| 25.91 | 198 | 110 | 68 | 0.285 | 0.549 | 1.702 | 60.18 | 89.24 |
| 26.83 | 189 | 70 | 60.4 | 0.283 | 0.562 | 2.016 | 64.95 | 97.02 |
| 27.78 | 181 | 76.8 | 42 | 0.281 | 0.519 | 2.735 | 71.99 | 106.3 |
| fcc B | | | | | | | | |
| $V(a_0^3)$ | $\omega_m$(meV) | $\bar{\omega}$(meV) | $\langle\omega\rangle$(meV) | $\mu^*(\omega_c)$ | $\eta$(Ry/$a_0^2$) | $\lambda$ | $A$ (meV) | $T_c$(K) |
| 16 | 236 | 143 | 136 | 0.277 | 0.926 | 0.842 | 57.52 | 50.01 |
| 18.52 | 199 | 116 | 108 | 0.269 | 0.752 | 1.039 | 57.28 | 66.62 |
| 19.87 | 183 | 102 | 94.4 | 0.266 | 0.744 | 1.305 | 63.30 | 87.70 |
| 21.30 | 167 | 88 | 77.6 | 0.262 | 0.797 | 1.787 | 75.12 | 113.9 |
| $MgB_2$ (Ref. 6) | | | | | | | | |
| $\omega_m$(meV) | $\bar{\omega}$(meV) | $\langle\omega\rangle$(meV) | $\mu^*(\omega_c)$ | $\eta$(Ry/$a_0^2$) | $\lambda$ | $A$ (meV) | $T_c$(K) | |
| 100 | 66.6 | 64.1 | 0.14 | 0.210 | 0.867 | 27.77 | 40 | |
| fcc Pb | | | | | | | | |
| $\omega_m$(meV) | $\bar{\omega}$(meV) | $\langle\omega\rangle$(meV) | $\mu^*(\omega_c)$ | $\eta$(Ry/$a_0^2$) | $\lambda$ | $A$ (meV) | $T_c$(K) | |
| 9.70 | 8.96 | 5.77 | 0.17 | 0.051 | 1.27 | 3.76 | 6.02 | |
| bcc Nb | | | | | | | | |
| $\omega_m$(meV) | $\bar{\omega}$(meV) | $\langle\omega\rangle$(meV) | $\mu^*(\omega_c)$ | $\eta$(Ry/$a_0^2$) | $\lambda$ | $A$ (meV) | $T_c$(K) | |
| 27.5 | 24.1 | 15.6 | 0.24 | 0.179 | 1.33 | 10.82 | 15.6 | |

proportional to $\eta/\langle\omega^2\rangle$, is less drastic (than in $\eta$) when compared with $MgB_2$ or a low $T_c$ superconductor like Pb or Nb. The area under the Eliashberg spectral function vs $\omega$ curve $A$ is 5–15 times larger for fcc or bct B than for a typical electron-phonon superconductor, because the coupling of electrons in these high pressure phases takes place via very high frequency phonons.

For pedagogical reasons, we have listed in Table II the values of $T_c$ obtained by using the Allen-Dynes form[14] of the McMillan expression,[15]

$$T_c = \frac{\omega_{\ln}}{1.2}\exp\left\{-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\}, \tag{4}$$

where $\omega_{\ln}$ is the logarithmically averaged phonon frequency,[14] obtained from our linear response calculations. Note that the Coulomb pseudopotential $\mu^*$ appearing in the McMillan equation above is related to $\mu^*(\omega_c)$ appearing in the Eliashberg equation via[14]

$$\mu^* = \mu^*(\omega_{\ln}) = \frac{\mu^*(\omega_c)}{[1+\mu^*(\omega_c)\ln(\omega_c/\omega_m)]}, \tag{5}$$

where $\omega_m$ is the maximum phonon frequency. Our results are computed with $\omega_c/\omega_m=10$. In Table II values of $\mu^*(\omega_{\ln})$ and the logarithmic average phonon frequencies $\omega_{\ln}$ are also listed. Note that, for the cases considered, the McMillan expression underestimates $T_c$, and the extent of the underestimation is usually higher for larger values of $\lambda$. The McMillan equation is also insensitive to small changes in the Eliashberg spectral function, as caused by a change in volume per atom in bct B, from 25.91 bohrs$^3$ to 26.83 bohrs$^3$. While $\lambda$ changes from 1.702 to 2.016, the Eliashberg equation produces a change of 8 K in $T_c$, while according to the McMillan expression $T_c$ remains virtually unchanged. We would like to point out that, in general, the McMillan expression would yield a $T_c$, that is different from, but not necessarily lower than, that given by the solution of the Eliashberg equation. For example, for hcp Fe under pressure[8] $T_c$ generated by the McMillan expression is found to be slightly higher than that obtained by solving the Eliashberg equation (see Table II of Ref. 8). Note that for hcp Fe the $T_c$ values calculated from the Eliashberg equation are all low, lying in the range 0.66–4.52 K. However, it would be highly speculative to suggest that in the case of low transition temperatures the McMillan expression yields slightly higher values and vice versa.

The trend that the Hopfield parameter $\eta$ increases with decreasing volume per atom is supported by the rigid muffin-tin approximation results of Papaconstantopoulos and

TABLE II. Transition temperatures $T_c^M$ obtained by using the McMillan equation [Eq. (4)], compared with the $T_c$'s obtained by solving the Eliashberg equation (last column), reported in Table I. $\omega_{ln}$ stands for the logarithmic average of the phonon frequencies, and $\mu^*(\omega_{ln})$ is the Coulomb pseudopotential used in the McMillan equation [given by Eq. (5)]. Results for $MgB_2$ are taken from Ref. 6.

| | | bct B | | |
|---|---|---|---|---|
| $V(a_0^3)$ | $\omega_{ln}$(K) | $\mu^*(\omega_{ln})$ | $T_c^M$(K) | $T_c$(K) |
| 20.80 | 1037 | 0.176 | 49.6 | 56.3 |
| 24.12 | 815.0 | 0.173 | 66.6 | 78.4 |
| 25.91 | 711.4 | 0.172 | 73.8 | 89.2 |
| 26.83 | 607.2 | 0.171 | 74.0 | 97.0 |
| 27.78 | 606.1 | 0.171 | 91.5 | 106 |
| | | fcc B | | |
| $V(a_0^3)$ | $\omega_{ln}$(K) | $\mu^*(\omega_{ln})$ | $T_c^M$(K) | $T_c$(K) |
| 16 | 1488 | 0.169 | 46.8 | 50.0 |
| 18.52 | 1172 | 0.166 | 61.3 | 66.6 |
| 19.87 | 1006 | 0.165 | 77.4 | 87.7 |
| 21.30 | 763.2 | 0.163 | 85.4 | 114 |
| | $\omega_{ln}$(K) | $\mu^*(\omega_{ln})$ | $T_c^M$(K) | $T_c$(K) |
| $MgB_2$: | 719.2 | 0.106 | 38.0 | 40.0 |
| fcc Pb | 163.1 | 0.12 | 5.35 | 6.02 |
| bcc Nb | 163.1 | 0.15 | 13.7 | 15.6 |

Mehl.[11] However, the rigid muffin-tin approximation consistently underestimates $\eta$. We have compared our linear response results for $\eta$ with those obtained by using the rigid muffin-tin (rigid atomic sphere) approximation scheme within the LMTO method. The details of the method have been discussed by Skriver and Mertig.[16] Our LMTO rigid muffin-tin approximation calculation of $\eta$ for fcc B with lattice parameter 4.6 a.u. gives a value 15.14 eV/Å$^2$, which compares well with the LAPW (linear augmented plane waves) rigid muffin-tin results 14.59 eV/Å$^2$ of Papaconstantopoulos and Mehl.[11] Note that for the lattice parameter of 4.6 a.u. we cannot compare the rigid muffin-tin value of $\eta$ with the linear response result, as the phonon frequencies at this lattice parameter are imaginary. However, our linear response calculations for lattice parameters for the stable fcc or bct phases (which produce real phonon frequencies) show that $\eta$ is always underestimated in the rigid muffin-tin approximation. Usually as the volume per atom decreases the difference between the linear response value and the rigid muffin-tin value increases. For fcc B with a lattice parameter 4.0 a.u. the rigid muffin-tin approximation gives a value 0.537 Ry/$a_0^2$ for $\eta$, while the linear response result is 0.926 Ry/$a_0^2$. Readers interested in a comparison of the rigid muffin-tin and linear response results for $\eta$ may consult Table II of Ref. 8, where such a comparison for hcp Fe is provided.

The variation of the superconducting transition temperature $T_c$ with volume per atom is shown in Fig. 8, where the vertical dashed line is drawn at the volume per atom equal to 21.3 bohrs$^3$, estimated to be the dividing line between the bct and the fcc phase. For both bct and fcc B the phonon frequencies rise faster with increasing pressure than the Hopfield parameter, resulting in a decrease in electron-phonon coupling and $T_c$. In the study of the fcc phase by Papaconstantopoulos and Mehl[11] no calculation of phonon spectra as a function of pressure was done, and the authors speculated that if the phonon frequencies do not rise as fast as the Hopfield parameter, $T_c$ should rise with increasing pressure. The present calculations reveal two important results; $T_c$ decreases with increasing pressure despite a rise in the Hopfield parameter and the calculated $T_c$'s are in the range 50–100 K, much higher than the measured values. In the fcc phase, electron-phonon coupling rises strongly with increasing volume due to the softening of $X$-point transverse phonons as the fcc→bct phase transition is approached. Similarly in the bct phase electron-phonon coupling is very

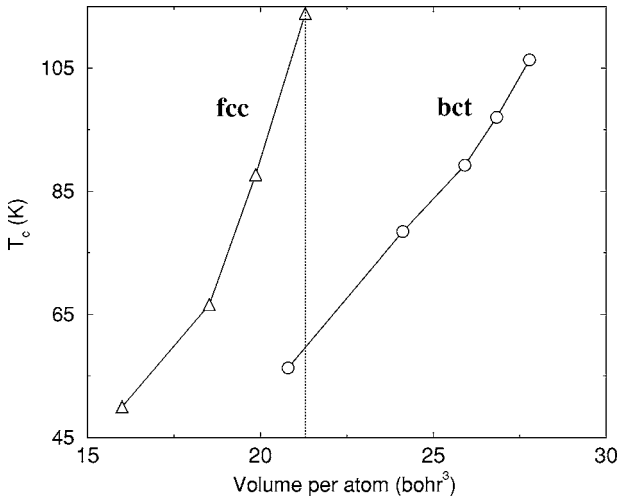


FIG. 8. Variation of the superconducting transition temperature $T_c$ with volume per atom. The vertical dashed line is drawn at volume per atom equal to 21.3 bohrs$^3$, estimated to be the dividing line between the bct and the fcc phases.

high near the bct→icosahedral phase change due to the softening of $N$ point transverse phonons. Unlike in $MgB_2$ there is no disproportionately high contribution to electron-phonon coupling from a particular phonon mode. The Eliashberg spectral function follows faithfully the phonon density of states.

The striking differences between the results of this theoretical investigation and the experimental results beg for a suitable explanation. While we cannot rule out the possibility that the electron-phonon coupling and therefore $T_c$ is somehow overestimated in the calculation, it would be hard to deny the validity of the results altogether. The trend in the variation of the Hopfield parameter with pressure is similar to that found via a less rigorous rigid muffin-tin approximation calculation of Papaconstantopoulos and Mehl.[11] Our values of the Hopfield parameter are larger than what would be given by a rigid muffin-tin calculation, and their rise with pressure is also steeper. Despite the steep rise in the Hopfield parameter, $T_c$ decreases with increasing pressure due to rapid increase in phonon frequencies. The phonon calculations correctly predict the fcc→bct transition and also the onset of instability of the bct phase (presumably against the icosahedral phase) as the pressure is lowered or the volume per atom is increased. Since the systems studied do not represent cases of extreme electron-phonon coupling (see, e.g., An *et al.*[9]) via a single mode or only a few modes, superconductivity in these systems does not seem to be special.

On the experimental front, the possibility that the measurements were not carried out for a single (pure) phase cannot be ruled out, as was pointed out by the authors themselves.[2] It is possible that the systems studied were in mixed phases with coexisting icosahedral and bct clusters and the superconductivity of the sample was due to the proximity effect of the bct clusters. This would explain why the measured $T_c$ was so much lower than what would be expected for the pure bct phase. It is also possible that with increasing pressure the samples were just evolving towards a pure bct phase, which would explain the observed increase in $T_c$ with pressure. The results of the present work strongly suggest that the experimental work on high pressure phases of B should be repeated, with particular emphasis on the phase of the sample. It is expected that if the phase is bct or fcc (or a mixture of the two), superconducting transition temperatures should be much higher than previously reported.

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