2008

Reduction of superconducting transition temperature and flux pinning in Al and C codoped MgB2 with insight from first-principles calculations

Aihua Li
University of Wollongong, aihua@uow.edu.au

Xiaolin Wang
University of Wollongong, xiaolin@uow.edu.au

S X. Dou
University of Wollongong, shi@uow.edu.au

Qiwen Yao
University of Wollongong, qy75@uow.edu.au

Zhenxiang Cheng
University of Wollongong, cheng@uow.edu.au

See next page for additional authors

Reduction of superconducting transition temperature and flux pinning in Al and C codoped MgB2 with insight from first-principles calculations

Abstract

We report for the first time the Al and C codoping effect on the structures and superconductivity in MgB_2. It was found that both the lattice parameters and the T_c decreased monotonically with increasing doping level of both Al and C. The T_c dropped to 27.5 and 7 K for x=0.2 and for x =0.4, respectively. The reduction of T_c for the codoping was found to be quicker than for individual Al doping and slower than for individual C doping at the same doping levels. First-principles calculations indicated that the observed decrease in T_c for the codoped MgB_2 can be understood in terms of a band filling effect due to the electron doping by both Al and C. However, it is suggested that other factors may also play a role in the T_c reduction in the real $Mg_{1-x}Al_xB_{2-x}C_x$ samples. Furthermore, the Al and C codoping also reduces J_c and weakens flux pinning in MgB_2.

Keywords

Reduction, superconducting, transition, temperature, flux, pinning, codoped, MgB2, insight, from, first, principles, calculations

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Li, A, Wang, X, Dou, SX, Yao, Q, Cheng, Z, Soltanian, S, Yoo, JM & Munroe, P (2008), Reduction of superconducting transition temperature and flux pinning in Al and C codoped MgB2 with insight from first-principles calculations, Journal of Applied Physics, 103(7), pp. 07C713-1-07C713-3.

Authors

Aihua Li, Xiaolin Wang, S X. Dou, Qiwen Yao, Zhenxiang Cheng, Saeid Soltanian, J M. Yoo, and P Munroe

Reduction of superconducting transition temperature and flux pinning in Al and C codoped MgB_2 with insight from first-principles calculations

A. H. Li, X. L. Wang,[a] S. X. Dou, Q. W. Yao, Z. X. Cheng, and S. Soltanian
Institute for Superconducting and Electronic Materials, University of Wollongong, New South Wales 2522, Australia

J. M. Yoo
Korea Institute of Materials Science, 531 Changwondaero, Changwon, Gyeongnam 641-831, South Korea

P. Munroe
Electron Microscope Unit, University of New South Wales, Sydney, Australia

(Presented on 8 November 2007; received 8 September 2007; accepted 8 November 2007; published online 7 March 2008)

We report for the first time the Al and C codoping effect on the structures and superconductivity in MgB_2. It was found that both the lattice parameters and the T_c decreased monotonically with increasing doping level of both Al and C. The T_c dropped to 27.5 and 7 K for $x=0.2$ and for $x=0.4$, respectively. The reduction of T_c for the codoping was found to be quicker than for individual Al doping and slower than for individual C doping at the same doping levels. First-principles calculations indicated that the observed decrease in T_c for the codoped MgB_2 can be understood in terms of a band filling effect due to the electron doping by both Al and C. However, it is suggested that other factors may also play a role in the T_c reduction in the real $Mg_{1-x}Al_xB_{2-x}C_x$ samples. Furthermore, the Al and C codoping also reduces J_c and weakens flux pinning in MgB_2. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2837246]

Since the discovery of superconductivity in MgB_2 with an unusually high critical temperature T_c of 39 K, extensive efforts have been made toward the understanding and improvement of its superconductivity via chemical doping and physical processing. For all the studies of chemical doping, the T_c of MgB_2 decreases at different rates for various dopants. It has been accepted that MgB_2 is a BCS-type superconductor with an exceptionally high T_c. The reduction of the density of states (DOS) at the Fermi level increases the band scattering, and changes in the phonon frequencies are the main factors responsible for the reduction of T_c. Al substitution[1] at Mg sites and C substitution[2,3] at B sites are the most potent doping elements in terms of having an effect on T_c. Al substitution takes place in the Mg plane, keeping the B plane intact. However, the C dopes into the B sites instead of the Mg sites and forms a strong covalent bond with B. Despite the difficulties in accurately determining the carbon concentration in relation to T_c, theoretical studies have shown that the decrease in T_c for the Al or C doped MgB_2 samples can be understood mainly in terms of a band filling effect due to the electron doping by Al and C.[4] In addition to the interest in the understanding of the T_c variations for the Al or C doped MgB_2, the flux pinning enhancement due to the doping effect is also of great interest because of the potential practical applications. C doping has been proved to be very effective in enhancing the upper critical field H_{c2} and the flux pinning.[5] However, C causes a significant drop in T_c even at a low doping level. In contrast, Al doping reduces the T_c much more slowly. It should be noted that the Al and C doping effects were studied for either Al or C substituting into either Mg or C sites individually. In this work, we report for the first time on the codoping effect of Al and C on the structures and superconductivity in MgB_2.

The $Mg_{1-x}Al_xB_{2-x}C_x$ ($x=0-0.4$) polycrystalline bulks used in this study were prepared using an *in situ* reaction method. High purity powders of Mg, Al, C, and amorphous boron were mixed well according to the desired atomic ratios. The mixed powders were pelletized and sintered at 900 °C for 30 min in a high purity Ar atmosphere. The phases, lattice parameters, microstructures, and superconductivity were characterized by x-ray diffraction (XRD), Rietveld refinement, transmission electron microscopy (TEM), and magnetic measurements using a commercial physical properties measurement system.

The XRD patterns for all the samples with x from 0 up to 0.2 demonstrate that single phase MgB_2 can be formed

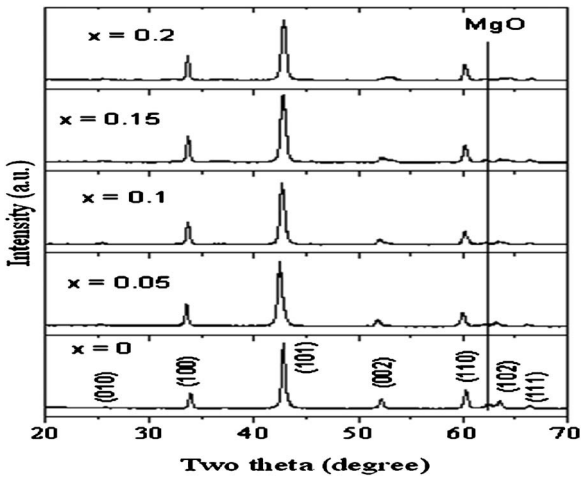

FIG. 1. XRD patterns of $Mg_{1-x}Al_xB_{2-x}C_x$. Indexed peaks are from MgB_2.

[a]Electronic mail: xiaolin@uow.edu.au.

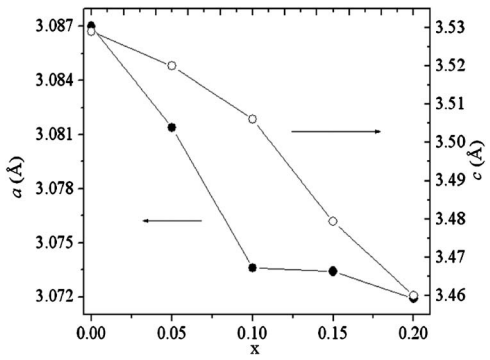

FIG. 2. Lattice parameters vs doping level.

within this range of doping levels, as shown in Fig. 1. A small amount of MgO is present in all the samples, as is very common in MgB_2 samples. The peaks gradually shift to high diffraction angles, indicating a reduction in the lattice parameters caused by the codoping. The lattice parameters a and c calculated by using Rietveld refinement are shown in Fig. 2. It clearly illustrates that both lattice parameters decrease with increasing codoping levels, in agreement with the fact that the Mg (1.60 Å) and C (0.70 Å) atomic sizes are smaller than those of Al (1.43 Å) and B (0.88 Å), respectively.

In order to further prove that both Al and C were incorporated into the MgB_2 lattice, a careful investigation using high resolution TEM was carried out. It was observed that all these samples with $x \leqslant 0.2$ were well consolidated and homogeneous in nature. A high resolution TEM image of a typical sample with $x=0.15$ is shown in Fig. 3. The energy dispersive spectroscopy (EDS) spectra done at several points on several MgB_2 particles indicate that Mg, Al, C, and B, along with a small amount of O, were all detected, as shown in the inset of Fig. 3. Calculated atomic ratios from the EDS are in line with the nominal compositions of the starting materials, indicating that both Al and C were incorporated into the MgB_2 lattice.

The temperature dependence of the magnetic moment for some typical samples is shown in Fig. 4. It can be seen that the T_c drops from 37.5 K to 34.5, 27.5, and 7 K for $x=0$, 0.15, 0.2, and 0.4, respectively.

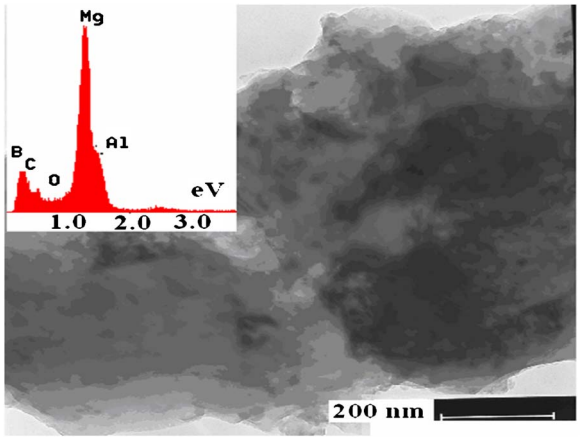

FIG. 3. (Color online) High resolution TEM image of a grain from a sample with $x=0.15$. The inset shows the corresponding EDS spectrum.

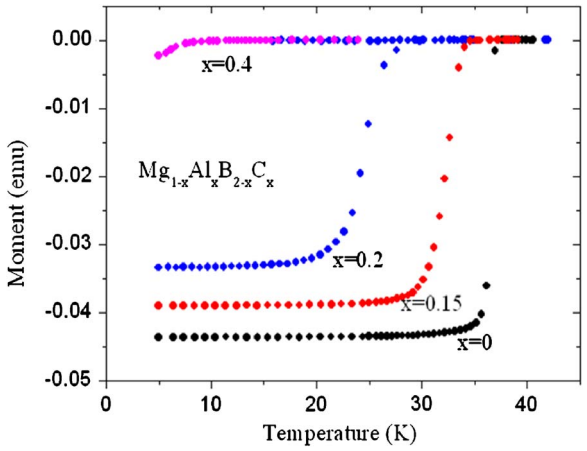

FIG. 4. (Color online) Temperature dependence of the zero field cooled dc moment measured in 20 Oe.

To understand the reduction in T_c caused by the Al and C codoping, first-principles calculations were performed using density functional theory.[6] A cutoff energy of 340 eV and a self-consistent field tolerance of 10^{-6} were used. The quality of the k-point separation for the band structure calculation is 0.015 A^{-1}. The ultrasoft pseudopotential basis set and the general gradient approximation corrected Perdew, Burke, and Enzerhof functional[6] were adopted. The total and partial densities of states of both C and B atoms were computed. The calculations were performed on a $2\times2\times2$ supercell containing 8 Mg and 16 B atoms. C or Al individual doping effects or codoping effects were calculated by replacing B using one, two, or three C atoms or replacing one Mg using one Al, or two B and one Mg atom were replaced by two C and one Al atoms, respectively. The doping levels thus correspond to $x=0.06$, 0.13, 0.18, or 0.13 for one, two, or three C, or one Al, or one Al with two C cosubstitution, respectively. Figure 5 is the supercell structure containing one Al and two C atoms that was used for the calculations. It has been well established that MgB_2 has a total of 0.26 holes, and both C and Al dopings reduce T_c because the band filling effect due to the electron doping by Al and C reduces the total number of holes.[4] If Al and C are codoped into the MgB_2 lattice, it is expected that more electrons could be introduced and the total holes should be reduced. The reduction in the total holes simply corresponds to a shift in the Fermi level or a

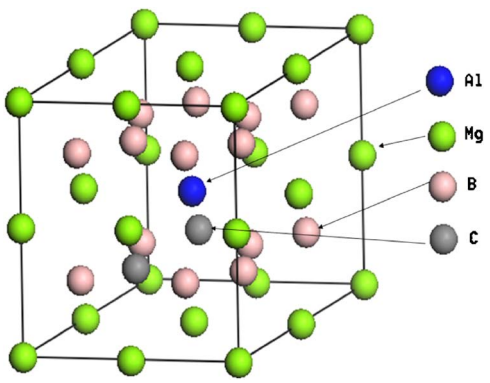

FIG. 5. (Color online) $2\times2\times2$ supercell of MgB_2 doped with one Al and two carbon atoms.

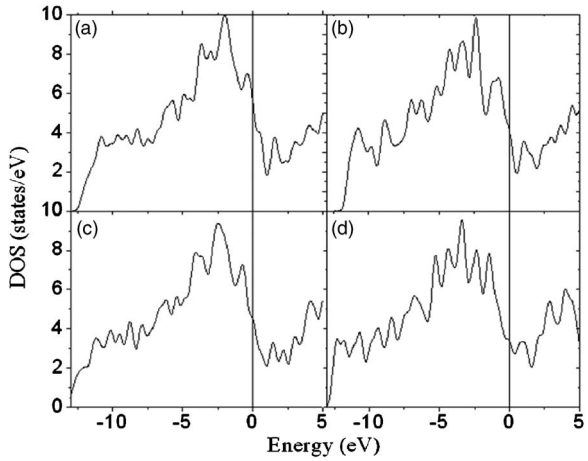

FIG. 6. The calculated total DOS of pure MgB_2 (a), $MgB_{1.8}C_{0.2}$ (b), $Mg_{1.9}Al_{0.1}B_2C$ (c), and $Mg_{1.9}Al_{0.1}B_{1.8}C_{0.2}$ (d).

decrease in the total density of states, $N(E_F)$.

We found that the DOS decreases gradually from 0.6 down to 0.4 states/eV per unit cell when the number of either C or Al atoms increases, in accordance with what has been reported from band structure calculations.[4] The typical calculated total DOS of MgB_2 doped with one Al or two C atoms, and one Al and two C codoped MgB_2 are shown in Fig. 6. It can be seen that the DOS gradually decreases for doping with individual C or Al, and it further drops for the Al and C codoping. Generally, a decrease in $N(E_F)$ leads to a reduction in T_c. Therefore, the T_c of the codoped MgB_2 should drop faster than for individual Al or C at a similar level of doping.

To compare the T_c reduction caused by individual C or Al doping with the Al and C codoping, T_c as a function of doping level x in $Mg_{1-x}Al_xB_2$, $MgB_{2-x}C_x$, and $Mg_{1-x}Al_xB_{2-x}C_x$ is shown in Fig. 7. The data extracted from the literature on both polycrystalline and single crystal samples show a relative narrow range of variations in T_c for both Al and C doped MgB_2. It can be seen that the reduction in T_c due to the C doping is much faster than with the Al doping. The T_c for the C doping drops significantly to 7–10 K for $x=0.1-0.15$,[7,8] while the T_c for the Al doping

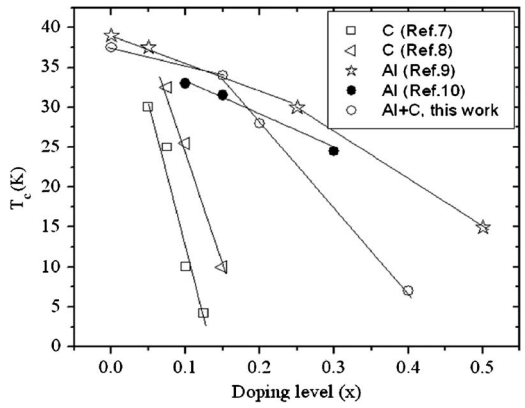

FIG. 7. Variation of T_c of MgB_2 with doping levels for individual Al or C doping and for Al and C codoping.

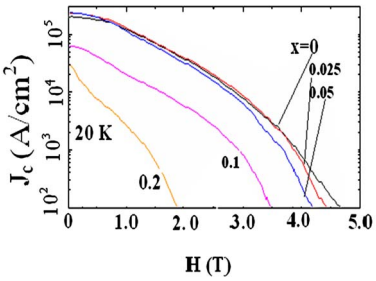

FIG. 8. (Color online) Magnetic J_c vs field for $Mg_{1-x}Al_xB_{2-x}C_x$ at 20 K.

decreases slowly from 39 to 37 down to 25 or 15 K as x changes from 0 to 0.1 and then to 0.3 or 0.5, respectively.[7,8] However, for the Al and C codoping, we can see that the T_c values are in the range between those resulting from individual Al and C dopings.[9,10] This means that the codoping leads to a quicker or slower drop in T_c than individual Al or C doping, respectively. The former fact is understandable, given that both C and Al are electron dopants that reduce the total holes. However, as mentioned earlier, the T_c changes for the codoping should also be more dramatic than for C doping, as more electrons are introduced by both Al and C compared to individual C doping. As the T_c of MgB_2 is also associated with other factors, such as the lattice parameters, the distances between B or Mg atoms, interband scattering, and distortions in the B–B plane, the T_c of the Al and C codoped MgB_2 may be controlled by all these factors in addition to the predicted reduction in $N(E_F)$. Furthermore, it is also possible that the real solubility of C in the codoped MgB_2 may be lower than the nominal composition. A further study is needed to further elucidate the T_c variations due to the Al and C doping effects. The Al and C at low doping should play a positive role in flux pinning enhancement compared to individual Al and C dopings as the T_c remains high for $x<0.2$. However, the experimental results contradict our expectations, as shown below.

The magnetic field dependence of J_c at 20 K is shown in Fig. 8. Note that at 20 K, the J_c at low fields remain almost the same as for the undoped material for $x<0.1$, but it drops much more quickly at high field for all the doped samples. At 30 K, J_c at both low and high fields is reduced significantly as compared to the undoped MgB_2.

This work is supported by funding from the Australian Research Council (ARC) under Linkage and ARC International Linkage projects and is partially supported by the Global Partnership Program through the Ministry of Science and Technology in Korea.

[1] J. S. Slusky *et al.*, Nature (London) **410**, 343 (2001).
[2] M. Paranthaman *et al.*, Physica C **355**, 1 (2001).
[3] R. A. Ribeiro *et al.*, Physica C **383**, 166 (2002).
[4] J. Kortus *et al.*, Phys. Rev. Lett. **94**, 027002 (2005).
[5] X. L. Wang *et al.*, Physica C **408**, 63 (2004).
[6] M. D. Segallm *et al.*, J. Phys.: Condens. Matter **14**, 2717 (2002); J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
[7] T. Masui, S. Lee, and S. Tajima, Phys. Rev. B **70**, 024504 (2004).
[8] S. M. Kazakov *et al.*, Phys. Rev. B **71**, 024533 (2005).
[9] B. Renker *et al.*, Phys. Rev. Lett. **88**, 067001 (2002).
[10] M. Monni *et al.*, Phys. Rev. B **73**, 214508 (2006).