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Compressibility and electronic structure of MgB_2 up to 8 GPa

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The lattice parameters of MgB_2 up to a pressure of 8 GPa were determined using high-resolution x-ray powder diffraction in a diamond anvil cell. The bulk modulus, B_0, was determined to be 151 ± 5 GPa. Both experimental and first-principles calculations indicate nearly isotropic mechanical behavior under pressure. This small anisotropy is in contrast to the two-dimensional nature of the boron *p* states. The pressure dependence of the density of states at the Fermi level and a reasonable value for the average phonon frequency $\langle \omega \rangle$ account within the context of BCS theory for the reduction of T_c under pressure.

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The recent discovery of superconductivity in MgB_2 close to 40 K (Ref. 1) has pushed T_c beyond what was thought to be possible in intermetallic compounds within the context of the BCS theory.[2,3] However, the boron isotope effect was measured to be consistent with MgB_2 being a conventional phonon-mediated BCS superconductor.[4] The temperature-dependent electrical resistivity in the normal state was observed to obey a T^3 power law by Finnemore *et al.*,[5] whereas Jung *et al.*[6] found a T^2 behavior to be more appropriate. Within the context of hole superconductivity[7] it was proposed that a decreasing *B-B* intraplane distance should increase T_c. However, ac magnetic susceptibility measurements revealed that T_c actually decreases.[8] The response of the crystal and electronic structures of MgB_2 to pressure is not only important to distinguish a conventional from a non-BCS mechanism, but it might also give valuable clues for guiding chemical substitutions. Slusky *et al.*[9] have established the loss of superconductivity in $Mg_{1-x}Al_xB_2$ and conjecture that MgB_2 is on the edge of a structural instability at slightly higher electron concentrations. These authors furthermore indicate the presence of a two phase region between $0.1 \leqslant x \leqslant 0.25$. To investigate the intrinsic electronic properties of MgB_2 and to avoid complications from possible extrinsic effects such as compositional fluctuations and phase separations in substituted systems, we have determined the bulk compressibility and compared it to the one derived from first-principles calculations based on the density functional theory (DFT).

The sample, obtained from Alfa, was of excellent quality without any impurities visible in a high-resolution x-ray powder diffraction pattern taken at room temperature. All reflections could be indexed to the AlB_2-type structure in spacegroup $P6/mmm$ with $a = 3.08589(1)$ Å and $c = 3.52121(3)$ Å at room temperature and ambient pressure. The magnetic susceptibility showed a sharp transition at 38.2 K (Fig. 1). The compressibility up to 8 GPa was measured using a Merrill-Bassett diamond anvil cell. The lattice parameters (Table I) were determined using the high-resolution powder diffractometer X7A at the National Synchrotron Light Source at the Brookhaven National Laboratory. An asymmetrically cut triangular shaped Si (220) monochromator was cylindrically bent to focus a photon beam with a wavelength of 0.68613(2) Å down to 200 μm. A steel gasket was preindented and a 200 μm hole drilled in the center. The sample and several small ruby chips were loaded along with the pressure transmission fluid of methanol:ethanol:water (ratios 16:3:1). Pressure was determined by measuring the shift of the R1 emission line of ruby using an argon ion laser.[10] Diffraction patterns up to $2\theta = 35°$ were recorded using a position-sensitive detector.[11] Further experimental details are described in.[12] There were no indications of any splitting or significant broadening of the Bragg reflections indicative of a possible phase transition. The width of the R1 emission line of ruby at higher pressures also indicated that the sample was well within a hydrostatic pressure regime. The unit cell volumes, *V*, normalized to the one at ambient pressure, V_0, at various pressures *P* were fitted to a first-order Murnaghan equation of state $V = V_0(1 + B_0' P/B_0)^{-1/B_0'}$ where B_0 is the bulk modulus at ambient conditions and $B_0' = 4$. We obtained a value of 151 ± 5 GPa. For comparison, B_0 of YNi_2B_2C, a related borocarbide, was measured to be 200 GPa.[13]

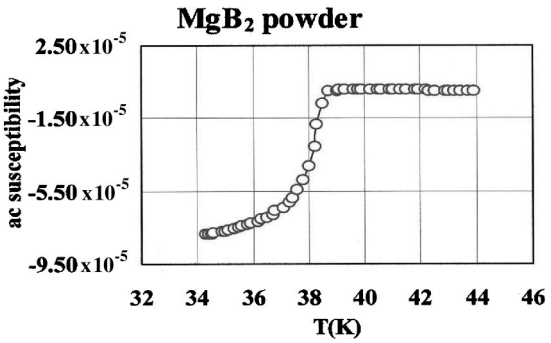

FIG. 1. ac susceptibility of MgB_2 as a function of temperature.

TABLE I. Measured lattice parameters for MgB_2 as a function of applied pressure. The error in pressure is estimated to 0.2 GPa.

pressure (GPa)	volume (Å^3)	a (Å)	c (Å)	c/a
0.0	29.0391	3.08589(3)	3.52121(9)	1.1411
1.17	28.8494	3.08017(28)	3.51121(29)	1.1399
2.14	28.5835	3.07149(21)	3.49854(52)	1.1390
3.05	28.5017	3.06709(49)	3.48857(58)	1.1374
4.07	28.2994	3.06349(15)	3.48188(25)	1.1366
5.09	28.0519	3.05449(19)	3.47180(24)	1.1366
6.53	27.8583	3.04972(31)	3.45863(24)	1.1341
8.02	27.8228	3.04843(14)	3.45715(28)	1.1341

We calculated the electronic structure and mechanical properties within the DFT (Ref. 14) using the full-potential linearized augmented plane wave method FLAPW (Ref. 15). For the exchange-correlation potential we used the generalized gradient approximation of Perdew *et al.*[16] A relatively large basis set was required to accurately calculate small changes in the electronic structure and lattice parameters with applied pressure.[17] Calculated equilibrium parameters are $a=3.089$ Å, $c=3.548$ Å, and $c/a=1.149$. They differ from the experimental values by 0.1%, 0.8%, and 0.7%, respectively. The calculated bulk modulus of $B_0=139\pm10$ GPa is in good agreement with the measured value of 151 ± 5 GPa. Both calculated and experimental lattice parameters as a function of volume are shown in Fig. 2. The agreement between theory and experiment is excellent. Over the range of pressure considered, the c/a ratio is essentially constant, indicative of the three-dimensional character of MgB_2. The small observed anisotropy of the compressibility as given by the observed reduction in the c/a ratio with decreasing volume is reproduced by our calculations, although the rate of change is overestimated.

The superconducting properties of MgB_2 as a function of pressure have been investigated by Lorenz *et al.*,[8] who found that the transition temperature T_c decreases linearly and reversibly at a rate of -1.6 K/GPa. Within the BCS theory the pressure dependence of T_c can be calculated from the McMillan formula

$$T_c=\frac{\langle\omega\rangle}{1.45}\exp\left(\frac{-1.02(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right),$$

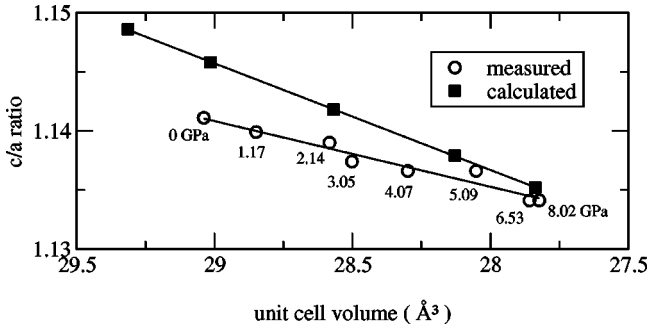

FIG. 2. c/a ratio as a function of unit-cell volume from both experiment and calculation.

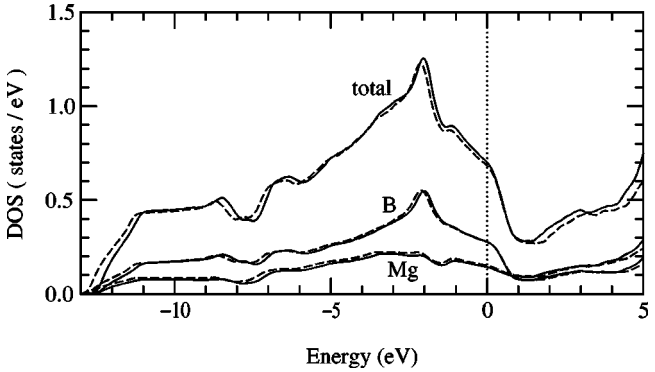

FIG. 3. Total and partial densities of states (PDOS) of MgB_2 for two sets of lattice parameters: ($a=3.09$ Å, $c=3.55$ Å) (full lines) and ($a=3.05$ Å, $c=3.46$ Å) (dashed lines). The difference in lattice parameters corresponds to a pressure of ≈8 GPa. The energy zero is the Fermi energy. The PDOS is calculated inside the muffin tin spheres ($R_{MT}=1.6$ and 2.7 a.u. for B and Mg, respectively.)

where $\langle\omega\rangle$ is an average phonon frequency, μ^* denotes the Coulomb pseudopotential, $\lambda\propto N(0)/\langle\omega^2\rangle$ is the electron-phonon interaction parameter and $N(0)$ denotes the density of states at the Fermi energy.[2]

The calculated change in the density of states of MgB_2 for a pressure of ≈8 GPa is shown in Fig. 3. We observe the expected increase in bandwidth, but the overall changes are very small and in particular $N(0)$ decreases by only 3% from 0.70 states/eV to 0.68 states/eV. Assuming that T_c continues to decrease linearly at higher pressures we can estimate that at 8 GPa, $T_c\approx26$ K which is 30% lower than T_c at ambient pressure. Comparing this large decrease in T_c to the minute change in $N(0)$, it becomes apparent that the pressure dependence of $N(0)$ alone cannot account for the large rate with which T_c decreases with applied pressure. Taking our value for $d\ln N(0)/dP\approx-0.004$/GPa and assuming $\mu^*=0.1$ and $\lambda=1.0$, which is the average of published calculations and estimates ranging from 0.7 to 1.4,[18,19] we find that in order to reproduce the experimentally observed pressure dependence of T_c, $d\ln\langle\omega^2\rangle^{1/2}/dP\approx+0.012$/GPa is needed. This value appears reasonable.

The volume dependence of T_c within the BCS theory has been characterized using

$$\frac{d\ln(T_c/\Theta_D)}{d\ln V}=\ln\frac{\Theta_D}{T_c}\frac{d\ln\lambda}{d\ln V}\equiv\ln\frac{\Theta_D}{T_c}\varphi,$$

where φ is a material dependent parameter describing the volume dependence of the electron-phonon coupling parameter and Θ_D is the Debye temperature. For superconducting sp metals one generally finds $\varphi\approx2.5$.[20] Using for the Debye temperature the recently determined value of $\theta_D=800$ K,[21] we find $\varphi=2.4$ for MgB_2, a value not inconsistent with the BCS theory.

The importance of the mostly two-dimensional B p_{xy} states for the superconductivity of MgB_2 has been pointed out by several authors.[18,19] The change with pressure in the partial density of states (PDOS) of B p states separated into p_{xy} and p_z characters is shown in Fig. 4. The B p_z PDOS

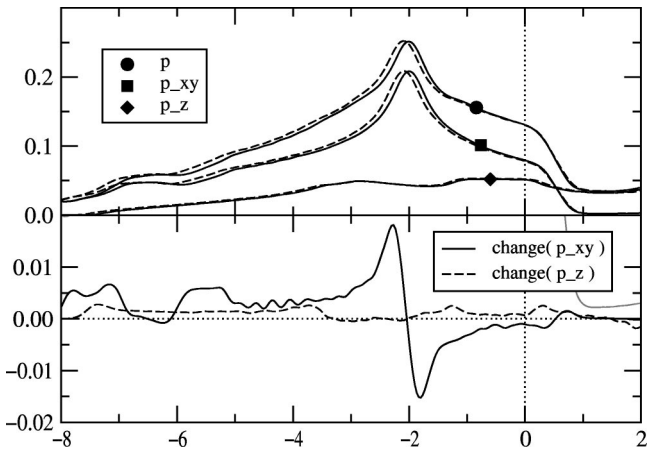

FIG. 4. Single boron p partial density of states (PDOS) (top panel) for two sets of lattice parameters (see Fig. 3), corresponding to 0 Gpa (full lines) and ≈ 8 GPa (dashed lines). The change in the $B\ p_{xy}$ PDOS (full line) and p_z PDOS (dashed line) is shown in the bottom panel. The energy zero is the Fermi energy.

remain essentially unchanged, but the $B\ p_{xy}$ PDOS shows an overall shift to lower energies, leading to a loss of states in the energy range from just below the Fermi energy to ≈ -2 eV. In general one expects the PDOS inside a fixed sphere to increase with pressure. The qualitatively different behavior of the $B\ p_{xy}$ PDOS in MgB_2 can be attributed to the two-dimensional character of these $B\ p_{xy}$ states. However, the $B\ p_{xy}$ PDOS at the Fermi energy does not change significantly.

In conclusion, we have experimentally and theoretically determined the bulk modulus of MgB_2 and lattice parameters up to pressures of 8 GPa. Despite an overall isotropic behavior of MgB_2, there are small anisotropies in the mechanical properties. The electronic structure under pressure reveals the two-dimensional character of the $B\ p_{xy}$ states whose occupancy is altered by pressure in contrast to the $B\ p_z$ states.

Furthermore, the pressure dependence of the density of states at the Fermi level and a reasonable value for the average phonon frequency $\langle\omega\rangle$ account for the reduction of T_c under pressure within the context of the BCS theory. We find that the material dependent constant φ describing the volume dependence of the electron-phonon coupling parameter agrees well with the BCS theory for an sp metal.

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