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Carbon-substitution dependent multiple superconducting gap of MgB_2: A sub-meV resolution photoemission study

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"Sub-meV" resolution photoemission spectroscopy was used to study carbon-substitution dependence of the multiple superconducting gap of $Mg(B_{1-x}C_x)_2$. Two features corresponding to σ and π gaps are clearly observed in the raw spectra up to carbon concentration $x=0.075$. The observed x dependence of the two gaps shows a qualitatively different behavior: the σ gap is proportional to T_c while the π gap shows negligible change. Doping as well as temperature dependence can be explained within the two-band mean-field theory. Implications from the present study are discussed.

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Superconductivity is a fundamental quantum phenomenon, which was first explained by the Bardeen-Cooper-Schrieffer (BCS) theory[1] for the low transition temperatures (T_c) superconductor. Subsequent discoveries of new superconducting materials with higher T_c have made the field continuously attractive. New theories and new materials have motivated the search for higher T_c. The discovery[2] of superconductivity in magnesium diboride (MgB_2) has thus induced many studies to clarify the superconducting (SC) transition mechanism because it has the highest T_c among intermetallic superconductors. In fact, the T_c of MgB_2 ($T_c=39$ *K*) is even higher than some of the cuprate superconductors, and is also close to the upper limit predicted by the BCS theory.[1] It is now generally accepted that MgB_2 has a multiple SC gap,[3] originating in the two types of Fermi surface sheets with very different character, which simultaneously plays an important role for the high T_c. Theoretically, a possibility of the multiple SC gap was proposed more than 40 years ago in terms of "two-band superconductivity." However, further experimental verification is essential for a complete understanding of this unique superconductor. Here, we show carbon-substitution dependence of the two gaps of MgB_2 with "sub-meV" resolution photoemission spectroscopy (PES). The result clearly shows two gaps and different substitution dependence for the two gaps. These results confirm theoretical predictions of the two-band superconductivity in MgB_2, and also suggest a new road to explore higher-T_c materials.

The crystal structure of MgB_2 consists of alternate hexagonal layers of boron and magnesium, respectively.[2] First-principles calculations[4,5] have indicated that MgB_2 is a band metal, where four bands cross the Fermi level (E_F). Two of them originate in the boron $2p$ σ orbital with a two-dimensional character, namely, the σ band, and the other two originate in the boron $2p$ π orbital with a three-dimensional character, namely, the π band. The calculated band structure is consistent with experimental band structure obtained from angle-resolved PES studies.[6–8] The transition mechanism is explained by electron-phonon coupling,[9,10] where the coupling strength depends on the symmetry of the Fermi surface. This two band model, within an Eliashberg theory, has succeeded in explaining the multiplicity of the SC gap qualitatively and the T_c quantitatively.[9–12] Conventional BCS theory[1] predicts that a reduction of the density of states (DOS) at E_F reduces T_c and the SC gap value. According to band calculations, doping of electrons in MgB_2 is supposed to decrease T_c because of a decrease of the total DOS at E_F: the hole character σ band at E_F would get occupied, and consequently the σ-band DOS would be reduced by the doped electrons. In contrast, the DOS at E_F originating in the π band is not expected to change significantly.[5]

Chemically doped MgB_2 has been studied extensively as listed in Refs. 13–16 for the examples on the carbon substitution case. All the carbon substitution suppresses the T_c. For application, lower T_c is not suitable. Nevertheless many studies have been done on the chemical substitution. One of the reasons is giving a perturbation on the electronic structure of MgB_2 that gives us further understanding of the SC mechanism. As mentioned above, the electronic state around E_F is composed of two kinds of the electronic state with different symmetry. Those states should be mixed with chemical substitution, which reduces the difference of the two states. This effect is reflected in the SC gap sizes through the interband coupling in the two-band model. Thus systematic study of the SC gap of chemically substituted MgB_2, using ultrahigh-resolution photoemission spectroscopy, can reliably and directly reveal the changes in the multiple SC gaps.[17] Moreover, the recent development of laser photoemission spectrometer with a "sub-meV" resolution[18] provides us an opportunity to do a more quantitative and reliable study for

the multiple gap, including the role of the interband coupling. While tunneling spectroscopy allows observation of the SC gap, it is known to depend on the surface and/or contact conditions very strongly. The ultraviolet laser excited PES is much more bulk sensitive than tunneling spectroscopy and conventional PES with a He lamp because of the higher escape depth of the photoelectron.[19]

Photoemission measurements were performed on a spectrometer built using a Scienta R4000 electron analyzer and an ultraviolet laser (6.994 eV). The energy resolution was set to ~0.4 meV. Samples were cooled using a flowing liquid He refrigerator with improved thermal shielding. The pressure of the spectrometer was better than 1×10^{-10} Torr during all the measurements. All the photoemission measurements have been done for *in situ* fractured surfaces. Temperature-dependent spectral changes were confirmed by cycling temperature across T_c. E_F of samples for high-resolution measurements was referenced to that of a gold film evaporated onto the sample substrate and its accuracy is estimated to be better than ±0.2 meV.

Here, we selected carbon substitution for B in MgB_2 to control T_c, and thus modulate the superconductivity. Carbon is the only atom which can replace boron, giving us a unique opportunity to study changes in boron electronic states which plays a crucial role for the superconductivity. Moreover, systematic carbon concentration (x) dependent studies on T_c, the axis length, etc., using single crystals are already available.[16] The carbon substituted $Mg(B_{1-x}C_x)_2$ polycrystalline samples were synthesized at high-temperature and high-pressure conditions using the same technique described in Ref. 16. The polycrystalline sample was cut to typically $2\times2\times2$ mm^3, which is much larger than the probing size of ~0.2 mm diameter. The x and T_c's used in this study are listed in Table I, where x values are nominal C concentration and T_c's were determined by SQUID measurements. No significant difference between nominal and actual C content was observed from Auger analysis within the accuracy of the analysis.[16,20,21] The estimated T_c obtained from PES supposing BCS temperature dependence of the SC gap[1] is consis-

TABLE I. Relation between the carbon concentration and the T_c.

Carbon concentration (x)	T_c (K)
0.0	38
0.02	35.5
0.05	30
0.075	24

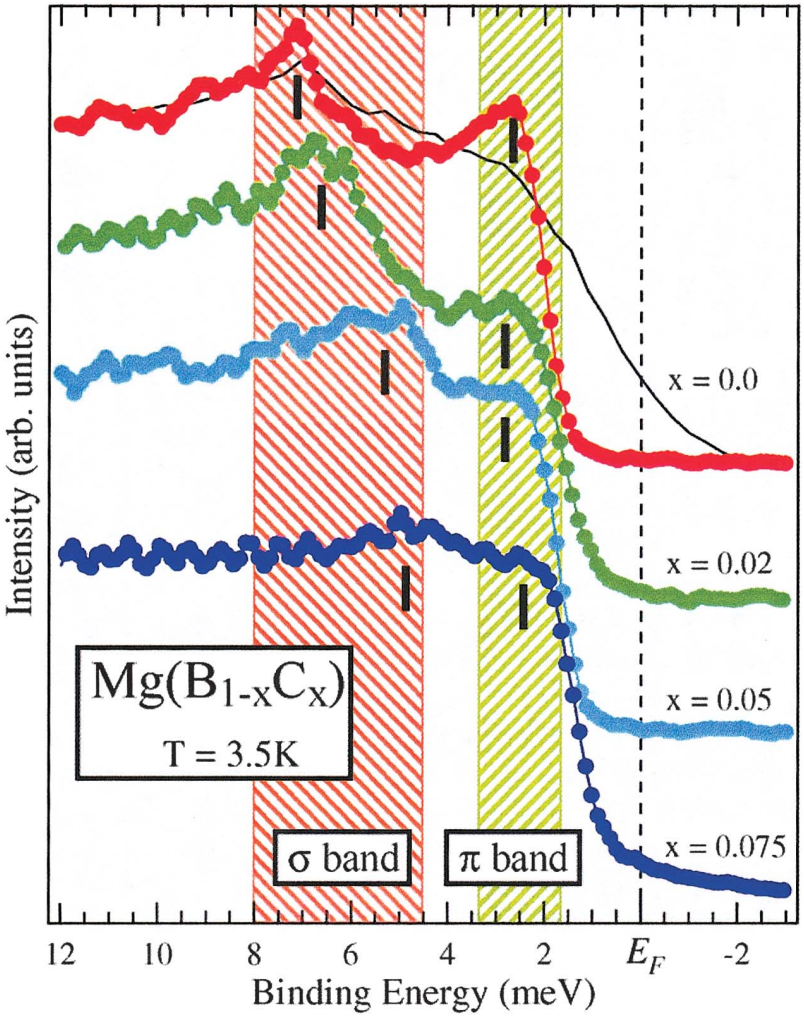

FIG. 1. (Color) "Sub-meV" resolution photoemission spectra of carbon substituted MgB_2 polycrystalline samples for the carbon concentrations x=0.0, 0.02, 0.05, and 0.075. The black thin line indicates the photoemission spectrum of a pure MgB_2 polycrystalline sample obtained using a conventional He discharge lamp with an energy resolution of ~3.0 meV. Each vertical short bar is a guide to the eyes, corresponding to the position of the superconducting gap, and hatched areas emphasize two gaps. The larger gap corresponds to the gap of the σ band and the smaller gap corresponds to the gap of the π band.

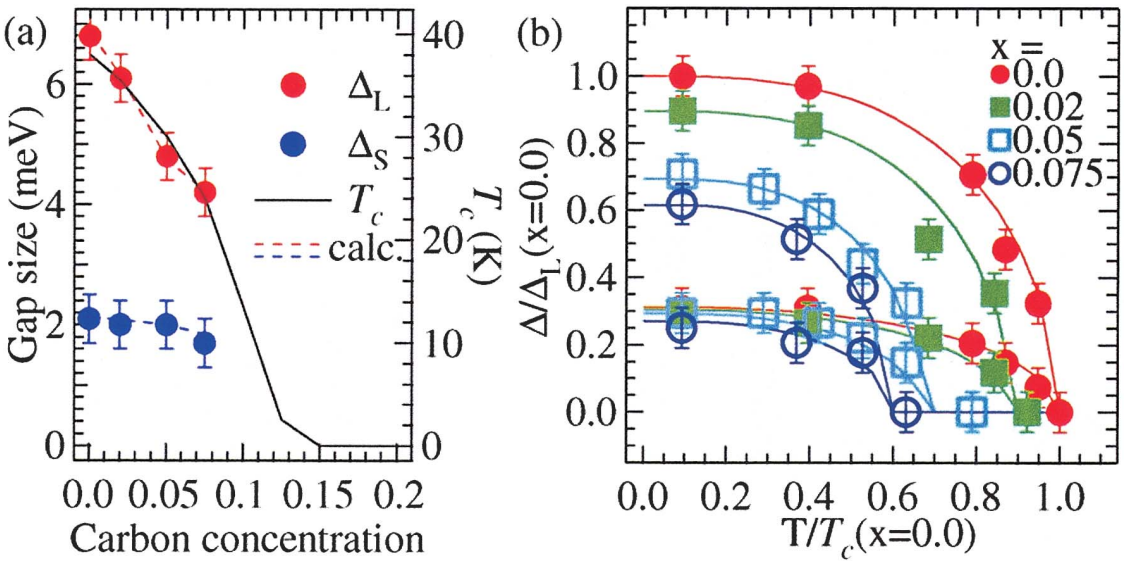

FIG. 2. (Color) (a) Carbon concentration dependence of the superconducting gap for the larger and smaller gaps. The carbon concentration dependence of the transition temperature[16] is indicated by a solid line (right axis). The experimental results are compared with model calculation results indicated by broken lines.[11] The experimental results are well reproduced by the calculations. The larger gap and the T_c show very similar carbon concentration dependence up to $x=0.075$. (b) Temperature dependence of the superconducting gaps for each carbon concentration (marks) determined using the Dynes function analysis. The vertical axis is normalized by the larger gap size of $x=0.0$ and the horizontal axis is normalized by the T_c of $x=0.0$. The calculated result indicated by solid curves reproduces the experimental result well.

tent with the T_c obtained from SQUID, indicating that inhomogeneous substitution of C in our polycrystalline samples does not give major contribution to the present PES study.

Figure 1 shows "sub-meV" resolution photoemission spectra as a function of x obtained at 3.5 K (superconducting state). In the spectrum for $x=0.0$, we clearly observe two well-separated peaks at 2.6 and 7.1 meV binding energy, which are attributed to SC gaps on the π and σ bands. Compared with the spectrum obtained using a conventional He discharge lamp (indicated by a black thin line), the quality of the spectrum is drastically improved and the multiplicity of the SC gap is certain because of the marked increase of the energy resolution and the possible increase in the bulk sensitivity. Moreover, no photoemission intensity was observed around E_F, directly indicating that MgB_2 is a full gap superconductor. As x is increased, the higher binding energy peak shifts clearly while the lower binding energy structure stays nearly the same position. For the measured x concentrations, the two structures do not merge, indicating that $Mg(B_{1-x}C_x)_2$ has two gaps up to $x=0.075$, consistent with the magnetic torque and tunneling experiments.[15,22] These observations, which clearly identify the carbon-substituted change in the SC gap from the raw data alone, are very important, demonstrating the advantage of "sub-meV" resolution PES.

To quantitatively estimate the SC gap size, we tried to fit the spectra using the Dynes function.[23,24] Figure 2(a) shows the x dependence of the gap size at $T=0$ K. The gap sizes at $T=0$ K were determined by an extrapolation from the fitting result using the known BCS temperature dependence of the SC gap.[1] The larger gap, corresponding to the σ band, decreases with increasing x, while the smaller gap, corresponding to the π band, is independent of x within the fitting error up to $x=0.075$. Bussmann-Holder and Bianconi calculated the x dependence of the two gaps for Al substituted case and predicted that the smaller gap increases up to $x=0.2$.[25] The theoretical result is different from the present experiment as well as specific-heat measurements for the Al substituted case.[26] The specific heat measurements for the Al substituted case shows good correspondence of the substitution dependence on the two gaps with the present case. The x dependence of T_c shown in Fig. 2(a) as a solid line seems very similar to that of the larger gap and in contrast to that of the smaller gap. The similar x dependence of the larger gap and

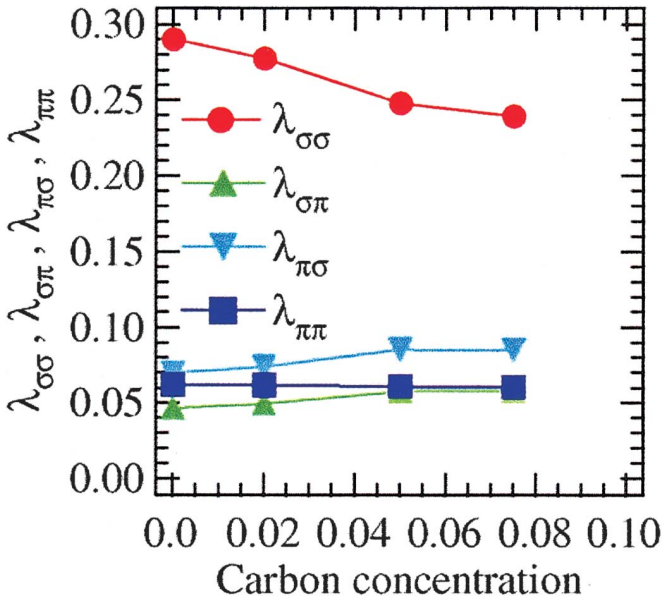

FIG. 3. (Color) Carbon concentration dependence of the coupling parameters. It is clear that the intraband coupling of the σ band decreases while the interband coupling increases with increasing carbon concentration.

T_c means the reduced gap $2\Delta/k_BT_c$, which is a measure of coupling strength of Cooper pairing, is independent of x. In the weak coupling limit, this value is 3.52, which is known as the mean field BCS value.[1] In the present case for the larger gap, this value is 4.1, which is surely larger than the BCS value, and is almost independent to x. This result suggests that electron-phonon coupling of the σ band is strong and also T_c, or, in other words, superconductivity is governed by the σ band.

To get further insight into the nature of inter- and intraband couplings, it is useful to compare the experimental result with a simple model. Here we use the multiband BCS theory for the case of multigap superconductivity, as discussed by Suhl *et al.*[11] For the present case, this model is formulated by the following expression:

$$\Delta_\sigma\left[1-\lambda_{\sigma\sigma}\int \tanh\left[\frac{\sqrt{\varepsilon^2+\Delta_\sigma^2}}{2k_BT}\right]\Big/\sqrt{\varepsilon^2+\Delta_\sigma^2}d\varepsilon\right] = \Delta_\pi\lambda_{\pi\sigma}\int \tanh\left[\frac{\sqrt{\varepsilon^2+\Delta_\pi^2}}{2k_BT}\right]\Big/\sqrt{\varepsilon^2+\Delta_\pi^2}d\varepsilon,$$

$$\Delta_\pi\left[1-\lambda_{\pi\pi}\int \tanh\left[\frac{\sqrt{\varepsilon^2+\Delta_\pi^2}}{2k_BT}\right]\Big/\sqrt{\varepsilon^2+\Delta_\pi^2}d\varepsilon\right] = \Delta_\sigma\lambda_{\sigma\pi}\int \tanh\left[\frac{\sqrt{\varepsilon^2+\Delta_\sigma^2}}{2k_BT}\right]\Big/\sqrt{\varepsilon^2+\Delta_\sigma^2}d\varepsilon,$$

where k_B is Boltzmann's constant and T is temperature. The gap sizes, Δ_σ and Δ_π, for given T are determined by solving this simultaneous equation self-consistently. $\lambda_{\sigma\sigma}$ and $\lambda_{\pi\pi}$ are intraband couplings for the larger and smaller gaps. $\lambda_{\pi\sigma}$ and $\lambda_{\sigma\pi}$ are interband couplings between the larger gap and the smaller gap. These are obtained by a fourmula $\lambda_{ij}=V_{ij}N_i$ $(i,j=\sigma,\pi)$, where V_{ij} is the electron-phonon coupling matrix element and N_i is calculated partial DOS at E_F.[4,5] For simplicity, we assume a rigid band shift of E_F with carbon substitution, which corresponds to electron doping. Then, the model has three independent parameters: $\lambda_{\sigma\sigma}$, $\lambda_{\pi\pi}$, and one of $\lambda_{\pi\sigma}$ or $\lambda_{\sigma\pi}$, which can be determined to reproduce the T dependence of the two gaps for each x. In Figs. 2(a) and 2(b), we plot the x-dependent and T-dependent σ and π gap values (marks), respectively, together with results using the multiband BCS theory mentioned above. We found that this simple model can reproduce the gap sizes for both the gaps at $T=0$ and their temperature dependence very well.[27] For the calculation, there are four coupling constants (three independent parameters), which are plotted in Fig. 3. From Fig. 3, it is clear that the intraband coupling of the σ band decreases while the interband coupling increases with increasing x. The 20% suppression of the $\lambda_{\sigma\sigma}$ cannot be explained by the DOS at E_F of the σ band alone, since the decrease of the calculated DOS at E_F of the σ band due to electron doping[4,5] is estimated to be, at most, 10% for $x=0.075$ within the rigid band model. This suggests that a suppression of the electron-phonon coupling, as discussed from Raman studies,[20] and/or an increase of interband coupling are also responsible for the reduction of T_c. Theoretical studies have reported negligible interband coupling effects for the carbon substitution.[28] Very recently, point contact spectroscopy reported carbon substitution dependence of the two SC gaps of MgB_2.[15] The result is similar to present result, though the interpretation of the result is different for the smaller gap.

Thus present results confirm the two-band superconductivity of MgB_2. Lastly, we would like to comment on an implication for T_c from the two-band model. The multiband model gives T_c by

$$T_c=\Theta_D\exp(-1/\lambda),$$

where Θ_D is the Debye temperature and λ is the total coupling constant given by

$$\lambda=\frac{\lambda_{\sigma\sigma}+\lambda_{\pi\pi}}{2}+\sqrt{\left(\frac{\lambda_{\sigma\sigma}-\lambda_{\pi\pi}}{2}\right)^2+\lambda_{\sigma\pi}\lambda_{\pi\sigma}}.$$

If the interband coupling constants are zero, T_c is completely governed by $\lambda_{\sigma\sigma}$. However, if the interband coupling is not zero, T_c will always become larger than the case of $\lambda_{\sigma\pi}\lambda_{\pi\sigma}=0$. Thus the role of the interband coupling is to make T_c higher than the case without interband coupling. In the present case, using obtained parameters, T_c is estimated to be pushed up about 5 K by the interband coupling. Normally, it is believed that a larger electron-phonon coupling, which is necessary for an increase of T_c can also lead to a CDW transition making the system insulating. In MgB_2, the existence of the π band may play a role in preventing such an instability occurring in the σ band with strong electron-phonon coupling. This possibly allows the σ band to become a strong coupling superconductor with higher T_c. Thus searching a new two-gap superconductor, with strong electron-phonon coupling, is meaningful and hopeful to obtain a much higher T_c.

In conclusion, the present study provides a direct observation of the multiple gap and its carbon substitution dependence using the "sub-meV" PES. In addition, it provides a qualitative estimate of the substituted dependence of interband and intraband coupling between the σ and the π band using a simple two-band model, giving strong verification for the two-band superconductivity in MgB_2.

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