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Lattice properties of MgB_2 versus temperature and pressure

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We have determined the structural properties of the superconducting compound MgB_2 as a function of temperature from 11 to 297 K and as a function of hydrostatic pressure up to 0.62 GPa using neutron powder diffraction. This compound, when compared to other diborides with the same structure, is characterized by unusually large anisotropies of both the thermal expansion and compressibility, with the c-axis responses being substantially larger. We speculate that the comparatively weaker metal-boron bonding in MgB_2 manifested by these lattice responses, is important for establishing the structural features that give rise to high-T_c superconductivity in this structure type.

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The remarkable discovery of superconductivity at 39 K in MgB_2 (Ref. 1) illustrates the critical role of electronic and crystal structure properties in achieving superconductivity in a given structure type. MgB_2 possesses the simple hexagonal AlB_2-type structure (C32 structure),[2,3] which is perhaps the most common structure type among the borides.[4] This structure type has previously been investigated extensively for superconductivity. In 1970, Cooper *et al.*[5] reported a search for superconductivity in this structure type in the series of compounds YB_2-ZrB_2-NbB_2-MoB_2. They were able to achieve superconducting transition temperatures, T_c, of 3.87 K in a ''boron-rich'' NbB_2 compound and above 11 K in $Zr_{0.13}Mo_{0.87}B_2$. Their experimental approach for achieving superconductivity was to adjust the formal electrons-per-atom (e/a) count to what they considered to be an optimal value of 3.8. In 1979, Leyarovska and Leyarovski[6] searched again for superconductivity in hexagonal diboride compounds, MeB_2 (Me = Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo), and found superconductivity only in NbB_2, which displayed a T_c of 0.62 K.

Following the discovery of superconductivity in MgB_2,[1] Slusky *et al.*[7] reported studies of how the behavior responds to incremental changes in chemical composition. They investigated the substitution of Al on the Mg site, i.e., $Mg_{1-x}Al_xB_2$, and observed that T_c decreases smoothly with increasing x for $0 \leqslant x \leqslant 0.1$, accompanied by a slight decrease of the c axis. At $x \approx 0.1$, there is an abrupt transition to a nonsuperconducting isostructural compound which has a c axis shortened by about 0.1 Å. They concluded that the compound MgB_2 is near a structural instability, at slightly higher electron concentration, that can destroy superconductivity. Clearly, the loss of superconductivity associated with decreasing the c axis length with no change in cell symmetry and only a small change in the formal electron count suggests that there is something special about the structural parameters of MgB_2 that leads to superconductivity in this compound. The importance of the c axis length is reminiscent of the earlier work of Cooper *et al.*[5] who had, in retrospect, observed that the highest T_c vs composition corresponded to a maximum of the c axis length.

An and Pickett[8] calculated the effects of various phonon modes on the electronic structure of MgB_2. They concluded that the superconductivity results almost exclusively from B σ bands that contribute strongly to the Fermi-level density of states because of the two-dimensional nature of the compound. Their calculations showed that B in-plane phonons, the E_{2g} modes at a calculated[9] energy of 58 meV, are strongly coupled to this band. They explained the instability observed by Slusky *et al.*[7] in terms of the disappearance of this band upon doping. These results suggest that both the appropriate structure, with a sufficient two-dimensional character which gives rise to the presence of significant density of states in the B σ band, and the correct electron count, to place this band near the Fermi energy, are required to achieve superconductivity in this structure type.

In this paper, we report the structural parameters of MgB_2 as a function of temperature from 11 to 297 K and as a function of hydrostatic pressure, at room temperature, to 0.62 GPa and compare the behavior with that of other compounds with the same structure type. The thermal expansion can be nicely modeled with a simple Einstein function using a single phonon energy around 500 K (43 meV). Both the thermal expansion and compression exhibit pronounced anisotropy, with the c-axis responses being substantially larger. Comparison with other structural measurements vs pressure[10,11] shows that the full anisotropy is observed only when a hydrostatic pressure fluid is used.

Because natural abundance B has a large neutron absorption cross section, a 1.6 g sample for this study was made using isotopically enriched ^{11}B (Eagle Picher, 98.46 atomic % enrichment). A mixture of ^{11}B powder (less than 200 mesh particle size) and chunks of Mg metal was reacted in a capped BN crucible at 800 C under an argon atmosphere of 50 bar for 1.5 h. The resulting sample displayed a sharp superconducting transition (0.4 K wide) with an onset at 39 K. Both x-ray and neutron-diffraction data showed the sample to be single phase with the AlB_2-type structure.

Neutron powder diffraction measurements were made on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratory.[12] For the low-temperature measurements, the sample was contained in a sealed thin-walled vanadium can along with helium exchange gas and cooled using a Displex refrigerator. The measurements vs pressure were made in a helium gas pressure cell,[13] at room temperature. Typical data

TABLE I. Refined structural parameters for MgB_2 at 297 and 37 K based on Rietveld refinements using neutron powder diffraction data. Space group $P6/mmm$, No. 191, with Mg at (0,0,0) and B at (1/3,2/3,1/2). Numbers in parentheses are statistical standard deviations of the last significant digit.

	297 K	37 K
a (Å)	3.08489(3)	3.08230(2)
c (Å)	3.52107(5)	3.51461(5)
V ($Å^3$)	29.019(1)	28.917(1)
U_{11}(Mg) ($Å^2$)	0.00545(26)	0.00347(18)
U_{33}(Mg) ($Å^2$)	0.00559(42)	0.00328(29)
U_{12}(Mg) ($Å^2$)	0.00272(13)	0.00173(9)
U_{11}(B) ($Å^2$)	0.00454(15)	0.00333(11)
U_{33}(B) ($Å^2$)	0.00648(25)	0.00455(18)
U_{12}(B) ($Å^2$)	0.00227(8)	0.00166(6)

collection times were 1 h at each temperature or pressure. The data were analyzed by the Rietveld technique using the GSAS code.[14] In initial refinements, the Mg/^{11}B ratio was refined. There was no indication of non stoichiometry within a refinement precision of about 0.5%. Figure 1 shows the raw data and refined diffraction pattern at 34 K. The sample is single phase and the diffraction pattern is nicely fit with peak widths near the instrumental resolution. This is true at all temperatures and pressures. There is no evidence for any structural transitions. Refined structural parameters at 297 and 37 K are listed in Table I.

The simple hexagonal AlB_2-type structure (space group $P6/mmm$, No. 191) (Ref. 4) is shown in Fig. 2. The structure contains graphitelike boron layers which are separated by hexagonal close-packed layers of metals. The center of a hexagonal boron ring lies both directly above and below each metal.

The lattice parameters and cell volume vs temperature are shown in Fig. 3. The thermal expansion can be nicely mod-

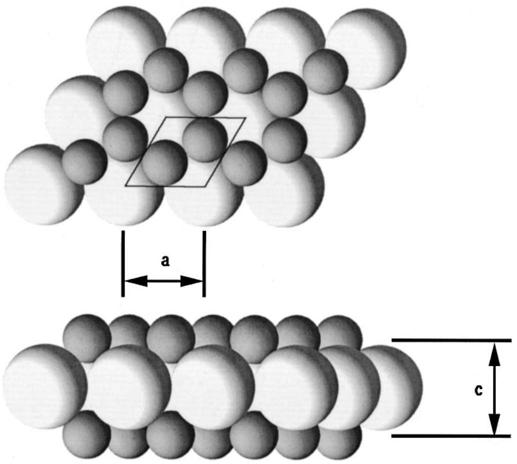

FIG. 2. Crystal structure of MgB_2 [AlB_2-type structure; hexagonal space group P6/mmm, No. 191, with Mg at (0,0,0) and B at (1/3,2/3,1/2)] viewed along the c axis (top) and perpendicular to an a axis (bottom). Small spheres are B atoms; larger spheres are Mg atoms.

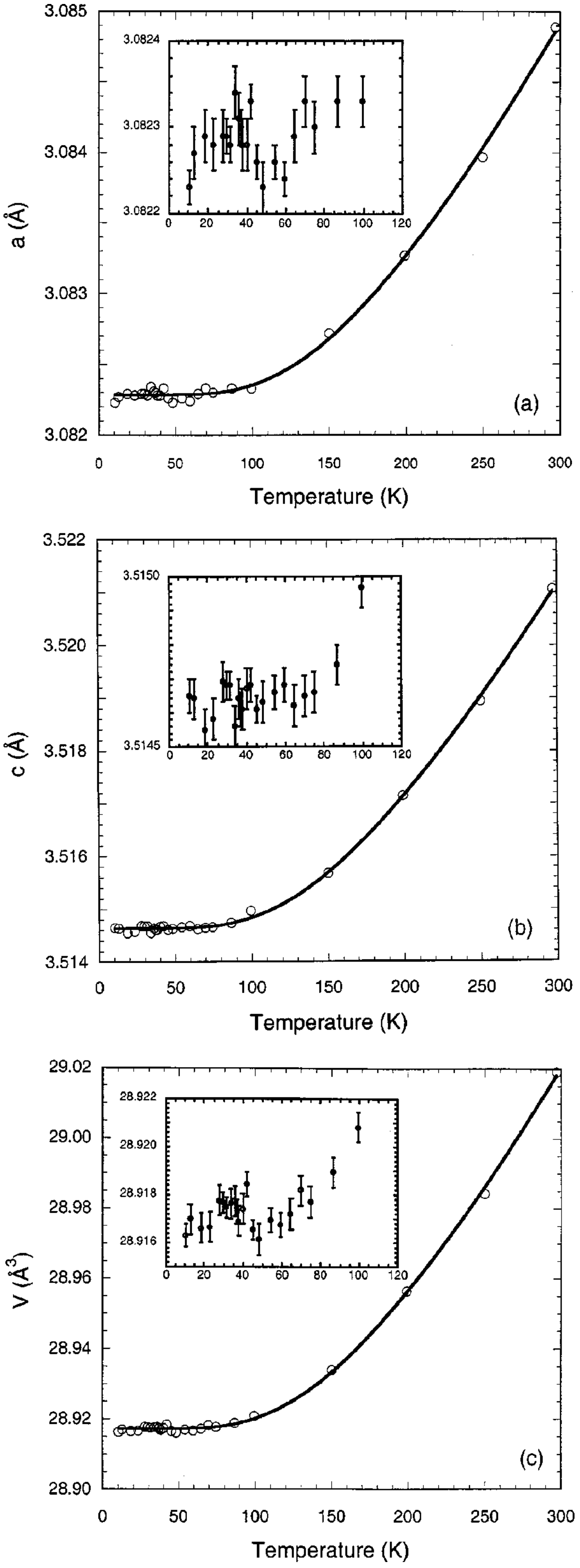

FIG. 3. a and c lattice parameters and unit cell volume, V, of MgB_2 vs temperature based on neutron powder diffraction measurements. The solid lines are least-squares fits using a simple Einstein model with a single phonon energy [Eq. (1) in the text]. The insets show the low-temperature data in more detail. Where not shown, standard deviations are smaller than the symbols.

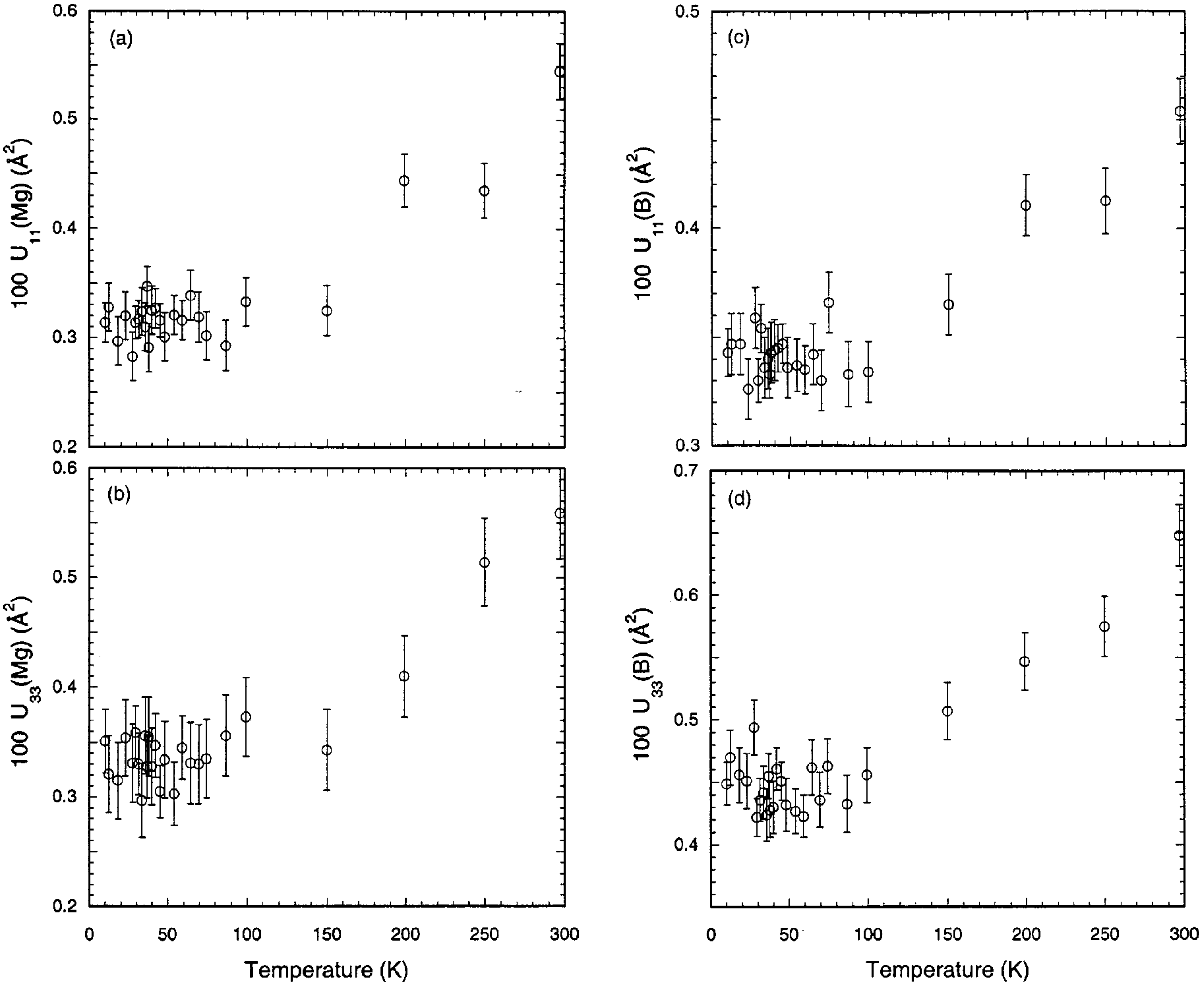

FIG. 4. Diagonal components, U_{11} and U_{33}, of the anisotropic Debye-Waller tensors for Mg (a) and (b) and B (c) and (d) atoms in MgB_2 vs temperature determined by Rietveld refinement using neutron powder diffraction data.

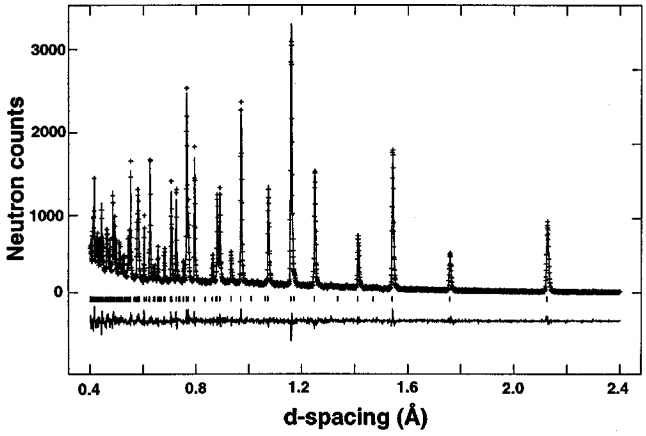

FIG. 1. Observed neutron powder diffraction data and best-fit Rietveld refinement profile for MgB_2 at 34 K. Data collection time was 1 h. Crosses (+) are the raw data. The solid line is the calculated profile. Tick marks indicate the positions of all allowed reflections. A difference curve (observed minus calculated) is plotted at the bottom.

eled with an Einstein equation using a single phonon energy:

$$\ln\left(\frac{a}{a_0}\right)=\frac{A\theta}{e^{(\theta/T)}-1}, \tag{1}$$

where a is the lattice parameter (a or c) or cell volume (V) and a_0 is its value at $T=0$, θ is the phonon energy, T is the temperature, and A is a scaling coefficient. The data of Fig. 3 have been fit with this equation to determine the values of a_0, A, and θ. Independent fits to a, c, and V give the same phonon energy, θ, within the standard deviations: 517(20), 494(12), and 508(13) K for the fits to a, c, and V, respectively.

The thermal expansion along the c axis is about twice that along the a axis. Linear thermal expansions near room temperature are $\alpha_a \approx 5.4\times 10^{-6}\,\mathrm{K}^{-1}$ and $\alpha_c \approx 11.4\times 10^{-6}\,\mathrm{K}^{-1}$ [where α is defined as $(\Delta l/\Delta T)/l_0$]. The thermal expansion of MgB_2 lies generally within the range observed for other hexagonal diborides,[15] although only VB_2 (for which $\alpha_c = 14\times 10^{-6}\,\mathrm{K}^{-1}$ at room temperature) has a larger c-axis thermal expansion. Larger thermal expansion along the *c* axis than along the *a* axis is not unusual for the AlB_2-type diborides, but most do not display such a large anisotropy as does MgB_2. This anisotropy results from the difference in bond strengths.[4] The B-B bonds in the basal plane are much stronger than the Mg-B bonds that connect layers of Mg and B atoms.

Thermodynamics requires a small positive response of the lattice parameters at T_c that is often beyond the limits of sensitivity of conventional diffraction measurements.[16] The details of our lattice parameter measurements at low temperature are shown in the insets of Fig. 3. Small positive effects may be seen near T_c for the cell volume and the *a*-axis lattice parameter, but these are admittedly within the experimental uncertainties. A more sensitive technique, such as higher resolution diffraction or dilatometry, will be required to properly investigate this behavior. However, in light of the conclusions of An and Pickett[8] that the in-plane B σ bands are responsible for the superconductivity, it is intriguing that we may observe a tiny structural response in the basal plane, but nothing perpendicular to the basal plane. This could be a manifestation of the change in B-B bonding as the bonding electrons condense at T_c.

The refined Debye-Waller factors in the basal plane and perpendicular to the plane for Mg and B vs temperature are shown in Fig. 4. The larger vibrational amplitudes along the *c* axis than along the *a* axis for the B atoms are another manifestation of the weaker Mg-B bonding. The mean squared displacements decrease as expected, but have significantly nonzero values at low temperature, especially for U_{33}(B). This could result from the inability of the Debye-Waller factor model of the Rietveld code (which assumes harmonic thermal vibrations) to fit anharmonic behavior, or a small static displacement of the B atoms that persists to low temperatures. Such displacements, if ordered, would give rise to supercells of the basic AlB_2-type structure. No evidence for such supercells is visible in our data.

The variation of the *a* and *c* lattice parameters vs pressure is shown in Fig. 5. Over the pressure range of this study, the changes are linear and can be expressed as

$$a = a_0(1 - 0.00187P), \text{ and}$$

$$c = c_0(1 - 0.00307P),$$

where a_0 and c_0 are the zero-pressure lattice parameters and *P* is the pressure in GPa. The bulk modulus $[V_0(\Delta P/\Delta V)]$ obtained from these measurements is 147.2(7) GPa. Loa and Syassen[17] used electronic structure calculations vs cell volume to calculate a bulk modulus of 140.1(6), in good agreement with the experimental result. They also calculated the pressure dependence of the c/a ratio, getting a result in nice agreement with the observed compression anisotropy.

Compression along the *c* axis is 64% larger than along the *a* axis, consistent with the comparatively weaker (Mg-B) bonds that determine the *c* axis length. A similar anisotropy, but not as large, has been reported in the refractory diboride TiB_2,[18] which is of considerable technological interest because of its high elastic moduli, high hardness, and high electric conductivity. By comparison, the compression anisotropy in the layered cuprate $YBa_2Cu_3O_7$ is about a factor of two.[13] Not surprisingly, the intrinsic compression anisotropy is not observed when pressure measurements are made in nonhydrostatic media. Recent room-temperature x-ray diffraction measurements in diamond anvil cells using methanol:ethanol:water[10] and silicone oil[11] as the pressure fluids gave anisotropies of 1.5 and 1.4, respectively. These differing results emphasize the importance of making pressure measurements in hydrostatic media for materials with anisotropic compression. Large differences in results have been reported for the pressure dependence of T_c of MgB_2. A measurement in helium gas yields $dT_c/dP = -1.11(2)$ K/GPa,[19] while two measurements in nonhydrostatic frozen pressure media[20,21] yield significantly higher values of -1.6 and -2.0 K/GPa. The differences among these results suggest that pressure measurements done in helium gas, which is hydrostatic at the temperatures of both measurements, provide the only opportunity for quantitative comparison of T_c and (room temperature) structural data because the properties of nonhydrostatic media are temperature dependent.

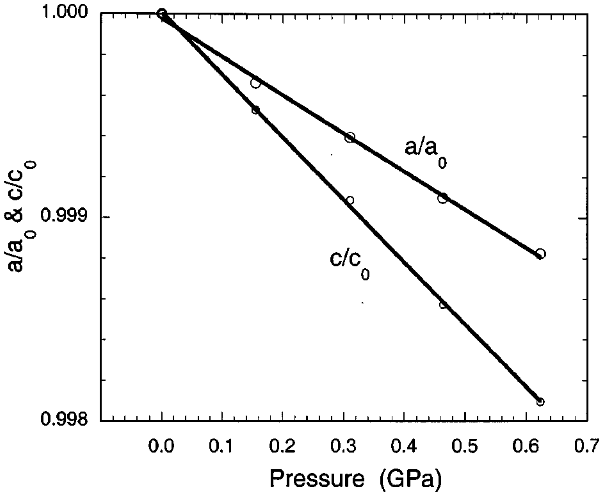

FIG. 5. Normalized *a* and *c* lattice parameters vs pressure at room temperature for MgB_2 based on neutron diffraction measurements at five pressures using helium as the pressure transmitting medium. Standard deviations of the individual points are smaller than the symbols. The straight lines are linear least-squares fits to the data

The structural data vs temperature and pressure reported here, when considered in the context of previous efforts to achieve and characterize superconductivity in the AlB_2-type structure and what is currently being learned about MgB_2, allow us to speculate about what structural features are important for achieving superconductivity in this structure type. Comparatively weak metal-boron bonding, which is manifest by a comparatively long *c* axis, larger thermal expansion and compression along the *c* axis, and larger vibrational amplitudes along the *c* axis, is a characteristic feature of MgB_2 and leads to its somewhat two-dimensional-like electronic structure that is thought to be of critical importance.[8] This relatively weak bonding is to be expected when a divalent metal is used in the hexagonal metal diboride structure, in contrast to the compounds based on transition metals that have been most extensively studied. The early work on hexagonal diborides by Cooper *et al.*[5] and the recent work of Slusky *et al.* on $Mg_{1-x}Al_xB_2$,[7] both of which show a sensitivity to the c/a ratio, are consistent with this hypothesis. Bianconi *et al.*[22] drew a similar conclusion, which they express in terms of a critical strain, or c/a ratio, by comparing the structures of a number of diboride compounds. Following the logic that has typically been applied to raise T_c in a given structure type, researchers will undoubtedly focus attention on changing the electronic structure such that the Fermi energy is positioned at a peak in the electronic density of states. Electronic structure calculations of hypothetical hexagonal diboride compounds illustrate how this might be accomplished.[23] As the search for higher T_c's in compounds with the AlB_2-type structure proceeds, it will be important to realize that chemical/structural changes that modify the metal-boron bonding strength could be unusually important in these compounds.

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