Effects of carbon doping on superconductivity in magnesium diboride

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We introduce carbon onto boron sites in MgB_2. The resulting changes in crystal lattice constants and superconducting transition temperature T_c are characterized by x-ray-diffraction, magnetic susceptibility, and electrical resistance measurements. The consequence of approximately 10% carbon doping of boron sites is a 1% contraction of the intraplane lattice dimension (with no appreciable change in the interplane dimension) and a lowering of T_c by approximately 7 K. The relative contributions to the shift in T_c from lattice contraction and charge transfer are evaluated.

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I. INTRODUCTION

The discovery of superconductivity in magnesium diboride MgB_2 at 39 K (Ref. 1) has sparked new research to further understand this interesting material. MgB_2 is the highest transition temperature noncuprate, nongated superconductor. Previous work has shown that the superconducting transition temperature T_c decreases with applied (isotropic) pressure[2] suggesting that, electronic effects aside, T_c decreases with decreasing lattice constant. Efforts have been made to introduce dopants into the host structure to elucidate how the crystal structure, internal charge states, and T_c are interrelated. Replacement of Mg with Al,[3] for example, decreases the *c*-axis lattice parameter (while leaving the *a-b* plane relatively unaffected) and depresses T_c, but from these results alone it is difficult to distinguish between charge-transfer and lattice-contraction effects. No successful attempts to dope foreign species into the boron sites or independently vary the *a-b* plane lattice parameters have been published.

In this paper, we report the effects of doping on the boron sites of MgB_2. Carbon substitution results in a significant contraction in the in-plane (*a* axis) lattice constant, while the *c*-axis lattice parameter is virtually unchanged. X-ray-diffraction, elemental analysis, electron energy-loss spectroscopy (EELS), dc magnetization, and electrical resistance measurements are used to characterize the structure and superconducting properties of the doped material. With approximately 10% of the boron sites substituted, the *a* axis contracts by 0.03 Å (1%) and T_c is decreased by 7 to 32 K. These results, taken together with previous pressure and Mg-site doping measurements, help identify which material parameters critically affect the unusual superconductivity.

II. EXPERIMENTAL SETUP

Both pure MgB_2 and carbon-doped ($MgB_{2-x}C_x$) polycrystalline samples were synthesized using variants on established methods.[1–3] To produce the carbon-doped material, magnesium turnings (99.8%, Alfa Aesar) and boron carbide (B_4C) powder (1–7 μm, 99.7%, Sigma-Aldrich) were mixed in a 1:2 stoichiometric ratio and placed in tantalum foil, which was crimped shut. The tantalum foil was heated to 600 °C and then 700 °C for 1–3 h each in a tube furnace under Ar atmosphere. To produce the pure material, amorphous boron powder (−325 mesh, 99.99%, Alfa Aesar) is substituted for the boron carbide and undergoes the same synthesis technique. The resulting material had a typical grain size of 1 μm as determined by scanning electron microscope.

X-ray-powder-diffraction measurements were performed on pure and carbon-doped samples. The diffraction pattern of the pure material was consistent with published results.[1] Figure 1 shows the x-ray powder diffraction of the carbon-doped product, taken with a siemens diffraktometer D5000. The diffraction pattern indicates that this doped sample consists of a majority phase with a distorted "MgB_2" structure,[1] together with a minority phase, which is MgB_2C_2.[4] The majority phase shows a shift in the diffraction pattern from that of MgB_2 to larger angle, consistent with lattice contraction of the *a* axis from $a=3.087$ to 3.055 Å, while the *c* axis remains unchanged at 3.524 Å. The diffraction peaks of the minority phase are consistent with undistorted and previously known MgB_2C_2.

In order to determine the volume fraction of the minority phase in the doped sample, along with the precise degree of carbon doping of the majority phase, two independent chemical analysis experiments were performed. In the first, the bulk, doped material was analyzed for magnesium and boron concentrations by an inductively coupled plasma

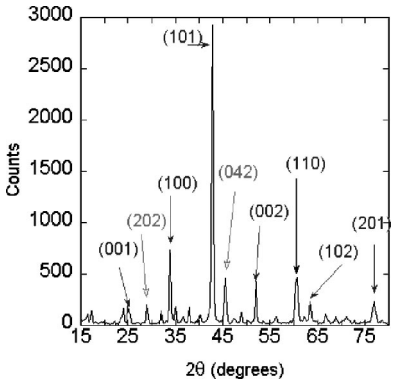

FIG. 1. X-ray-powder-diffraction pattern of $MgB_{1.8}C_{0.2}$ (blue, solid arrows) and MgB_2C_2 (red, hollow arrows) material.

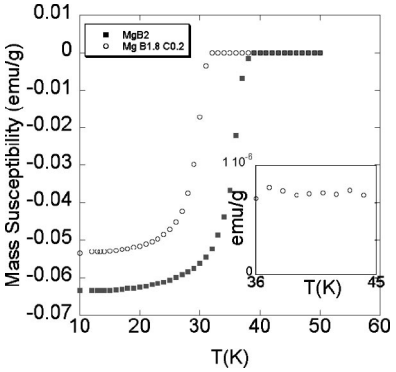

FIG. 2. Mass Susceptibility vs Temperature of product in an applied field of 5 Oe of MgB_2 (squares) and $MgB_{1.8}C_{0.2}$ (circles) Inset: Zoom-in on 35–45 K of $MgB_{1.8}C_{0.2}$, showing no MgB_2 signal.

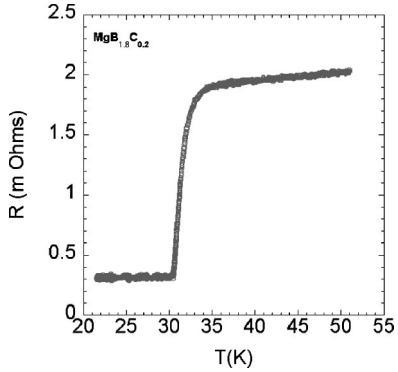

FIG. 3. A four-wire resistance of $MgB_{1.8}C_{0.2}$ vs temperature plot measured with a He gas flow probe from 20–55 K.

method and for carbon concentration by a combustion technique (both by Galbraith Laboratories). This revealed for the total sample an atomic Mg:B:C ratio of 1:1.84:0.55, with errors of less than 10%. Since there are no other major phases aside from "MgB_2" and MgB_2C_2 in the sample, this indicates that the bulk material is about 80% $MgB_{2-x}C_x$ and 20% MgB_2C_2. With the minority phase identified as MgB_2C_2, the majority phase has a B:C ratio of 9:1, i.e., $x=0.2$ in $MgB_{2-x}C_x$. This ratio was confirmed by EELS, which found a B:C ratio of $10\pm1.5:1$ for individual grains of the majority $MgB_{2-x}C_x$ phase. Hence, our doping method yields an "MgB_2" material where approximately 10% of the boron sites have been filled by carbon atoms. This ratio was further confirmed by a *ab initio* calculation of the lattice parameters as a function of carbon doping, which gave approximately 1% contraction of the *a* axis and no change for the *c* axis for a B:C ratio of 9:1.[5]

Figure 2 shows dc magnetization vs temperature curves for pure MgB_2 and $MgB_{2-x}C_x$ samples, both measured with a quantum design (MPMS-5S) magnetometer at 5 G. Strong diamagnetism associated with superconductivity is observed for both specimens (the slightly smaller saturated low-temperature mass susceptibility of the doped sample is consistent with approximately 80% volume fraction, consistent with the presence of a nonsuperconducting minority phase). Most importantly, the pure MgB_2 sample has a T_c of 39 K, while the doped material has a T_c of 32 K. The inset shows an expanded plot of the susceptibility of the doped sample, indicating no evidence for diamagnetic signal near 39 K, i.e., the doped sample has no hint of superconductivity above 32 K, consistent with no pure MgB_2 in the sample. Thus, carbon-doping results in a depressed yet still sharp T_c.

Figure 3 shows a four-probe resistance measurement of the doped material. The onset of superconductivity is around 34 K, with full resistive transition width of 4 K. The resistive midpoint occurs at $T_c=32$ K, consistent with the magnetization measurements.

Experiments were carried out to ensure that the minority MgB_2C_2 phase in the doped samples was not the source of the superconductivity. Magnesium, amorphous boron, and graphite in a 1:1:1 stoichiometric ratio were put in a tantalum foil under argon and heated to 1100 °C for 4 h. (Excess Mg was added due to its high vapor pressure at these temperatures). The resulting material was paramagnetic down to 10 K, while x-ray diffraction showed that it had the same structure and lattice constants as the minority phase of the $MgB_{2-x}C_x$ material, as well as previously published data.[4]

III. RESULTS AND DISCUSSION

We now discuss our experimental results. Carbon doping MgB_2 results in highly anisotropic lattice contractions and a substantial depression of T_c. The in-plane (*a* axis) dimension is sharply reduced, while the interplane (*c* axis) is unaffected. A larger change of the *a* axis is expected upon carbon doping, since the carbon atoms covalently bond with the adjacent boron in the plane parallel to the *a* axis and interact more weakly with the out-of-plane Mg atoms.

Are the structural changes the main contribution to the change in T_c, or does the C-doping change the electrical properties as well?

Lattice contraction, by means of isotropic pressure, has been shown to decrease T_c in MgB_2.[2] Although in those experiments the lattice contracts in all directions (as opposed to the extreme contraction anisotropy due to carbon doping), the results are relevant to the discussion at hand. The bulk modulus of MgB_2 is 151 ± 5 GPa.[6] An isotropic lattice contraction of 0.03 Å would require an effective pressure of 4.4 GPa. According to Monteverde *et al.*,[2] this would cause the MgB_2 transition temperature to drop by only about 3.5 K. This result suggests that the rather large T_c shift we observe for carbon doping is not due to lattice contraction alone.

It is reasonable to assume the additional shift in T_c observed upon 10% carbon doping is due to "electronic" (i.e., charge transfer) effects. For a first-order estimate, we assume that structural and electronic effects are independent and additive (i.e., the changes brought about by shifts in the lattice parameters are independent of changes in electron concentration). Here, we relate the dependence of T_c on charge transfer in C doped MgB_2 with that in Al-doped MgB_2. The electronic changes brought about by adding carbon into the lattice, which has one more electron that boron, are then responsible for a T_c shift of 3 K. By replacing every 10th boron by a carbon atom, the electron concentration n_e in the

lattice is increased by one electron for every five MgB_2 unit cells. If the dependence of the critical temperature on electron concentration is linear, then $dT_c/dn_e = -15$ K/e$^-$/unit cell.

It is insightful to compare this calculation to previously published data. According to Slusky *et al.*,[3] for $Al_{0.1}Mg_{0.9}B_2$ the shift in T_c is 2 K, and the lattice parameters contract by 0.004 Å in the *a* direction and 0.008 Å in the *c* direction. This contraction would require a pressure between 0.6 and 1.0 GPa. According to Monteverde,[2] these pressures would cause a T_c shift of between 0.5 and 0.8 K. Thus, leaving between 1.2 and 1.5 K unaccounted for by structural change. If this is due to an increase in the electron concentration in the lattice, then dT_c/dn_e is between -11.2 and -15.3 K/e$^-$/unit cell, which is in agreement with the calculation for C-doped MgB_2, indicating that the critical temperature depends strongly on the electron concentration and the lattice constant, and seemingly independent of the actual elements used. This shows promise that substituting elements into MgB_2 that would hole dope (accept electrons from the lattice), in addition to elements that would expand the lattice, would increase the critical temperature.

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