

Intralayer carbon substitution in the MgB_2 superconductor

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We report that the ternary $\text{MgB}_{2-x}\text{C}_x$ compounds adopt an isostructural AlB_2 -type hexagonal structure in a relatively small range of nominal carbon concentration, $x < 0.1$. The lattice parameter a decreases almost linearly with increasing carbon content x , while the c parameter remains unchanged, indicating that carbon is exclusively substituted in the boron honeycomb layer without affecting the interlayer interactions. The superconducting transition temperature T_c decreases quasilinearly as a function of the carbon concentration, with a slope steeper than that for the isoelectronic $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$.

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Discovery of superconductivity in MgB_2 at $T_c = 39$ K (Ref. 1) is attracting wide attention because of the simplicity in the chemical composition, the crystal and electronic structure of the system, and its highly promising potential applications. Detailed information on the properties of MgB_2 , particularly related to the nature of superconductivity, is being currently rapidly accumulated by means of structural and electronic probes on the parent compound, MgB_2 . An alternative approach is to synthesize related materials by partial chemical substitution on either the Mg or the B interleaved layers and follow the evolution of the properties.

MgB_2 adopts a hexagonal structure² (AlB_2 type, space group $P6/mmm$) that is analogous to intercalated graphite with all hexagonal prismatic sites of the primitive graphitic structure (found in hexagonal BN) completely filled and resulting in two interleaved B and Mg layers. In addition, allowing for full charge transfer from Mg to the boron two-dimensional (2D) sheets, the latter are themselves isoelectronic with graphite. Also, it is known that various metal borides form an isostructural series of compounds.² Moreover, theoretical calculations predict that substitution of Mg results in significant changes of the density of states at the Fermi level without introducing any disorder, potentially allowing access to increased T_c .³⁻⁵ These structural features have motivated attempts to substitute Mg with alkali,⁶ alkaline earth, group III metals,^{7,8} and other elements. However, a significant difference of MgB_2 from graphite-intercalation compounds is that both the structural and electronic properties are substantially more isotropic. For example, high-pressure synchrotron x-ray diffraction experiments revealed that the isothermal compressibility of MgB_2 is only moderately anisotropic between the boron intralayer and interlayer directions.^{9,10} Also, band structure calculations showed that the electronic states of this superconductor are essentially three dimensional.^{3-5,11} Thus, the substitution of Mg sites is not entirely analogous to the case of intercalation of the strongly bonded strictly 2D graphitic sheets.¹² Instead, appropriate substitution on the more weakly bonded boron sheets offers an alternative route of modulating the structural and electronic properties of this system. In this paper, we report the synthesis of carbon-doped MgB_2 superconductors, $\text{MgB}_{2-x}\text{C}_x$ and their solid solution behavior in the range of

carbon concentrations $0 \leq x \leq 0.1$. The observed structural and superconducting properties of $\text{MgB}_{2-x}\text{C}_x$ ternaries display an amazing coincidence to the isoelectronic $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ series, despite the difference in substitution sites. These results indicate that the electronic structure of MgB_2 and related ternary systems is well described by the band theory and that T_c is controlled by the density of states at the Fermi level.

The $\text{MgB}_{2-x}\text{C}_x$ ($x = 0.02, 0.04, 0.06, 0.1, 0.2,$ and 0.5) samples were synthesized by heating mixed powders of amorphous boron, carbon black, and magnesium at 900°C for 2 h. The powders were placed in stainless steel tubes and sealed inside quartz tubes. Figure 1 shows the (002) and (100) Bragg reflections taken on an x-ray powder diffractometer with $\text{Cu } K_\alpha$ radiation for $x = 0.0, 0.02, 0.04, 0.06,$ and 0.1 . While the position of the (002) peak remains unchanged with increasing x , the (100) peak shifts continuously to higher angles up to $x = 0.06$. Other reflection peaks with different combinations of Miller indices show consistent behavior with these typical reflections. At $x = 0.1$, the diffraction peaks display a considerable broadening, which is attributable to the reduction in crystallinity or to the onset of phase separation. The diffraction profiles of the nominal $x = 0.2$ and 0.5 compositions clearly show a two-phase behavior with a large number of extra peaks that cannot be accounted for within the AlB_2 -type structure.

The lattice parameters were extracted by a Le Bail pattern

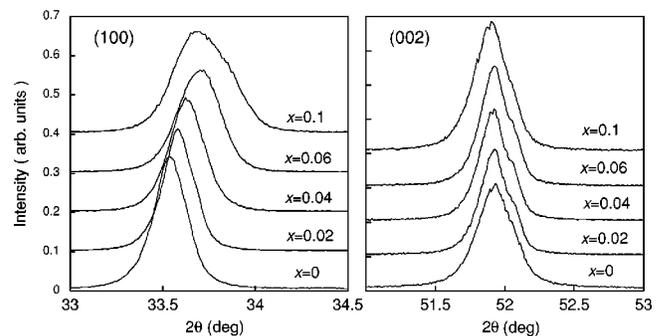


FIG. 1. The (100) and (002) Bragg reflections for the $\text{MgB}_{2-x}\text{C}_x$ compositions ($x = 0.0, 0.02, 0.04, 0.06,$ and 0.1).

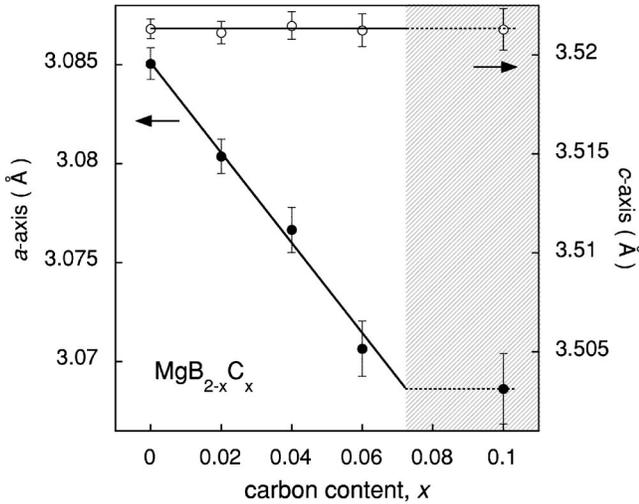


FIG. 2. Lattice parameters a and c as a function of the nominal carbon content x . The shaded area indicates a region showing inhomogeneity of samples.

decomposition technique.¹³ Figure 2 shows the evolution of the hexagonal-lattice constants with carbon concentration. The a and c lattice parameters display strongly contrasting behavior: a contracts essentially in a linear fashion up to $x = 0.06$, while c is invariant with x , unambiguously indicating that carbon is substituted in the boron layers without affecting their interlayer separation. This type of substitution effect has been also encountered in Li-doped MgB_2 ,⁶ but is in sharp contrast with the results of Al substitution,⁷ in which the in-plane B-B separation is essentially invariant. The homogeneous and random nature of the carbon substitution is also evident in the linewidths of the reflections that remain sharp and are independent of x up to $x = 0.06$. On the other hand, an abrupt broadening occurs at $x = 0.1$ implying incipient sample inhomogeneity. Such inhomogeneity could be the signature of the onset of phase separation, as multiphase behavior is encountered for the $x = 0.2$ and 0.5 samples. The structural data provide unambiguous evidence of solid solution behavior, with an extremely small miscibility region of $0 < x < 0.1$.

Magnetic susceptibility of the compositions with $x = 0.0, 0.02, 0.04, 0.06, 0.1, 0.2,$ and 0.5 has been measured with a quantum design superconducting quantum interference device magnetometer. Figure 3 displays the temperature dependence of the susceptibility in zero-field cooled experiments at 10 Oe. All the samples up to $x = 0.1$ show well-defined one-step transitions and shielding fractions of above 100% at 10 K before correction for demagnetization effect, implying that superconductivity is of bulk nature. The transition temperature T_c , defined by the intersection of line extrapolations made both below and above T_c , decreases with increasing x at the rate of $-dT_c/dx = 57$ K. Above $x = 0.1$, the transition becomes too broad to allow accurate definition of T_c and the volume fraction continuously decreases. The increase of T_c , suggested by the resistivity measurements on the multiphase $x = 0.2$ composition¹² is not observed in the present bulk characterization.

Figure 4 displays the variation of T_c with x in the solid

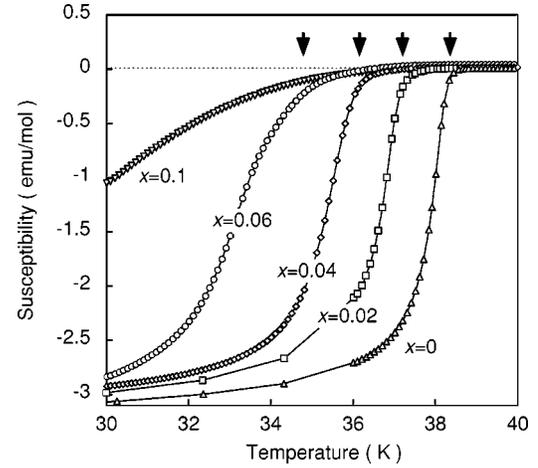


FIG. 3. Zero-field cooled magnetic susceptibility measured at 10 Oe for the $\text{MgB}_{2-x}\text{C}_x$ compounds ($x = 0.0, 0.02, 0.04, 0.06,$ and 0.1). The arrows indicate T_c s for $x = 0.0, 0.02, 0.04,$ and 0.06 .

solution region for $\text{MgB}_{2-x}\text{C}_x$. The results for $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ ⁷ are also included (dotted line) for comparison. The carbon substitution appears to cause more serious effect on superconductivity, but its physical background should be carefully examined. Since C has one more electron than B, electron doping is anticipated in $\text{MgB}_{2-x}\text{C}_x$ in direct analogy with the $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ case. In fact, band structure calculations predict a reduction in the density of states at the Fermi level for both $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ and $\text{MgB}_{2-x}\text{C}_x$,^{14,15} being consistent with the experimental results. Another important effect of Al or C substitution is the resulting lattice contraction, which is also known to decrease T_c from the high-pressure experiments on the parent MgB_2 .¹⁶⁻¹⁸ If the lattice contraction is a dominant reason for the T_c reduction in Al or C substitution, the relation between T_c and the volume V is expected to be uniquely scaled between chemical substitution and pressure experiments. The experimental results are $-d \ln(T_c)/dV = 0.85$ (Al substitution),⁷ $= 0.37$ (C substitution, present result), and $= 0.28$ (high pressure).^{9,10} The considerably larger coeffi-

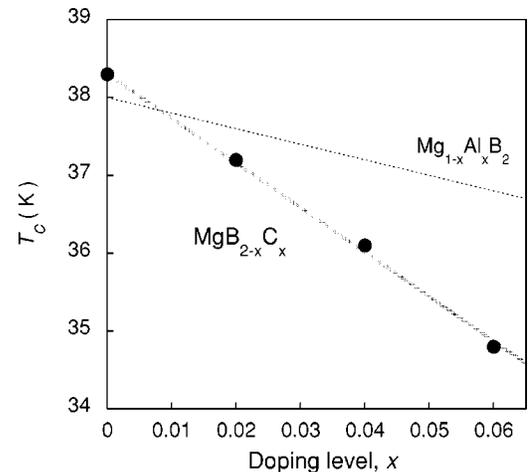


FIG. 4. T_c vs substitution concentration that corresponds to the excess electron count for $\text{MgB}_{2-x}\text{C}_x$ (filled circle) and $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ (dotted line) taken from Ref. 7.

cients in the substitution experiments clearly indicate that the reduction of T_c is not simply caused by the volume contraction, but there exist additional factors to reduce T_c . We postulate that this additional effect is the electron doping.

In contrast to the Al substitution, the $-d \ln(T_c)/dV$ value in the C substitution is fairly small. This is possibly due to the incomplete charge transfer from Mg to C, in contrast to the complete charge transfer from Al to B. In other words, the count of introduced electron in $\text{MgB}_{2-x}\text{C}_x$ is considerably smaller than the x value, while in Al substitution, the x value directly corresponds to the doped electron count. In the case of C, both the electron doping and lattice contraction should be taken into account.

Even so, we note that the rate of decrease in T_c in the case of C substitution is 2–3 times that in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$, as shown in Fig. 4. This may reflect the details of the proposed somewhat anisotropic electronic structure of MgB_2 , in which electronic conduction is mostly dominated by the boron sheets

and could be more sensitive to disorder effects in, rather than between, the layers.

To summarize, a solid solution of $\text{MgB}_{2-x}\text{C}_x$ is obtained in a small range of carbon concentration. The decrease of T_c with increasing x is possibly understood by a lattice contraction and electron-doping effect. The change of electronic structures of MgB_2 and related ternary systems is described by the band theory and that the value of T_c is controlled by the density of states at the Fermi level, consistent with a conventional BCS-type origin of superconductivity. Despite the reduced T_c , the availability of families of well-characterized electron-doped MgB_2 compositions should allow the systematic study of the electronic properties of these intriguing superconductors with the variation of the doping level.

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