Definitive Experimental Evidence for Two-Band Superconductivity in MgB$_2$

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The superconducting-gap of MgB$_2$ has been studied by high-resolution angle-resolved photoemission spectroscopy. The results show that superconducting gaps with values of 5.5 and 2.2 meV open on the $\sigma$ band and the $\pi$ band, respectively, but both the gaps close at the bulk transition temperature, providing a definitive experimental evidence for the two-band superconductivity with strong interband pairing interaction in MgB$_2$. The experiments validate the role of $k$-dependent electron-phonon coupling as the origin of multiple-gap superconductivity as well as the high transition temperature of MgB$_2$.

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Bardeen-Cooper-Schrieffer (BCS) theory in the simplest form assumes that phonons mediate electron pairing with a momentum ($k$)-independent electron-phonon coupling constant, giving rise to a simple isotropic superconducting (SC) energy gap [1]. For MgB$_2$, with an unexpectedly high transition temperature ($T_c$) [2] among the phonon-mediated superconductors [3], however, evidence for a multiple gap, exhibiting marked deviation from expectations for a simple isotropic gap, has been obtained from $k$-integrated probes [4]. Therefore, the origin of the multiple gap and its relation to the mechanism yielding such a high $T_c$ are strongly debated [5–9]. The most plausible candidate so far widely accepted is the two-band superconductivity model, which predicts a large difference in SC-gap size on different bands [or Fermi surface (FS) sheets] [10]. In the case of MgB$_2$, SC gaps with significantly different magnitudes are expected to open on the $\sigma$- and $\pi$-orbital derived bands (namely, $\sigma$ and $\pi$ bands), respectively, originating in strong $k$ dependence of the electron-phonon coupling [5,11]. The model explains the $T_c$ fairly well, too [12]. However, possibilities of other scenarios explaining similar multiple-gap structures [8,9] cannot be totally ruled out unless genuine $k$-resolved experimental evidence is reported.

The size of the SC gap on the $\sigma$ and $\pi$ bands (or FS’s) can be studied by using angle-resolved photoemission spectroscopy (ARPES) that measures the $k$- and temperature-dependent electronic states of a solid. These capabilities of ARPES are unique and have been used for studying the $k$-dependent SC gap in high-temperature superconductors [13,14] and the FS sheet-dependent SC gap in transition metal dichalcogenide 2H-NbSe$_2$ [15]. However, in MgB$_2$, the limitation of obtained sizes for single crystal samples (typically a few hundred micrometers) has prevented measurements of SC gaps due to the very small count rate when used with higher resolution, though a medium-resolution ARPES study has reported the valence band dispersions of MgB$_2$ [16]. In this Letter, we show high-resolution ARPES studies of the SC gap of MgB$_2$. The results clearly identify a larger gap on the $\sigma$ band and a smaller gap on the $\pi$ band, both of which close at the same temperature ($T_c$), giving definitive experimental evidence for the two-band superconductivity of MgB$_2$.

The single crystals of MgB$_2$ used in this study were prepared by a high pressure synthesis technique as described earlier [17]. Magnetization measurements confirmed that the samples have a midpoint of the SC transition at 36 K. ARPES measurements were performed on a spectrometer built using a Scienta SES2002 electron analyzer and a GAMMADATA high-flux discharging lamp with a toroidal grating monochromator using HeI$\alpha$ (40.814 eV) resonance lines. The energy and angular resolution for the wide-energy range valence band spectra were set to $\sim$100 meV and $\pm$0.1$^\circ$ (corresponding to 0.010 Å$^{-1}$), respectively. The high-resolution measurements for the SC gap on the $\sigma$ band and the $\pi$ band were set to energy resolution of 5.0 and 3.9 meV, respectively, depending on the count rate. Samples are cooled using a flowing liquid He refrigerator with improved thermal shielding. A sample temperature was measured using a silicon-diode sensor mounted below the samples. The base pressure of the measurement chamber was better than 3 x 10$^{-11}$ Torr. The sample orientation was checked by symmetry of ARPES spectra and further confirmed by electron diffraction studies after the ARPES measurements. All the ARPES measurements have been done for in situ cleaved surfaces. Temperature-dependent spectral changes were confirmed by cycling temperature across $T_c$. The Fermi level ($E_F$) 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 $\pm$0.2 meV.

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The crystal structure of MgB$_2$ consists of honeycomb boron layers separated by magnesium layers [2]. Band structure calculations have indicated that magnesium is substantially ionized, and the bands at $E_F$ are derived mainly from boron orbitals with very different characters [18]. As a result, MgB$_2$ possesses a total of four FS sheets that can be classified into two types; two 2-dimensional (2D) cylindrical FS sheets around the $k_z$-plane. Besides, two 3-dimensional (3D) tubular FS sheets derived from $\pi$-bonding and $\pi$-antibonding states of the boron $p_z$ orbitals. The intersections of the FS's with the $k_z = 0$ plane are shown in Fig. 1(a), where two small (solid lines) and one large (broken line) circular sheets correspond to the 2D FS sheets and one of the 3D sheet [19]. Figure 1(b) shows an intensity plot of ARPES spectra of MgB$_2$ measured along the $\Sigma(R)$ high symmetry line [line 1 in Fig. 1(a)], compared with the calculated band dispersions [19] on the $k_z = 0$ plane (solid lines for the $\sigma$ band and broken lines for the $\pi$ band). One can clearly see a prominent feature that disperses toward $E_F$ in the first Brillouin zone (BZ). Having a fairly good agreement with the calculated boron $2p\ \pi$-orbital derived band in terms of the dispersion and the peak position where it crosses $E_F$ ($k_F$), this band can be ascribed to the $\pi$ band in the $k_z = 0$ plane. Observation of the $\pi$ band in the $k_z = 0$ plane suggests that the measured $k_z$ position with the photon energy we used is located near the $k_z = 0$ plane. Besides the prominent structure, we also find another dispersive feature that crosses $E_F$ near the $\Gamma(A)$ point in the second BZ. It is found that this band follows the dispersion of one of the calculated bands derived from the boron $2p\ \sigma$ orbital and can be assigned to the $\sigma$ band. Inability to observe the $\pi$ band in the second BZ and the other $\sigma$ band in the second BZ can be attributed to matrix element effects, which strongly affects the intensity of photoelectrons as has been demonstrated for single crystal graphite [20]. Figures 1(c) and 1(d) are the ARPES intensity plots measured along lines 2 and 3 in Fig. 1(a), respectively. In both measured directions, we see a band crossing and can obtain $k_F$'s. As shown in Fig. 1(a), the $k_F$'s determined from the present ARPES (red open circles) correspond to the calculated $\sigma$- and $\pi$-orbital derived FS sheets and can be clearly attributed to that of the $\sigma$ and $\pi$ bands, respectively. The previous medium-resolution ARPES measurements [16] in the first BZ observed the $\sigma$ and $\pi$ bands with an additional surface derived band superimposed on the $\sigma$ band in the near $E_F$ region. In the present study, we found no evidence for the surface derived band in the second BZ facilitating the SC-gap measurements on the $\sigma$ band.

The identification of $\sigma$- and $\pi$-band derived FS sheets provides us the opportunity to measure the SC gap independently on each band (or each FS sheet). Figures 2(a) and 2(b) show temperature-dependent high-resolution ARPES spectra near $E_F$ obtained along lines 2 and 3 in Fig. 1(a), respectively. Here we employ higher resolution (5.0 meV for the $\sigma$ band and 3.9 meV for the $\pi$ band) and smaller step size (0.9 meV) to detect spectral changes as a function of temperature. To make up for the very low count rate when using higher resolution and due to the small sample size, the spectra shown are the sum of the APRES spectra obtained along lines 2 and 3 containing $k_F$, and, thus, correspond to angle-integrated spectra but for each individual band. This justifies the use of the modified BCS function analysis for angle-integrated spectra, as described below. The temperature-dependent spectra measured for the $\sigma$ band show redistribution of spectral weight from the region near $E_F$ to higher binding energy as the temperature is lowered, indicating the opening of a SC gap below $T_c$. At 6 K, the spectrum has a peak around 10 meV and a leading-edge shift of 3.6 meV. The leading-edge shift of a SC spectrum has been used to qualitatively estimate the...
size of a SC gap [21]. The spectra measured at the π band also show similar temperature dependence. The spectrum measured at 6 K has a more pronounced condensation peak but shows a leading-edge shift of only 0.9 meV. The larger shift on the σ band than on the π band in spite of the lower resolution used for the σ band strongly indicates that sizes of the SC gap are highly dependent on the character of the bands. The small shoulder structure near $E_F$ of 30 K spectra of the π band [inset of Fig. 2(b)] is indicative of persistence of the SC gap close to the bulk $T_c$ of 36 K, indicating that the smaller gap on the π band originates in the bulk electronic structure, too. Therefore, we can conclude that these raw data themselves provide first definitive experimental evidence for the two-band superconductivity of MgB$_2$.

For a more quantitative discussion, we estimated the size of the gap using a modified BCS function that includes the magnitude of a SC gap $\Delta$ and the quasiparticle lifetime broadening $\Gamma$ [22]. For the calculations, we first simulated the normal-state spectrum by assuming a linear spectral function multiplied by the Fermi-Dirac (FD) function of 40 K and convolved with a Gaussian of full width at half maximum for the known energy resolution. The obtained spectrum is then multiplied with a modified BCS function ($\Gamma = 0.8 \pm 0.4$ meV) and with the FD function of corresponding temperatures, and further convoluted with a Gaussian to reproduce the SC-state spectra. The results are superimposed as lines on the energy-enlarged spectra shown in the insets of Figs. 2(a) and 2(b). It can be seen that the function reproduces well the raw spectra, even for the small shoulder structure above $E_F$ of the π band that can be explained by thermally excited electrons over the gap [23]. The size of the SC gap for the σ and π bands are plotted as a function of temperature with open circles and diamonds [Fig. 2(c)], respectively, together with theoretical predictions [11] for two gaps (lines). As was implied by the raw data, the smaller gap of the π band persists up to the bulk $T_c$, further confirming the bulk origin. Furthermore, the temperature dependence of the SC gaps on different bands can also provide an insight into the nature of the interband pairing interaction of the Cooper pairs. The theoretical studies have shown that the two gaps close (or nearly close) at different temperatures in the condition of absence of an interband pairing interaction (or presence of a very weak interband pairing interaction), while they close at the same temperature in the condition of a strong interband pairing interaction [10]. Therefore the experimental observation showing both the gap closing at the same temperature indicating the existence of strong interband pairing interaction in MgB$_2$. This is the first experimental observation by ARPES of strong interband interaction effects predicted theoretically [10]. Compared to the very recent theoretical predictions in detail [11], while the gap of the π band shows a similar temperature dependence to the theoretical prediction, the gap of the σ band deviates for higher measured temperatures. The lowest temperature gap values are 5.5 meV for the σ band and 2.2 meV for the π band. Correspondingly, the reduced gap parameter $2\Delta/k_BT_c$, where $k_B$ is the Boltzmann’s constant, is 3.54 for the σ band and 1.42 for the π band, indicating weak coupling of σ electrons most likely with the in-plane $E_{2g}$ phonon mode [24] and anomalously weak coupling of π electrons with the same mode.

The present σ- and π-band SC-gap values agree well with the previous angle-integrated (AI) PES results [25] with a slightly smaller value for the gap on the π band in ARPES compared to that of the smaller gap in AIPES, including the temperature dependence of the gap values. The consistent values obtained with ARPES and AIPES for the gap on the σ band suggests that the anisotropy of the SC gap on the σ band is very small. As for the gap on the π band, we measured and found that the SC-gap values on the π band along the $\Gamma$-$M$ and $\Gamma$-$K$ directions are consistent within our experimental and fitting accuracy (2.2 ± 0.4 meV). This indicates that the gap on the two bands does not have nodes and may at best be an anisotropic s-wave gap, with a maximum
anisotropy of $\pm 20\%$ on the $\pi$ band. Comparing with recent tunneling studies [26], while the gap value of the $\sigma$ band is slightly smaller than the largest tunneling gap values ($2\Delta/k_B T_c = 4.12$–$4.24$), the gap value of the $\pi$ band is very consistent with the smaller tunneling gap values ($2\Delta/k_B T_c = 1.28$–$2.26$).

The present ARPES studies identify the larger gap on the $\sigma$ band and the smaller gap on the $\pi$ band and thus provide firm and direct experimental evidence for the two-band superconductivity in MgB$_2$. This is inconsistent with the novel two-band scenario [7] which reports that the nesting of $\pi$-FS sheets induces a large SC instability originating in Coulomb interaction and leads to a larger gap on $\pi$-FS than on $\sigma$-FS. The present results also emphasize the importance of a FS sheet-dependent gap, not an anisotropic gap [9]. The experimental confirmation of the two-band superconductivity predicted by the first-principles band calculations dealing with $k$-dependent electron-phonon coupling [11,12], in turn, confirms the importance of the $k$-dependent electron-phonon coupling to the SC properties of MgB$_2$, including the high transition temperature. The present results also imply that experimental efforts in combination with first-principles calculations [27] will succeed in discovering new MgB$_2$ related materials with higher $T_c$ based on the two-band superconductivity.

The only other known case of ARPES identifying a FS dependence of a SC gap was reported for $2H$-NbSe$_2$ with a $T_c$ of 7.2 K [15]. An unambiguous difference in the observed gap size between the Nb $4d$ and Se $4p$ derived FS sheets was observed. But, the gap closing temperature achieved for ARPES [15]. In the present case, the two-band superconductivity in MgB$_2$ provide firm direct experimental evidence for the two-band superconductivity predicted by first-principles band calculations with $k$-dependent electron-phonon coupling [11,12] confirms the importance of $k$-dependent electron-phonon coupling for the SC properties of MgB$_2$, including the high $T_c$.

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