Phonon-assisted electronic topological transition in MgB$_2$ under pressure

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We report measurements of the superconducting critical temperature $T_c$ of polycrystalline MgB$_2$ samples containing isotopically pure $^{10}$B and $^{11}$B under quasi-hydrostatic pressure conditions in He pressure media up to 44 GPa. Measurements to volume compressions $V/V_0 \sim 0.82$ allow us to observe a kink in the volume dependence of $T_c$ for Mg$^{10}$B$_2$ (at 20 GPa) and Mg$^{11}$B$_2$ (at 15 GPa). The pressure dependence of the $E_{2g}$ mode also changes abruptly around 20 GPa for the Mg$^{10}$B$_2$ sample. The anharmonic character of the $E_{2g}$ phonon mode and anomalies in $T_c$ pressure dependence are interpreted as the result of a phonon-assisted Lifshitz electronic topological transition.

The recently discovered high-temperature superconductor MgB$_2$ has attracted considerable interest in condensed-matter and materials physics. Experiment as well as theory indicate that MgB$_2$ can be treated as a phonon mediated superconductor. Calculations show that the strongest coupling is realized for the phonon branch in the Brillouin zone from Γ point ($E_{2g}$ phonon) to A point ($E_{2u}$ phonon), which is related to vibrations of the B atoms. This makes MgB$_2$ a unique system with a single phonon branch dominating the superconducting properties within the framework of phonon-mediated mechanism for superconductivity.

By knowing the pressure dependence of these phonons frequencies and pressure dependence of $T_c$, the electron-phonon coupling in this material can be directly addressed.

The pressure dependence of the $E_{2g}$ phonon was measured recently in our laboratory using Ne pressure media. The phonon mode is very anharmonic: it has large Raman linewidth and an unusually high Grüneisen parameter. Theoretically, the anharmonicity of this mode has been understood as arising from its strong coupling to the partially occupied planar B $\sigma$ bands near the Fermi surface. The theoretical calculations presented in Ref. predict high Grüneisen parameter values for the whole phonon branch from $E_{2g}$ to $E_{2u}$ phonon, and the frequency for the $E_{2g}$ phonon with anharmonic corrections was predicted to be close to 570 cm$^{-1}$. The effects of pressure on superconductivity in MgB$_2$ studied to 1.84 GPa in fluorinet and 0.7 GPa in a He pressure medium show a decrease of $T_c$ with the rate of 1.6 K/GPa and 1.11 K/GPa, respectively. Other measurements in He pressure media showed pressure coefficients 1.45 K/GPa, and 1.08 K/GPa for different samples. The pressure studies in a Bridgman anvil apparatus with steatite as a pressure medium showed different results for sintered and powder samples, with a highly non-linear pressure dependence measured for sintered sample.

Magnetic susceptibility studies in diamond anvil cells with alcohol pressure medium have been performed to 28 GPa, and an anomaly in the $T_c(P)$ dependence was observed around 10 GPa, which was interpreted as a signature of the electronic topological transition (ETT). Another diamond cell magnetic susceptibility experiment with a He medium to 20 GPa did not confirm the anomaly at 10 GPa, and showed a sublinear volume dependence of $T_c$. Our experiment on Mg$^{10}$B$_2$ to 15 GPa in a He pressure medium showed a linear volume dependence of $T_c$, different from Refs.

Compressibility data have been obtained by neutron diffraction (to 0.62 GPa) and synchrotron x-ray diffraction (to 6.15 GPa, 8 GPa, and 11 GPa). Based on theoretical calculations of the electronic density of states at the Fermi level, which show a very moderate decrease with pressure, the dominant contribution to the decrease in $T_c$ under pressure has been proposed to be due to an increase in phonon frequency.

Here we report quasihydrostatic measurements of $T_c$ in He pressure media in MgB$_2$ with isotopically pure $^{10}$B up to 44 GPa, and with isotopically pure $^{11}$B up to 33 GPa. Our low pressure data agree with previous measurements in hydrostatic conditions, with $dT_c/dP=1.1$ K/GPa. At higher pressures, however, $T_c$ deviates from a linear dependence as a function of pressure, although the volume dependence is linear for both isotopes to 15 GPa. Moreover, we observe a kink in the volume dependence of $T_c$ at 20 GPa for Mg$^{10}$B$_2$, and at 15 GPa for Mg$^{11}$B$_2$. The kink at 20 GPa for $^{10}$B isotope correlates well with a similar abrupt change in the pressure dependence of the $E_{2g}$ Raman mode, which suggests that the $E_{2g}$ phonon is involved in the observed behavior of the superconducting transition. We propose that pressure-induced changes in both the $E_{2g}$ phonon mode and $T_c$ result from a phonon-assisted electronic topological tran-
sition [13]. This finding further means that the zero point motion of B atoms should be taken into account in treatment of the electronic structure, as opposed to standard approaches which neglect the quantum character of the nuclei.

Samples of MgB$_2$ were similar to those used in Ref. [2,22], with isotopically pure $^{10}$B and $^{11}$B. They were essentially in a powdered form consisting of aggregates of 30-50 $\mu$m in linear dimensions, which is ideal for high-pressure experiments. Our experiments were done with Be-Cu nonmagnetic diamond anvil cells using magnetic susceptibility techniques [24]. We used diamond anvils with a flat tip 400 $\mu$m in diameter. A flake of MgB$_2$ approximately 40 $\mu$m in diameter and 10 $\mu$m in thickness was loaded into a 200-$\mu$m diameter hole, prepared in a nonmagnetic NiCr(Al) gasket [24]. He has served as the pressure transmitting medium. Pressure was increased at 40 to 50 K and measured using the standard ruby fluorescence technique. Thus, we can specify the conditions for this experiment as quasihydrostatic, because pressure was applied when the He medium was solidified. However, our results show very good agreement with low pressure hydrostatic data, so we believe that nonhydrostatic effects in our experiment are negligible. We warmed the Mg$^{10}$B$_2$ sample to room temperature twice during this experiment (at 10 GPa and 25 GPa), and kept it at room temperature for few days. This did not have any effect on the observed pressure dependence of $T_c$; we conclude that there is no substantial effect of thermal cycling on $T_c$.

Experiments with Mg$^{11}$B$_2$ were done in a similar manner, with the only difference being that we warmed the sample to room temperature when the pressure was below 11 GPa to achieve hydrostatic conditions on compression. Above 11 GPa the Mg$^{11}$B$_2$ sample was always kept below room temperature; however, it was warmed up occasionally to 120-130 K. We also performed a nonhydrostatic experiment (without pressure medium) to 25 GPa with Mg$^{10}$B$_2$; the observed pressure dependence differed from the run in the He medium, and resembled the data for powdered samples obtained by Monteverde et al [13].

In Fig.4 we show the $T_c$ as a function of pressure; temperature scans at selected pressures are also shown. The signal observed is close to the limit of the sensitivity of our setup, which we have recently improved [23]. The signal is superimposed on the nonlinear paramagnetic background from the gasket material at lower temperatures (below 25 K), which has a characteristic $\frac{1}{T}$ dependence (subtracted from the data) [23]. However, the onset of $T_c$ can be reliably identified with an accuracy 0.2-0.8 K (depending on the actual quality of the data, as illustrated in Fig.1) up to the highest pressures reached in this experiment.

We plot $T_c$ for Mg$^{10}$B$_2$ as a function of volume in Fig.5. One can clearly distinguish a kink in $T_c$($V$) curve at a volume that corresponds to 20 GPa. We have measured $E_{2g}$ Raman mode frequency at room temperature to 50 GPa to understand the anomaly in $T_c$, and we observed similar kink in pressure dependence of the Raman mode slightly above 20 GPa. The details of the Raman experiment will be published elsewhere [26]. Pressure dependence of the $E_{2g}$ Raman mode frequency is shown in Fig.6 together with the cartoons which illustrate our understanding of this anomalous behavior of the superconducting $T_c$ and the $E_{2g}$ phonon mode.

The left inset in Fig.6 illustrates that at lower pressures the zero-point motion of B atoms for the $E_{2g}$ mode splits the boron in-plane $\sigma$ bands strongly, so that the lower band moves below the Fermi level, thereby crossing it and fulfilling the condition for ETT. This means that for a frozen-phonon calculation there should be an anomalous contribution to the total energy, which behaves similar to suggested by Lifshitz [13] $\frac{1}{2}g$ power term in the free energy, with the amplitude of the phonon mode being a parameter, which drives the electronic subsystem through such a transition. As a result, the phonon frequency will be strongly anharmonic, and its volume derivative (the Grüneisen parameter) may even have an anomaly at the transition. At higher pressures the zero-point motion does not split $\sigma$ band strong enough for the lower band to cross the Fermi level (right inset). Thus, system is always at conditions when there is no anomalous contribution to the free energy from ETT-like $\frac{1}{2}g$ power terms, and the phonon mode and $T_c$ behave in a more regular manner. Between those two regimes there should be a small pressure range in which the amplitude of the zero-point motion is just enough for the top of the lower band to coincide with the Fermi level. We propose that this condition is almost fulfilled at the observed kinks in pressure dependencies of $T_c$ and $E_{2g}$ phonon mode frequency.

The volume dependence of $T_c$ for Mg$^{11}$B$_2$ is shown Fig.5. A similar kink is clearly visible around 15 GPa. We believe that the lower pressure for the observed transition is due to the isotope effect: the zero-point motion for a heavier atom is smaller, and the matching condition for the $\sigma$ band is fulfilled at lower compression of the lattice. We also note that the transition at room temperature from Raman data for Mg$^{10}$B$_2$ (Fig.6) occurs at slightly higher pressure, than the low-temperature transition as observed from the $T_c$($V$) plot (Fig.5). Although the difference is close to the observation error, we may tentatively attribute this small effect to the lattice expansion: higher pressure is needed to compress the structure at room temperature to reach the transition.

Several arguments support the observed isotope trend, following the reasoning proposed by An and Pickett [31]. They noticed that the $\sigma$ bands belonging to boron, which form cylindrical Fermi surface sheets [41], can be treated as quasi-two-dimensional. The states in these bands contribute most of the electron-phonon coupling responsible for superconductivity [41]. The overall splitting of the $\sigma$
band is characterized by $p-p$ matrix element $t_{ppσ} \sim d^{-3}$, where $d$ is B-B bond length. Thus, the deformation potential of the $σ$ band will be proportional to the derivative of the above matrix element with respect to $d$ ($E_{2g}$ mode modulates B-B distance), and thus $|\mathbf{D}| \sim d^{-4}$. We have determined earlier that the phonon frequency of the $E_{2g}$ mode scales as $ω \sim (a/a_0)^{-10.8} = (d/d_0)^{-10.8}$ below 15 GPa [3]. The amplitude of the zero-point motion $u \sim ω^{-1/2} \sim (d/d_0)^{5.4}$, which means that the splitting of $σ$ bands $ΔE \sim Δω \sim (d/d_0)^{1.4}$ is decreasing almost proportionally to the B-B bond length.

The low-pressure regime for both isotope compounds suggests a strong contribution from ETT anomalies to the observed properties of the materials. It should be noted that the electron-phonon coupling may be strongly affected by the non-adiabatic effects due to the violation of the condition that the Debye frequency is much less than the Fermi energy $ω_D/E_F \ll 1$ [27] close to the ETT regime. We also expect large effects of uniaxial stresses and impurities on the pressure dependence of the superconducting transition in MgB$_2$.

In summary, we have measured the superconducting transition temperature in isotopically pure Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ under quasihydrostatic conditions (He pressure media) to 44 GPa. Although the initial linear slope of $T_c$ is found to be in excellent agreement with previous hydrostatic experiments [11,12], we observed a kink in the volume dependence of $T_c$ at 20 GPa for Mg$^{10}$B$_2$, and at 15 GPa for Mg$^{11}$B$_2$. A similar anomaly was found in the pressure dependence of the $E_{2g}$ phonon in Mg$^{10}$B$_2$. We argue that observed anomalies are related to the phonon-assisted electronic topological transitions. This finding further means that the zero-point motion of the atoms should be taken into account in treatments of the electronic structure for this system. The nonhydrostatic stresses and impurity effects may be responsible for the most of the discrepancies in the available high pressure data for these intriguing materials.

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FIG. 1. Pressure dependence of $T_c$ in a He medium. $T_c$ is identified as the onset of the magnetic signal [24,25] as illustrated in the insets for selected pressures. The solid circles are data for Mg$^{10}$B$_2$ (dotted line is guide to the eye). The data for Mg$^{11}$B$_2$ are shown as solid squares for compression, and open squares for decompression. No decompression data were obtained for the Mg$^{10}$B$_2$ sample.

FIG. 2. Volume dependence of $T_c$ for Mg$^{10}$B$_2$. The Vinet equation of state [24] was used to calculate the P-V relation with a bulk modulus $B_0=150$ GPa, and its derivative $B_0'=4.0$.

FIG. 3. Pressure dependence of the $E_{2g}$ Raman mode in Mg$^{10}$B$_2$. The linewidth of the mode was anomalously large around 20 GPa [17].

FIG. 4. Volume dependence of $T_c$ in Mg$^{11}$B$_2$. Full symbols are for compression; open symbols for decompression. We calculated the equation of state using the same parameters as for Mg$^{10}$B$_2$. The variation of the bulk modulus by $\pm 5$ GPa does not shift volume position of the kink by more than $\delta V/V_0 \sim 0.005$. 