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, $T_c$, 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 $T_c$ has been pointed out in a number of studies: a considerable density of states (DOS) at the Fermi level, beneficial for high $T_c$, is often an indication of structural instability [6]. One of the remarkable exceptions is the stoichiometric MgB$_2$ material [12] with naturally hole-doped $\sigma$ bands and a $T_c$ 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, FeB$_4$, 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 FeB$_4$ 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]. Bialon et al. [17] suggested that the predicted FeB$_4$ 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 tetaboride 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.
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$_{1-0.49}$ (Ref. [21]) have also been reported in literature. Metastable cubic Fe$_3$B$_6$ and orthorhombic FeB$_2$ phases have also formed in a number of experiments [22–24].

We have undertaken a series of high-pressure experiments [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$_{1-0.49}$, 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$_4$, FeB$_2$$_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 capsules 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, wavelength dispersive x-ray, and energy dispersive x-ray microprobe 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 measurements (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 diffraction [25], FeB$_4$ adopts an orthorhombic Pnmm ($Z = 2$) 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 remarkably 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...
Tc to the demagnetization factor of N. Both estimates of extrapolated as downwards. The critical field at zero temperature is ¼ N with N for the ideal superconductor with the demagnetization factor of midpoints of the susceptibility drop (susceptibility (footprint of superconductivity. The drop in the volume 

ΔTc = 2.95 and 2.89 K for Tc onset or 2.82 and 2.70 K for Tc 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 ΔTc ≈ 0.05 K in good agreement with ΔTc ≈ 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_n T + β T^2 with γ_n = 10.2(2) mJ mol⁻¹ K⁻² and β = 0.025(1) mJ mol⁻¹ K⁻³ 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 FeB_4 (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 Tc ≈ 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 FeB_4. This finding is further corroborated by a fit of the zero-field C_p(T) with the BCS expression by Mühlenschlegel [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. 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.
The work was supported by the German Research Foundation (DFG). N. D. thanks DFG for financial support through the Heisenberg Program and the DFG Project DU 954-8/1. H. G. gratefully acknowledges financial support of the Alexander von Humboldt Foundation. A. M. A., D. B., and G. V. T. acknowledge support from the ERC Grant No. 246791 “COUNTATOMS”. A. A. T. was partly supported by the MTT77 Mobilitas Grant of the ESF. L. D., N. D., and A. N. K. conceptualized the work. L. D. and N. D. planned and coordinated the study. H. G. conducted all synthesis experiments and analyzed all samples; E. B. analyzed all single crystal x-ray diffraction data; A. A. T., D. K., and W. S. performed magnetic susceptibility and heat-capacity measurements and analyzed the data; experiments in DAC were carried out by E. B., M. M., M. H., L. D., and N. D.; A. M. A., D. B., and G. V. T. performed the TEM analysis; A. R. conducted nanoindentation measurements. Y. N. performed the microprobe analysis. The paper was prepared by N. D. with contributions of all authors.

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