Discovery of a Superhard Iron Tetraboride Superconductor

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Single crystals of novel orthorhombic (space group Pnmm) iron tetraboride FeB₄ were synthesized at pressures above 8 GPa and high temperatures. Magnetic susceptibility and heat capacity measurements demonstrate bulk superconductivity below 2.9 K. The putative isotope effect on the superconducting critical temperature and the analysis of specific heat data indicate that the superconductivity in FeB₄ is likely phonon mediated, which is rare for Fe-based superconductors. The discovered iron tetraboride is highly incompressible and has the nanoindentation hardness of 62(5) GPa; thus, it opens a new class of highly desirable materials combining advanced mechanical properties and superconductivity.

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Modern computational materials design is gaining broad recognition as an effective means of reducing the number of experiments that can ultimately lead to materials discovery [1–3]; successful examples now include thermoelectrics, catalysts, electrode materials for Li-ion batteries, to name a few. Superconductors remain among the most challenging materials to develop [2,4–6]. So far theory has only successfully guided experiment to a discovery in a few cases related to thoroughly studied elemental materials, namely, silicon [7] and lithium [8] under pressure. The progress can be attributed to the improvement of density functional theory-based methods [9,10], advances in compound prediction strategies [1,3], and the steady growth of computational resources. Nevertheless, the prediction of novel superconductors remains challenging [4]. First, only conventional (phonon-mediated) superconductors are understood well enough [4] to be described by theories with predictive power [5,11]. Calculation of the superconducting critical temperature, Tc, is possible but exceedingly demanding as a viable option in high-throughput screening for candidate materials. Second, the inverse correlation between the stability of a compound and its phonon-mediated superconducting Tc has been pointed out in a number of studies: a considerable density of states (DOS) at the Fermi level, beneficial for high Tc, is often an indication of structural instability [6]. One of the remarkable exceptions is the stoichiometric MgB₂ material [12] with naturally hole-doped σ bands and a Tc of 39 K.

The problem of thermodynamic instability can be mitigated under high pressure. When quenched to normal conditions, materials with a large DOS at the Fermi level may remain metastable and show superconductivity facilitated by this large DOS. Kolmogorov et al. [9] systematically examined the Fe-B system and showed that a previously unknown compound, FeB₄, may exist under normal conditions in a previously unobserved orthorhombic crystal structure. The material was predicted to have naturally electron-doped bands and a large electron-phonon coupling [9], which indicate that FeB₄ might be a “conventional” Fe-based superconductor (rare cases are known, see [13–15]), as opposed to the recently discovered family of “unconventional” Fe-based superconductors [2,16]. Balić et al. [17] suggested that the predicted FeB₄ phase could be synthesized under pressure. The wide and growing interest in Fe-based superconductors [2], simple chemical composition, and expected mild pressure-temperature conditions for synthesis [17] make iron tetraboride a good case for testing the computational predictive power and, thus, the degree of our theoretical comprehension of such a complex physical phenomenon as superconductivity. Here, we report synthesis of an iron boride with a so-far unknown composition, the verification of theoretical predictions regarding the structure and superconductivity of this material, and the finding of its unexpectedly low compressibility and very high hardness.
cracks in the orthorhombic FeB (Ref. [19]), although hexagonal further experiments. The largest pieces of phase-pure probe analysis (performed in SEM and TEM) [25] prior to length dispersive x-ray, and energy dispersive x-ray micro-
carefully characterized them with x-ray diffraction, wave-
common edges of the adjacent polyhedra, whose centers (Fe atoms) are displaced with respect to each other by 1/2 along the body diagonal of the unit cell.

The experimental Fe-B phase diagram [18] at ambient pressure shows only two compounds, tetragonal Fe$_2$B and orthorhombic FeB (Ref. [19]), although hexagonal FeB$_2$ (Ref. [20]) and rhombohedral FeB$_{0.49}$ (Ref. [21]) have also been reported in literature. Metastable cubic Fe$_2$B$_6$ and orthorhombic Fe$_2$B$_{12}$ phases have also formed in a number of experiments [22–24].

We have undertaken a series of high-pressure experi-
ments [25] aimed at the synthesis of the predicted boron-
rich Fe-B phases (FeB$_2$ and FeB$_{4}$ [9]). Independent of pressure, a major component of the reacted mixture was stoichiometric FeB (Table S1, Ref. [25]). At low pressures (3 GPa and below) and temperatures of 1323 to 1973 K only known phases, orthorhombic FeB and rhombohedral FeB$_{0.49}$, were produced. Experiments at pressures of 8 to 18 GPa and temperatures of 1523 to 2023 K (Table S1 [25]) led to the synthesis of previously unidentified orthorhombic FeB$_4$, Fe$_2$B$_7$, and tetragonal Fe$_{1+x}$B$_{30}$ ($x \approx 0.04$) phases. The compounds crystallize from the melt and by optimizing the sample geometry, heating duration, and temperature gradients along the capsule it was possible to increase the amount of boron-rich Fe-B phases. However, as seen in Fig. 1(a), all the products of the high-pressure synthesis, and particularly FeB$_4$ and Fe$_2$B$_7$, are found in a tight mutual intergrowth, so that the procedure of phase separation is challenging.

We have manually selected small pieces of FeB$_4$ and carefully characterized them with x-ray diffraction, wave-
length dispersive x-ray, and energy dispersive x-ray micro-
probe analysis (performed in SEM and TEM) [25] prior to further experiments. The largest pieces of phase-pure FeB$_4$ produced so far have dimensions on the order of 150 $\times$ 150 $\times$ 100 $\mu$m$^3$. Maximal weight of phase-pure polycrystalline samples is of about 0.14 mg. We note, however, that standard characterization techniques are not sensitive enough to detect trace amounts of ferromagnetic impurities, such as metallic iron that is almost inevitably present in samples recovered after the high-pressure synthesis. These impurities are seen in magnetic susceptibility measure-
ments (see [25]), but do not affect any of our conclusions regarding the superconductivity and superhardness of FeB$_4$.

The crystal structures of FeB$_4$, Fe$_2$B$_7$, and Fe$_{1+x}$B$_{30}$ have been solved from single crystal x-ray diffraction data (Table S2 [25]). A detailed description of Fe$_2$B$_7$ and Fe$_{1+x}$B$_{30}$ is out of the scope of the present Letter and will be published elsewhere.

According to the single crystal x-ray and electron dif-
fraction [25], FeB$_4$ adopts an orthorhombic $Pnnm$ ($Z = 2$) crystal structure. The refined structure was confirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images along the [100], [010], and [001] directions [Fig. 1(b), Figs. S10, S11]. Additionally, planar defects confined to the [010] planes were occasionally observed in FeB$_4$. These defects are not abundant in the material, as indicated by the absence of any related diffuse intensity on the electron diffraction patterns (Fig. S9).

A polyhedral model of the FeB$_4$ structure is shown in Fig. 1(c) and Fig. S1 (Ref. [25]). The structure is remark-
bly close to that theoretically predicted [9] (Table S2 [25]), and found very recently also for CrB$_4$ [26,27].

Despite the very small size of the available phase-pure samples, we were able to confirm the prediction of superconductivity in FeB$_4$. While resistivity measurements are presently unfeasible, magnetic susceptibility data collected on polycrystalline samples indicate superconductivity in FeB$_4$. Magnetic susceptibility measurements under zero-
field-cooling (ZFC) conditions reveal a strong diamagnetic response of FeB$_4$ samples below 3 K (Fig. 2). Above 3 K, FeB$_4$ is weakly paramagnetic with a nearly temperature independent susceptibility above 70 K. Additionally, our samples showed a weak ferromagnetic signal of unknown

FIG. 1 (color online). (a) The backscattered electron SEM image of the polished surface of a high-pressure sample. The central part of the image (dark gray field) represents FeB$_4$ produced by the reaction of Fe with B after melting. The adjacent area on the right appears brighter as it is composed of the phases with lower boron content, namely, Fe$_2$B$_7$ and FeB. The surrounding black field is nonreacted boron which, however, underwent a pressure-induced phase transformation from $\beta$-B to $\gamma$-B. Boron intrusions also fill the cracks in the FeB$_4$ phase. (b) The high resolution [001] HAADF-STEM image of FeB$_4$ (bright dots correspond to the Fe columns). Occasional planar defects (marked with arrowheads) are confined to the (010) plane and are visible as lines running parallel to the $a$ axis and consisting of pairs of the Fe columns with a shorter projected intercolumn distance in comparison with the FeB$_2$ matrix [25]. (c) Crystal structure of FeB$_4$ presented as a packing of columns of FeB$_{12}$ polyhedra along the $c$ direction; the columns are connected by common edges of the adjacent polyhedra, whose centers (Fe atoms) are displaced with respect to each other by 1/2 along the body diagonal of the unit cell.
FIG. 2 (color online). Magnetic susceptibility of FeB₄ measured in an applied field of 1 mT ZFC. The susceptibility is normalized to the unit of volume (χ₁) and multiplied by 4π to facilitate the comparison with the expected value of 4πχ₁ = -1 for the ideal superconductor with the demagnetization factor of N = 0. Two sets of data were collected on the samples enriched with ¹⁰B and ¹¹B isotopes. Dashed lines denote the procedure for determining the onset temperature T onset (see Ref. [25]). The midpoints of the susceptibility drop (T mid) are shown as well.

FIG. 3 (color online). Specific heat (Cₚ) of FeB₄ measured on the ¹⁰B-enriched sample. The jump in Cₚ indicates the bulk superconductivity with T onset ~ 2.9 K in zero field. External magnetic field shifts the transition to lower temperatures. The critical field H c2 estimated from T onset in different fields is plotted as an inset and approximated by the empirical formula $H_c^2(T) = H_c^2(0)(1 - (T/T_c)^{α})$ shown by the dashed line. The WHH estimate of $μ_0H_c^2(0) = 1.0$ T is shown as well. In the main figure, the solid line is the BCS fit including a Gaussian broadening [30] (see text for details).

The strong diamagnetic response of FeB₄ is a clear footprint of superconductivity. The drop in the volume susceptibility (χ₁) is 4π(Δχ₁) = -1.3 that corresponds to the demagnetization factor of N = 0.23 according to 4π(Δχ₁) = -1/(1 - N). This value of N is close to N = 1/3 expected for a spherical sample.

The bulk nature of superconductivity is confirmed by heat capacity measurements showing a jump at the superconducting transition around 3 K (Fig. 3). This jump is systematically shifted to lower temperatures in applied magnetic fields. Using the onset of superconductivity as a measure of T c, we mapped the temperature dependence of the upper critical field H c2. It increases upon cooling, with an initial slope of $μ_0dH_c^2/dT = -0.5$ T/K at $T_c(0) ~ 2.9$ K. At lower temperatures, H c2(T) bends downwards. The critical field at zero temperature is extrapolated as $μ_0H_c^2(0) = -0.693T_cμ_0(dH_c^2/dT) ~ 1.0$ T according to the Werthamer-Helfand-Hohenberg formula [28]. Alternatively, H c2(0) can be determined from a fit with the empirical formula $H_c^2(T) = H_c^2(0) \times (1 - (T/T_c)^{α})$ yielding $μ_0H_c^2(0) = 1.05$ T and α = 1.25. Both estimates of H c2(0) are far below the Pauli-paramagnetic limit for weak electron-phonon coupling $μ_0H_c^2[\text{Tesla}] = 1.86T_c[\text{Kelvin}] \times 5.4$ T [29] and corroborate phonon-mediated superconductivity in FeB₄. In contrast, unconventional superconductors may have critical fields above the Pauli-paramagnetic limit.

To elucidate the nature of the observed superconducting transition, we compared the transition temperatures in the samples containing different boron isotopes (Fig. 2). The sample enriched with the heavier B isotope shows a lower $T_c (2.95$ and 2.89 K for T onset or 2.82 and 2.70 K for T mid in the ¹⁰B and ¹¹B samples, respectively), as expected for a phonon-mediated superconductor. Indeed, our tentative estimate of the isotope effect [25] yields ΔT c ~ 0.05 K in good agreement with ΔT c ~ 0.06–0.12 K, as found experimentally. Specific heat data provide further evidence for phonon-mediated superconductivity. The specific heat of the normal state, as measured in the applied field of 1 T, follows $C_p = γ_nT + βT^2$ with $γ_n = 10.2(2)$ mJ mol⁻¹ K⁻² and $β = 0.025(1)$ mJ mol⁻¹ K⁻⁴ determined from the fit of $C_p/T$ vs $T^2$ up to $T = 12$ K [see (25), Fig. S8]. This β value yields the quite high Debye temperature $θ_D ~ 730$ K indicating predominantly hard phonons, which are indeed expected for superhard FeB₄ (see below). The value of $γ_n$ corresponds to $N(E_F) = 4.3$ states eV⁻¹ (f.u.)⁻¹ at the Fermi level and suggests a strong renormalization of the electronic DOS compared to the LDA result of $N(E_F) ~ 1$ state eV⁻¹ (f.u.)⁻¹ [9]. At zero field, the jump in $C_p$ at the superconducting transition is ΔC p ~ 35 mJ/mol K yielding ΔC p/γ n$T_c ~ 1.18$ in reasonable agreement with 1.43 expected for the BCS limit with weak electron-phonon coupling. The proximity of ΔC p to the BCS value is indicative of the conventional, phonon-mediated superconductivity in FeB₄. This finding is further corroborated by a fit of the zero-field C p(T) with the BCS expression by Mühlschlegel [30] yielding $γ_n = 8.8(1)$ mJ mol⁻¹ K⁻² in reasonable agreement with $γ_n$ derived from the 1 T data.

Metal borides are known for their high hardness [31], so that characterization of the elastic behavior of the newly synthesized boride and its stability under pressure is an
important issue. No phase transitions were observed under compression of FeB$_4$ at ambient temperature in a diamond anvil cell up to about 40 GPa [25]. Compressibility measurements on both compression and decompression revealed the remarkably high bulk modulus, $K = 252(5)$ GPa, $K' = 3.5(3)$, and $V_0 = 72.79(4)$ Å$^3$/unit cell. (b) The relative changes of the unit cell parameters as a function of pressure. The stiffness of the FeB$_4$ structure along the $b$ direction is the same as that of diamond (continuous line according to Ref. [32]). Closed symbols represent the data points obtained on compression, and open ones—on decompression. The uncertainties are not shown since they are smaller than the size of symbols. (c) Depth dependent average values of indentation modulus. (d) Hardness of FeB$_4$. Load-displacement curves without pop-ins have been used for evaluation with tip compression correction.

FIG. 4 (color online). Compressibility of FeB$_4$ and the results of nanoindentation measurements. (a) The pressure dependence of the unit cell volume based on single crystal x-ray diffraction data. The fit of the pressure-volume data with the third-order Birch-Murnaghan equation of state (solid line) gave the bulk modulus $K = 252(5)$ GPa, $K' = 3.5(3)$, and $V_0 = 72.79(4)$ Å$^3$/unit cell. (b) The relative changes of the unit cell parameters as a function of pressure. The stiffness of the FeB$_4$ structure along the $b$ direction is the same as that of diamond (continuous line according to Ref. [32]). Closed symbols represent the data points obtained on compression, and open ones—on decompression. The uncertainties are not shown since they are smaller than the size of symbols. (c) Depth dependent average values of indentation modulus. (d) Hardness of FeB$_4$. Load-displacement curves without pop-ins have been used for evaluation with tip compression correction.

In summary, we have prepared and characterized the novel superhard superconductor FeB$_4$. Our data not only support the predicted orthorhombic crystal structure [9], but also confirm the superconductivity of FeB$_4$ that was likewise predicted theoretically. We argue that the superconductivity of FeB$_4$ is mediated by phonons, which is highly unusual for Fe-based materials [2,4]. In addition, the FeB$_4$ compound was found to be superhard, well exceeding the expectations about its potential mechanical properties [26]. This finding, bridging the gap between the superhardness and superconductivity community, may lead, for example, to a possibility for designing new superconducting nanoelectromechanical systems and/or observation of new fundamental effects.
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