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 σ band and the π 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 σ- and π-orbital derived bands (namely, σ and π 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 σ and π 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 σ band and a smaller gap on the π 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 HeIIα (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 $\pm 0.1°$ (corresponding to 0.010 $Å^{-1}$), respectively. The high-resolution measurements for the SC gap on the σ band and the π 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 3×10^{-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 ± 0.2 meV.

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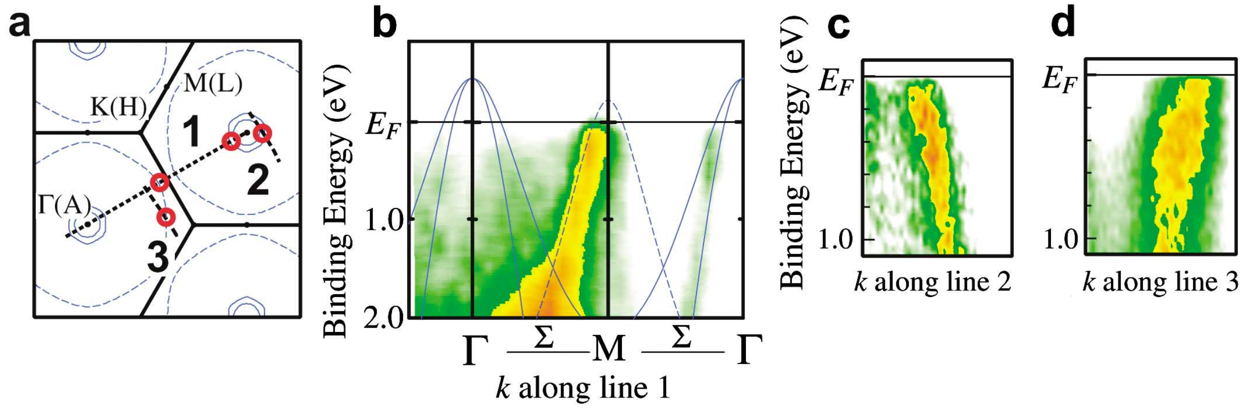

FIG. 1 (color). (a) Intersections of calculated FS sheets [19] at $k_z = 0$ and k_F's from the ARPES study of single crystal MgB_2 (0001). The full lines around the $\Gamma(A)$ point enclose the small 2D cylindrical FS sheets derived from the boron σ orbital, and the dashed line centered at the Γ point encloses the large 3D tubular FS sheets derived from boron π orbitals. (b) The ARPES intensity plot with respect to binding energy and k along line 1 of (a) (the high symmetry line Σ) compared with the calculated dispersions [19]. The intensity is higher as the color changes from white to red. (c),(d) The same as (b) but measured along lines 2 and 3 of (a), respectively.

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 Γ-A line derived from σ-bonding states of the boron $p_{x,y}$ orbitals and two 3-dimensional (3D) tubular sheets derived from π-bonding and π-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 σ band and broken lines for the π 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 $2p$ π-orbital derived band in terms of the dispersion and the$k$ point where it crosses E_F (k_F), this band can be ascribed to the π band in the $k_z = 0$ plane. Observation of the π 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 $2p$ σ orbital and can be assigned to the σ band. Inability to observe the π band in the second BZ and the other σ 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 σ- and π-orbital derived FS sheets and can be clearly attributed to that of the σ and π bands, respectively. The previous medium-resolution ARPES measurements [16] in the first BZ observed the σ and π bands with an additional surface derived band superimposed on the σ 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 σ band.

Thus, the identification of σ- and π-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 σ band and 3.9 meV for the π 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 σ 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

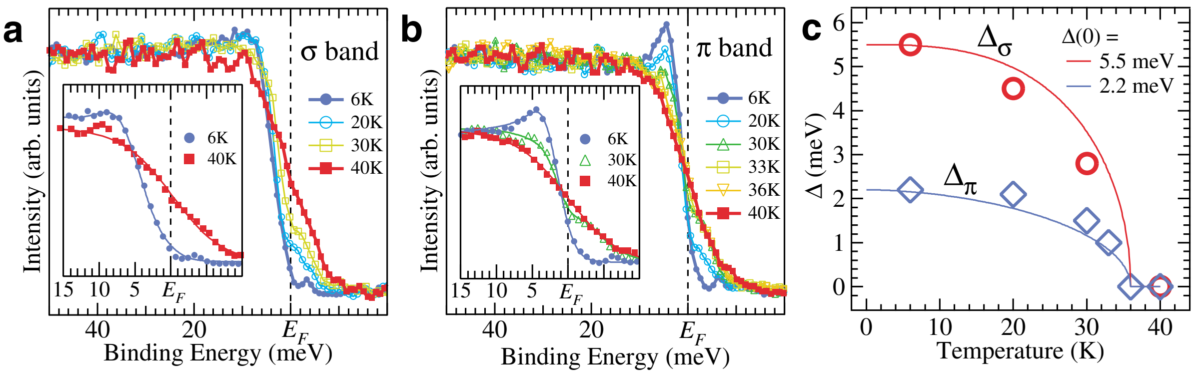

FIG. 2 (color). (a),(b) Temperature-dependent high-resolution spectra measured for the FS sheets derived from the boron σ- and π-orbital bands, respectively. The inset shows energy-enlarged spectra (symbols) for selected temperatures, as compared with the fitting results (lines), contrasting the difference in gap size on different FS's. (c) Plot of the superconducting gap size $\Delta(T)$ used for fitting the superconducting-state spectrum. Open circles and diamonds denote the gap values on the σ and π bands, respectively, as compared with theoretical predictions [11] (lines). The uncertainty of the estimated gap values is at most ± 0.4 meV.

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 Δ and the quasiparticle lifetime broadening Γ [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 convolved 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. Futhermore, 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 $2\Delta/k_B T_c$, 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 Γ-M and Γ-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 π band. Comparing with recent tunneling studies [26], while the gap value of the σ 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 π 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 σ band and the smaller gap on the π 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 π-FS sheets induces a large SC instability originating in Coulomb interaction and leads to a larger gap on π-FS than on σ-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 for the smaller gap could not be confirmed due to the limitation of energy resolution and the lowest temperature achieved for ARPES [15]. In the present case, the higher transition temperature makes MgB_2 a unique case for measuring the detailed temperature dependence of both the σ- and π-band SC gaps showing that both the gaps close simultaneously at the bulk T_c. The two-band superconductivity in MgB_2 and $2H$-$NbSe_2$, as measured by ARPES, and from a recent study on thermal conductivity [28], confirms the similarity between these materials and suggests that the two-band superconductivity is a general feature for superconductors having multiple FS sheets with different character. We hope the present work motivates more comparative studies between low-T_c and high-T_c two-band superconductors which will give further insight into characteristic properties of MgB_2 and related materials.

In conclusion, we have performed high-resolution ARPES of MgB_2 in order to study the origin of the multiple gap reported from k-integrated experimental probes. The ARPES spectra show the magnitude of the gap at 6 K to be 5.5 meV and 2.2 meV for the σ and π bands, respectively, and simultaneous gap closure at the bulk T_c. This provides direct experimental evidence for the two-band superconductivity of MgB_2. The experimental observation of 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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