Superconductivity in Boron

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Metals formed from light elements are predicted to exhibit intriguing states of electronic order. Of these materials, those containing boron are of considerable current interest because of their relatively high superconducting temperatures. We have investigated elemental boron to very high pressure using diamond anvil cell electrical conductivity techniques. We find that boron transforms from a nonmetal to a superconductor at about 160 gigapascals (GPa). The critical temperature of the transition increases from 6 kelvin (K) at 175 GPa to 11.2 K at 250 GPa, giving a positive pressure derivative of 0.05 K/GPa. Although the observed metallization pressure is compatible with the predictions of first-principles calculations, superconductivity in boron remains to be explored theoretically. The present results constitute a record pressure for both electrical conductivity studies and investigations of superconductivity in dense matter.

Predicting the superconducting properties of materials and searching for new superconductors remains a challenge for condensed-matter physics. Descriptions of the transition to superconducting states depend on a number of parameters that are difficult to determine from first-principles calculations. From conventional theory (*1*), it follows that low-Z elements are beneficial for increasing the temperature of superconductivity because of their typically high Debye temperatures; and of these materials, many require pressure to be produced. The highest superconducting transition temperature (T_c) is predicted for the lightest element, H (*2*, *3*), which is expected to become metallic at pressures of ~400 GPa (*4*). At ordinary pressures, the light metallic element Li does not show any evidence of superconductivity down to 4 mK (*5*), but recent calculations for Li predict that T_c can reach 70 K at high pressures (*6*). Be has a T_c of 0.25 mK, but in thin films this increases up to 10.5 K (*7*). In addition, there is much interest in superconductivity in B-containing compounds (*8*–*10*). It has been proposed that metallic B layers in the structure of the recently discovered MgB_2 superconductor play a crucial role in the mechanism of its superconductivity (*11*). B is predicted to be metallic at pressures of about 200 GPa (*12*), taking on the behavior of a trivalent metal such as Al, the next member of the group IIIa family, but no calculations of superconductivity in B have been reported. The goal of the present experiments was to transform B into the metallic state under high pressure to search for superconductivity.

Experimentally, B remains the least studied of the light elements at high pressure. Under ambient conditions, it has a molecularlike structure based on 12-atom icosahedral clusters, a feature that gives rise to complex polymorphism (*13*). In the simplest structure (α-B) the B clusters are linked at the corners, whereas in β-B they share common faces. High-pressure Raman spectra of α-B measured up to 32 GPa appear to indicate that intercluster bonds are much stronger than the intracluster bonds (*14*). Subsequent x-ray studies have confirmed the cluster-based nature of this material (*15*). X-ray diffraction of the material is difficult to perform at high pressures because B is a weak scatterer. In a recent study, x-ray diffraction of rhombohedral-105 (R-105) β-B was performed to above 30 GPa at temperatures up to 3500 K (*16*). B was found to transform to a tetragonal phase (T-192) above 10 GPa at high temperature. No experimental studies at higher pressures appear to have been reported.

The calculations of Mailhiot *et al.* (*12*) gave 200 GPa as the approximate pressure at which metallic B can be expected. This pressure is within the range of accessibility of recently developed electrical techniques, which are described in (*17*, *18*). In this method, the leads are insulated from the Re gasket by a layer formed by a cubic BN/epoxy mixture. A sample is placed on the top of the anvil and pressed into this layer together with the electrodes. Thus, the BN/epoxy layer serves also as a quasihydrostatic pressure medium for the sample. The variation in pressure across the sample was within 10 GPa. The ruby scale was used for pressure determination (*19*). Samples consisted of high-purity (99.999%) polycrystalline β-B that had been well characterized in our recent x-ray diffraction studies (*16*). We carried out two high-pressure experiments. In the first experiment, 0.25-carat type I diamonds with a 500-μm tip, 8° bevel angle, and 20-μm culets were used to generate pressure. A flake of β-B 14 to 16 μm in diameter and 1 to 3 μm in thickness was placed at the culet. Because of the small size of the sample in this run, we used a quasi–four-electrode scheme in which four 2-μm-thick Pt electrodes were electrically connected in pairs by crossing their tips near the sample. The sample was then connected to these joined leads with 2-μm-thick Pd electrodes. Thus, the resistance of the sample was measured in series with the two Pd electrodes.

The sample at ambient pressure showed no measurable resistance (R > 300 Mohm), but exhibited strong photoconductivity under illumination by a halogen lamp or Ar-ion laser (at 488 nm) as expected for β-B, which is a semiconductor with a 1.6-eV energy gap (*20*). With increasing pressure at 300 K, a measurable resistance appeared above 19 GPa, and visible darkening of the sample was observed at ~30 GPa. On further increase in pressure, the resistance dramatically decreased (Fig. 1). The pressure dependence of the resistance had clearly visible steps at 30, 110, and 170 GPa. We applied the load at 300 K to examine a possible change in conductivity from semiconducting to metallic, followed by cooling to check for possible superconductivity. The type of conductivity was checked by slight heating of the cell near room temperature. Up to 170 GPa, the material remained semiconducting, indicating the persistence of a band gap. Above 160 GPa, the sample also started to show visible reflectivity (although much less than that of the adjacent Pd electrodes), which increased under further compression. At approximately 175 GPa, the room-temperature conductivity clearly showed a change from semiconducting to metallic.

At 175 GPa, we cooled the sample to liquid helium temperatures. A sharp drop in resistance was observed at 6 K (Fig. 2). We then warmed the cell to room temperature to change pressure and subsequently cooled the sample. These warming and cooling cycles, which lasted more than 10 hours, were repeated at a series of pressures. The pressures were measured at room temperature and at intermediate and low temperatures on each cycle. By using a low-temperature diamond anvil cell equipped with a spring (*21*), we kept the pressure on the sample nearly constant during the temperature cycles, only slightly increasing with cooling (less than 10 GPa). The observed picture is consistent with superconducting behavior of the B sample in series with the Pd leads (*22*). The superconducting transition shifted on compression to higher temperatures, so that T_c reached 11 K at 250 GPa (Fig. 2).

In the second run, we employed a true four-electrode scheme for the resistance measurements. We used a larger sample (diameter, 40 μm) and anvils with 320-μm culets, an 8° bevel angle, and 50-μm flat regions (0.25-carat type I diamonds). This resulted in a lower maximum pressure reached in the experiment but allowed accurate measurements of the sample resistance to be performed without the input resistance of

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the electrodes. In this run, we also used different electrodes (only Pt), in order to prove that the measured superconducting steps in the first experiment belong to the B. In addition, we measured the true superconducting transition with zero resistance at low temperatures (Fig. 3). The measured superconducting steps agree with the data from the first run, and the combined data give a pressure derivative of the critical temperature (dT_c/dP) of 0.05 K/GPa above the transition (Fig. 4) (*23*). The pronounced kink in the pressure dependence of T_c at ~180 GPa correlates well with the kink in the pressure dependence of the room-temperature resistance (Fig. 1). The four-electrode measurement and the geometry of the sample allowed us to estimate the conductivity σ of the material, which at 195 GPa is ~500 ohm^{-1} cm^{-1}. Thus, B at this pressure is a very poor metal, with a value of σ close to that of minimum metallic conductivity (*24*).

In the superconducting phase, we note that the observation of metallization is compatible with the theoretical calculations of Mailhiot *et al.* (*12*), who predicted a transition from icosahedral B to a body-centered tetragonal (bct) structure at 210 GPa followed by a transition to face-centered cubic (fcc) at 360 GPa (*25*). Although 210 GPa was given as an upper bound, the stabilization of intermediate, perhaps partially polymerized, structures could shift the predicted transition pressure to the purely noncovalent (e.g., bct and fcc) phases to still higher values. We cannot yet rule out the existence of such intermediate phases. This is particularly important for understanding the mechanism of metallization (e.g., band overlap versus structural transition) as well as the mechanism of superconductivity. We consider the Allen-Dynes expression for T_c

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

where ω_{ln} is a characteristic phonon frequency, λ is the electron-phonon coupling strength, and μ^* is the coulomb pseudopotential. Assuming $\mu^* \approx 0.12$ and ω_{ln} is in the range from 900 to 1400 cm^{-1} (*26*), a T_c of 7 K gives λ between 0.48 and 0.44, which is a reasonably strong electron-phonon coupling for a normal *s-p* metal. However, compared to the typically observed pressure-induced decrease in T_c for *s-p* metals [e.g., Al (*27*)], we observe a significant increase in T_c for B. McMillan (*28*) pointed out that electron-phonon coupling in *s-p* metals can be represented by $\lambda = N(0)\langle I^2\rangle/(M\langle\omega^2\rangle) \sim C/\langle\omega^2\rangle$, where $N(0)$ is the density of states at the Fermi level, $\langle I^2\rangle$ is the average square of the electron-phonon matrix element, and $\langle\omega^2\rangle$ is averaged over the phonon spectrum. Assuming that

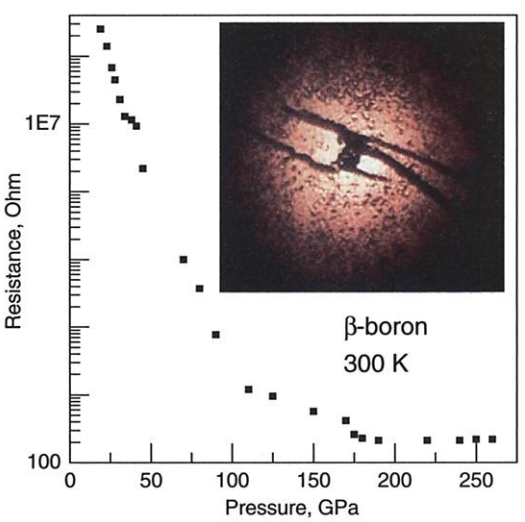

Fig. 1. Pressure dependence of the resistance of B at 300 K. The inset shows a view of a B sample of 14- to 16-μm-diameter in transmitted light with Pd electrodes at 175 GPa. The electrode in the upper part of the sample was duplicated for reliability. The cubic BN/epoxy gasket becomes transparent at pressures above 20 GPa, and the region of transparency spreads out with pressure. The apparent diameter of the sample did not change up to the highest pressures of the experiment (260 GPa), whereas the transparent part of the gasket increased substantially. The electrodes extruded with pressure and became thinner but remained intact. The sample was in series with the two Pd electrodes, which were ~200 μm in length and ~3 μm^2 in cross section. The sample reached a pressure of 260 GPa at 300 K, at which point one of the diamonds failed.

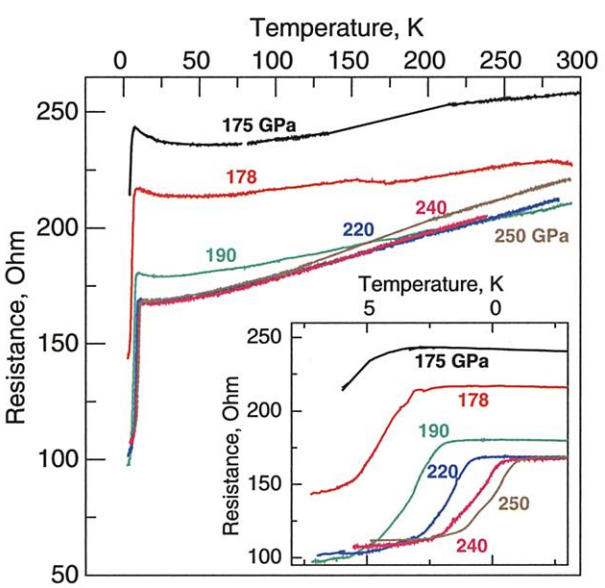

Fig. 2. Temperature dependence of the resistance of the B sample with a quasi–four-electrode measurement scheme. Superconducting steps are displayed enlarged in the inset. The height of the superconducting step decreases under compression, in accordance with increasing metallic conductivity of B. The resistance at the plateau at low temperature increases on compression and is naturally explained by the observed extrusion and thinning of Pd electrodes connected in series with the B. The transition curves are broadened somewhat, primarily because the pressure medium (the BN/epoxy mixture) was not hydrostatic. However, the pressure gradient over the sample did not exceed 10 GPa at the highest pressures, which allowed a consistent and reliable identification of T_c.

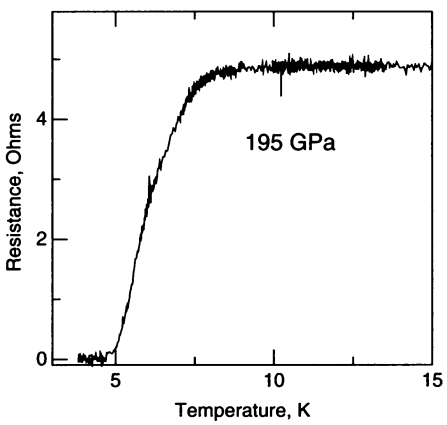

Fig. 3. Resistance of B as a function of temperature as measured with the four-probe technique, showing the transition to the zero-resistance superconducting state.

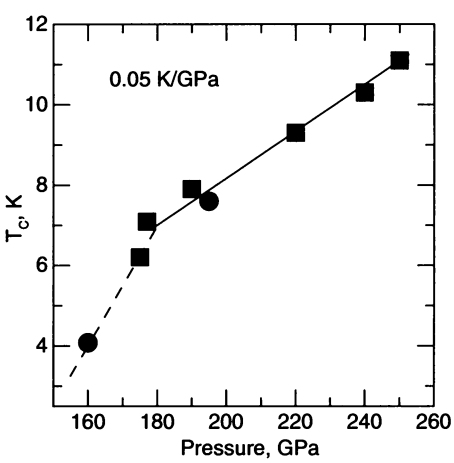

Fig. 4. Pressure dependence of T_c. The squares and circles represent data from the first and second experimental runs, respectively. The solid line is a fit to the data above 170 GPa. The dashed line is a fit to the lower pressure data (see text). T_c was determined from the intersection of tangent lines at the superconducting steps (Fig. 2). All data were taken during increasing pressure. In the second run, we attempted to release pressure after the 195-GPa point, but the electrodes failed after a small decrease in pressure.

pressure affects the phonon spectrum essentially by increasing all phonon frequencies, we can explain the decrease in T_c observed in many superconductors on compression, as has been done recently for MgB_2 (*10, 29*).

That T_c in boron increases substantially with pressure may be due to one of the following: (i) The factor $\eta = N(0)\langle I^2\rangle$ may increase with pressure in B, thus suppressing the effect of increasing $\langle\omega^2\rangle$. The Hopfield parameter, η, may also contribute to the increase in T_c if the character of the conduction electrons also changes under pressure, as in *s-d* transfer. (ii) The $\langle\omega^2\rangle$ factor may actually decrease with pressure if the phonon modes responsible for electron-phonon coupling soften under pressure. (iii) The parameter μ^* decreases on compression, which would be related to pressure-induced additional screening of the electron-electron interaction. Of these, the first and third options are possibilities: Both may be effective if B is approaching a covalent instability (with η increasing), as discussed by Allen and Dynes (*30*); or it transforms to a compensated metal, as in the cases discussed by Richardson and Ashcroft (*31*). A similar increase in critical temperature ($dT_c/dP \approx 0.05$ K/GPa) is observed in metallic S after transforming to the β-Po structure at 160 GPa (*32*), suggesting that the mechanism could be related.

We have found superconductivity in B at pressures above 160 GPa. The pressure of metallization is in the general range of (but somewhat lower than) theory, which predicted that the transition would be accompanied by the loss of covalent bonding to form a dense nonicosahedral structure (*12*). The magnitude of T_c appears to be consistent with such a transition and with an electron-coupling origin for the superconductivity. This work extends the range of electrical conductivity measurements to a record value of 250 GPa. These observations should stimulate theoretical calculations of superconductivity in elemental B and related low-*Z* substances.

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22. The superconducting step cannot be attributed to Pt or Pd electrical wires in series with the sample, because the same superconducting transitions were observed for both electrodes. In addition, we proved that the Pt electrodes did not reveal a superconducting transition on cooling down to 50 mK in previous experiments on CsI up to 220 GPa (*17*). In those experiments, the only superconducting transition was that of the CsI sample, which appeared at 1.6 K and 203 GPa and shifted to lower temperatures with pressure. We also did not observe any superconductivity in experiments on Xe to 155 GPa and 27 mK, using the same arrangement of Pt electrodes (*18*). Only recently has superconductivity been found in compacted Pt powder, but at very low temperatures; i.e., $T_c < 1.38$ mK [R. König, A. Schindler, T. Herrmannsdörfer, *Phys. Rev. Lett.* **82**, 4528 (1999)]. We note that the BN/epoxy layer is also in contact with the sample and electrodes. However, this mixture remains insulating to at least 240 GPa, as demonstrated by recent experiments on N [M. I. Eremets *et al.*, *Nature* **411**, 170 (2001)], and consistent with the experiments described above. Thus, although the Meissner effect was not examined (*17*), the resistance steps measured here can be attributed to superconductivity in the B samples.
23. The initial pressure derivative is very large (~0.2 K/GPa). Extrapolation of this line to lower pressure gives $T_c = 0$ K at ~130 GPa, which correlates with a kink in the room-temperature *R(P)* curve. This suggests the possibility that the transition to the metallic state occurs at ~130 GPa, whereas the change near 180 GPa arises from a phase transition.
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26. The modes in α-B extend to 1300 cm^{-1} at high pressure (*13*). The frequency of diatomic B is ~1000 cm^{-1} [K. P. Huber, G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979)].
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Observation of Chaos-Assisted Tunneling Between Islands of Stability

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We report the direct observation of quantum dynamical tunneling of atoms between separated momentum regions in phase space. We study how the tunneling oscillations are affected as a quantum symmetry is broken and as the initial atomic state is changed. We also provide evidence that the tunneling rate is greatly enhanced by the presence of chaos in the classical dynamics. This tunneling phenomenon represents a dramatic manifestation of underlying classical chaos in a quantum system.

Quantum-mechanical systems can display very different behavior from their classical counterparts. In particular, quantum effects suppress classical chaotic behavior, where simple deterministic systems exhibit complicated and seemingly random dynamics (*1*). Nevertheless, aspects of quantum behavior can often be understood in terms of the presence or absence of chaos in the classical limit. In this report, we focus on quantum transport in a mixed system, where the classical dynamics are complicated by the coexistence of chaotic and stable behavior. We study quantum tunneling between two stable regions (referred to as nonlinear resonances or islands of stability) in the classical phase space. The classical transport between these islands is

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