Evidence for a Multiple Superconducting Gap in MgB_2 from High-Resolution Photoemission Spectroscopy

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We study the new binary intermetallic superconductor MgB_2 using high-resolution photoemission spectroscopy. The superconducting-state spectrum measured at 5.4 K shows a coherent peak with a shoulder structure, in sharp contrast to that expected from a simple isotropic-gap opening. The spectrum can be well reproduced using the weighted sum of two Dynes functions with the gap sizes of 1.7 and 5.6 meV. Temperature-dependent study shows that both gaps close at the bulk transition temperature. These results provide spectroscopic evidence for a multiple gap of MgB_2.

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MgB_2 has attracted tremendous attention since the discovery of superconductivity by Nagamatsu *et al.,* because the simple intermetallic compound shows a remarkably high transition temperature (T_c) of 39 K (Ref. [1]). The value is actually the highest within intermetallic compounds, and it is even higher than those of some cuprate high temperature superconductors, where pairing driving forces other than phonon have been speculated [2]. For MgB_2, symmetry of the Cooper pairs has been confirmed to be of a spin-singlet type from nuclear magnetic resonance (NMR) study [3]. The boron isotope effect measurements [4] indicate phonon-mediated superconductivity. The next question to be addressed is why MgB_2 shows such a high T_c; T_c lies on or beyond the estimated upper limit of T_c for phonon-mediated superconductivity [5].

Band structure calculations [6–9] predict the coexistence of two-dimensional covalent in-plane (holelike B-$2p_{xy}$ or σ band) and three-dimensional metallic-type interlayer (electronlike B-$2p_z$ band or π band) conducting bands at the Fermi level (E_F) for a peculiar feature of MgB_2. For explaining its large T_c within the BCS framework [7–9], a strong coupling of high frequency phonons originating in the in-plane boron vibrations with the density of states at E_F is a plausible scenario. However, the conclusions from band calculations are not consistent with one another. Kong *et al.* conclude that MgB_2 seems to be an intermediate-coupling phonon-mediated s-wave superconductor [9], since they can explain the value of T_c using obtained electron-phonon coupling constant λ ($= 0.87$) and Coulomb pseudopotential μ^* ($= 0.14$). But other studies have reported that the value of T_c cannot be reproduced, if one uses obtained λ ($= 0.65 - 1$) and the commonly accepted values for μ^* (Refs. [7,8,10]), suggesting the need for a theory beyond ordinary BCS. On the other hand, alternative models [11–14] which propose a pairing mechanism other than phonon have also appeared.

Since the symmetry and magnitude of a superconducting gap reflect the nature of superconductivity, many experimental studies on the superconducting gap of MgB_2 have been performed. Tunneling [15–17] and photoemission [18] measurements, which directly measure superconducting electronic structures and hence the size of the gap, have reported the size of the superconducting gap (Δ) of 2–5.9 meV (the reduced gap value $2\Delta/k_BT_c = 1.2$–3.5) assuming an isotropic gap. Optical measurements roughly estimated $2\Delta/k_BT_c = 2.6$ from the energy position where normalized reflectivity changes [19]. For the symmetry of the gap, while some studies have reported an isotropic s-wave gap [3,20–22], evidence for a deviation from an expectation of a simple isotropic s-wave gap has been increasing [23–27]. Though the symmetry and size of the gap seems not to be settled down completely even within the same experimental probe, these conflicts might hint on the shape of the superconducting gap. Indeed, the results from specific heat [25] and microwave surface resistance [27] measurements have been discussed in the light of a multiple gap.

In this Letter, we report high-resolution photoemission results on high density MgB_2 samples. The spectrum measured at 5.4 K reveals a characteristic spectral shape which cannot be explained by a simple isotropic gap opening. From fittings to the temperature dependence of the gaps, we find the spectral shape is well described with two Dynes functions with different gap values and both of the gaps close at the bulk transition temperature. This gives rise to a reduced-gap value of 1.08 for the smaller gap and that of 3.56 for the larger one. These results provide direct evidence that the superconducting gap of MgB_2 is not a simple isotropic one, but is rather a multiple gap.

High-density MgB_2 samples were prepared with a high-pressure synthesis, details of which are described elsewhere [28]. Magnetization measurements show a superconducting transition with an onset and a midpoint at 38.0 and 36.5 K, respectively. Photoemission measurements were performed on a spectrometer built using a GAMMADATA-SCIENTA SES2002 electron analyzer and a high-flux discharging lamp with a toroidal grating monochromator. The total energy resolution (analyzer and light) used the He Iα (21.2182 eV) resonance line was set to 3.8 meV. The sample temperatures were measured using a silicon-diode sensor mounted just close to it. The base pressure of the spectrometer was better than 5×10^{-11} Torr. Samples were fractured *in situ* to obtain clean surfaces and no spectral changes were observed within the measurements. Fermi energy of samples 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.

Figure 1 shows photoemission spectra of MgB_2 measured at 5.4 K (superconducting state: opened circles connected with a line) and 45 K (normal state: open squares connected with a line) with a He Iα resonance line. In contrast to the normal-state spectrum having a Fermi-edge-like structure, the superconducting-state spectrum shows a clear peak around 7 meV. We also note that there is a weak feature around 18 meV binding energy, which might relate to the unusual phonon peak at 17 meV observed by the neutron scattering study [29]. To see the superconducting-state spectrum more in detail, we expanded the same spectrum at 5.4 K near E_F, as shown in the inset in Fig. 1. We observe an intensity maximum at ~7 meV and a shift of the leading edge, indicative of the opening of a superconducting gap. More importantly, we find a shoulder structure at 3.5 meV as indicated with an arrow. These structures were not clearly observed in the recent photoemission study [18]. However, we find that the leading edge spectral shape of the present 20 K spectrum [shown in Fig. 2(d)] is very similar to that of the 15 K spectrum by Takahashi *et al.* in spite of the difference in preparation method and/or quality of samples, if we take the difference in energy resolution, temperature, and procedure to get fresh surfaces into consideration and broaden our spectrum. The observed anomalous leading edge spectral shape is in sharp contrast to those of elemental metals, Pb and Nb, where resolution-limited leading edges are observed [30]. These results suggest a deviation from a simple isotropic s-wave gap.

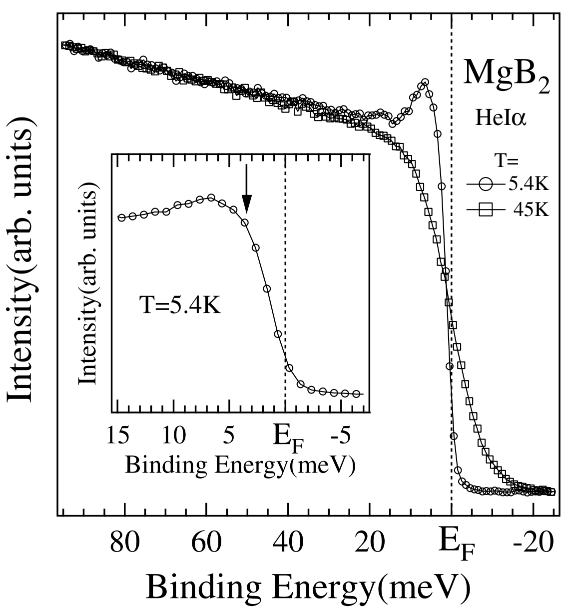

FIG. 1. High-resolution photoemission spectra of MgB_2 measured at 5.4 K (open circles connected with a solid line) and 45 K (open squares connected with a solid line) with a He Iα resonance line (21.2182 eV). The inset shows an expanded spectrum at 5.4 K in the vicinity of E_F. Please note that the spectrum has a peak with a shoulder structure as is emphasized with an arrow, which indicates a nonsimple isotropic gap.

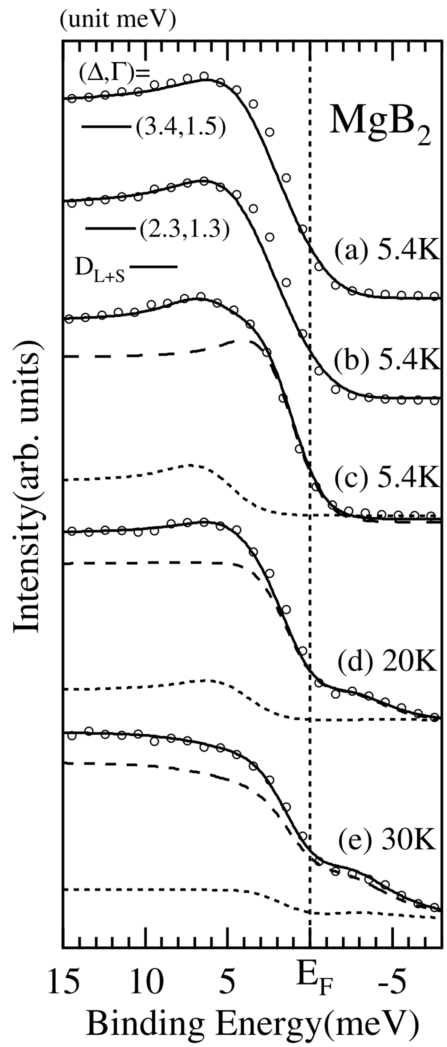

FIG. 2. Results of fittings (solid lines) and temperature-dependent experimental spectra (open circles). (*a*) Single Dynes function with $\Delta = 3.4$ meV and $\Gamma = 1.5$ meV and (*b*) single anisotropic Dynes function with $a = 1$, $\Delta = 2.3$ meV, and $\Gamma = 1.3$ meV for 5.4 K. The results of fittings are to reproduce the peak position. (*c*)–(*e*) The weighted sum of two Dynes functions (*c*) for 5.4 K with $\Delta_S = 1.7$ meV (broken line) and $\Delta_L = 5.6$ meV (dotted line) having the same $\Gamma = 0.10$ meV, (*d*) for 20 K with $\Delta_S = 1.7$ meV (broken line) and $\Delta_L = 4.5$ meV (dotted line) having the same $\Gamma = 0.20$ meV, and (*e*) for 30 K with $\Delta_S = 1.2$ meV (broken line) and $\Delta_L = 2.2$ meV (dotted line) having the same $\Gamma = 0.20$ meV. For a detailed fitting procedure, see the text.

In order to get further insight into the shape of the superconducting gap, we analyzed the experimental spectrum with the Dynes function [31] multiplied by the Fermi-Dirac (FD) function of 5.4 K and convolved with a Gaussian having a full width at half maximum (FWHM) of the known instrumental resolution. The Dynes function is a modified BCS function in the form of $D(E, \Delta, \Gamma) = \mathrm{Re}\{(E - i\Gamma)/\sqrt{(E - i\Gamma)^2 - \Delta^2}\}$, where E is the energy and Γ is the thermal broadening parameter [31]. Figure 2(a) is an example of fitting results with $\Delta = 3.4$ meV and $\Gamma = 1.5$ meV (solid line) together with the experimental data (open circles), where one can see the leading edge part is not reproduced well. We actually found that both the peak and shoulder structures were not fit at the same time using any sets of parameters. Next, we considered the case of the anisotropic gap, as discussed by Haas and Maki [32] as well as Chen *et al.* [33], who treat all the possible anisotropic gaps from the group theory that include the function used by Haas and Maki. We substitute each anisotropic gap function for isotropic Δ of the Dynes function and integrate it over momentum (k) space. We tried to fit the experimental results with these functions, but, again, we found every possible anisotropic gap function cannot reproduce the peak and shoulder structures at a time, either. In Fig. 2(b), we show an example of the fitting results using one of the anisotropic gap functions with the gap value $\Delta(a, z) = \Delta_0 \times (1 + az^2/1 + a)$, where $z = \cos\theta$ (θ is the polar angle on k space) and the parameter a, which determines the anisotropy, is set to 1 as in the Ref. [32]. We find the fitting result cannot explain the experimental result successfully.

Supposing that the shoulder structure comes from another gap, we try to fit using the weighted sum (D_{L+S}) of two Dynes functions for a larger gap (D_L) and a smaller one (D_S), $D_{L+S} = \frac{1}{1+R} D_L(E, \Delta_L, \Gamma) + \frac{R}{1+R} D_S(E, \Delta_S, \Gamma)$, where R is an amplitude ratio of the smaller gap to the larger one. Here, we used the same value of Γ for the two Dynes functions for simplicity. In Fig. 2(c), we show a result of fittings (D_{L+S}, solid line), together with Dynes functions for the larger gap ($\Delta_L = 5.6$ meV, broken line) and the smaller gap ($\Delta_S = 1.7$ meV, dotted line) with $\Gamma = 0.10$ meV and $R = 5.2$. It is evident that D_{L+S} reproduces the experimental result for both the peak and shoulder structures significantly. We note the magnitude ratio of the two gaps at 5.4 K, Δ_L/Δ_S, is ~3.3. These analyses show that the superconducting gap of MgB_2 is not a simple isotropic one, but rather contains two dominant components. This is consistent with the transport [23–27] and most recent optical [34] measurements, which indicate the inconsistency with an ordinary s-wave gap and some of which suggest a multicomponent gap.

To see how the two gaps behave as a function of temperature, we analyzed temperature-dependent spectra with D_{L+S} assuming that R is temperature independent. In Figs. 2(d) and 2(e), we show the spectra measured at 20 and 30 K (open circles) superimposed by fitting results (solid lines), respectively. Though it is clear that the weighted sum of two Dynes functions works well in explaining the experimental temperature-dependent spectra, the shoulder structure is smeared out as the temperature is increased. This relates to the fact that the intensity of the superconducting coherent peak of the smaller gap is reduced since electrons are thermally excited into unoccupied states, which can be understood to be temperature-dependent D_S (broken lines) in Figs. 2(c) to 2(e). Figure 3 shows obtained temperature-dependent gap values, where open and filled circles show the sizes of the larger and smaller gaps, respectively [36]. Theoretical temperature dependence of gaps with $\Delta(0) = 1.7$ and 5.6 meV is also shown with broken and dotted lines, respectively [35]. We find, while the temperature dependence of the smaller gap follows the BCS prediction, that of the larger gap decreases faster than the prediction. We do not know the reason for the deviation so far, but the result is similar to that obtained from MgB_2/Ag and MgB_2/In junctions [37]. More importantly, the smaller and larger gaps close nearly at the midpoint of T_c (36.5 K) obtained from the magnetization measurements with the smaller gap having more certainty [36]. This rules out the possibility that the smaller gap originates in the impurities in the surface regions and has lower T_c, as discussed in tunneling studies [17]. Therefore we think that the multiple gap of our results represents the bulk electronic structure. From these results, we obtain the reduced gap size $2\Delta(5.4\ \mathrm{K})/k_B T_c$ of ~3.56 for the larger gap, which is nearly consistent with the mean field value of 3.52, and that of 1.08 for the smaller

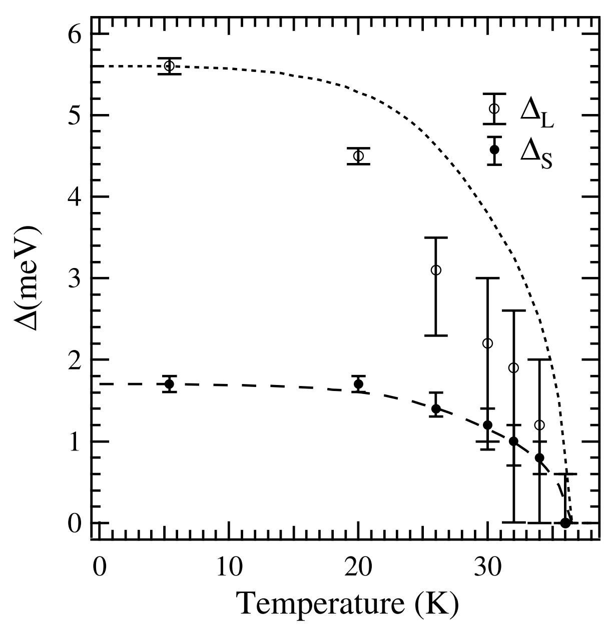

FIG. 3. Temperature dependence of the two gaps obtained from the Dynes function analyses as described in the text. Filled and open circles represent the sizes of the smaller and larger gaps, respectively. Broken and dotted lines show the predicted temperature dependence of superconducting gap from BCS theory [35] for $\Delta(0) = 1.7$ and 5.6 meV, respectively.

gap. The value of the smaller gap agrees well with that from the tunneling measurements by Rubio-Bollinger *et al.* [15], while the values from the other tunneling [16,17], photoemission [18], and optical measurements [20] lie between the obtained values of smaller and larger gaps.

Currently, there are active discussions on the mechanism of the superconductivity of MgB_2, as briefly described above. Within the weak or strong coupling BCS models, it seems necessary to think of a multiple gap [38] in order to explain the high value of T_c using reasonable λ and μ^*, as well as experimentally observed physical properties [23–27]. Liu *et al.* [38] calculated a temperature dependence of two gaps in the weak-coupling multiple-gap model, showing that the larger and smaller gaps close at the same temperature and the magnitude ratio of the larger one to the smaller one is approximately 3. These predictions can describe the present results very well. Present results are also consistent with the alternative models proposing the exsotic mechanism to explain large T_c (Refs. [12,13]), as long as they predict a multicomponent gap. Further detailed studies to show the calculated density of states are desired so as to be compared with the present study. We do not attempt to assign whether the experimentally observed larger and smaller gaps relate to the bands with what kind of character, σ band or π band, since there is a conflict on the assignment between models. To directly study the relation between the multicomponent gap and the bands with different characters, angle-resolved photoemission using single crystals is necessary and urgent.

In conclusion, we report on high-resolution photoemission results on the superconducting gap of a new binary intermetallic superconductor, MgB_2. The superconducting-state spectrum measured at 5.4 K shows a coherent peak with a shoulder structure, in sharp contrast to that expected from a simple isotropic-gap opening. We find that a simulation using two Dynes functions with the gap sizes of 1.7 and 5.6 meV reproduces the superconducting-state spectrum better than that using single isotropic and anisotropic Dynes functions. We also find that the smaller gap as well as the larger gap seems to close at the bulk transition temperature. These results are consistent with transport measurements and thus indicate the superconducting gap of MgB_2 is a multiple gap.

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[1] J. Nagamatsu *et al.,* Nature (London) **410**, 63 (2001).
[2] P. W. Anderson, *The Theory of Superconductivity in the High-T_c Cuprates* (Princeton University Press, Princeton, NJ, 1997).
[3] H. Kotegawa *et al.,* Phys. Rev. Lett. **87**, 127001 (2001).
[4] S. L. Bud'ko *et al.,* Phys. Rev. Lett. **86**, 1877 (2001).
[5] V. L. Ginzburg, J. Supercond. **13**, 665 (2000).
[6] K. D. Belashchenko, M. van Schilfgaarde, and V. P. Antrov, Phys. Rev. B **64**, 092503 (2001).
[7] J. Kortus *et al.,* Phys. Rev. Lett. **86**, 4656 (2001).
[8] J. M. An and W. E. Pickett, cond-mat/0102391.
[9] Y. Kong *et al.,* Phys. Rev. B **64**, 020501(R) (2001).
[10] K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. **86**, 5771 (2001).
[11] J. E. Hirsch, Phys. Lett. A **282**, 392 (2001); J. E. Hirsch and F. Marsiglio, Phys. Rev. B **64**, 144523 (2001).
[12] M. Imada, J. Phys. Soc. Jpn. **70**, 1218 (2001).
[13] K. Yamaji, J. Phys. Soc. Jpn. **70**, 1476 (2001).
[14] K. Voelker, V. I. Anisimov, and T. M. Rice, cond-mat/0103082.
[15] G. Rubio-Bollinger, H. Suderow, and S. Vieira, Phys. Rev. Lett. **86**, 5582 (2001).
[16] G. Karapetrov *et al.,* Phys. Rev. Lett. **86**, 4374 (2001).
[17] H. Schmidt, J. F. Zasadzinski, K. E. Gray, and D. G. Hinks, Phys. Rev. B **63**, 220 504 (2001).
[18] T. Takahashi *et al.,* Phys. Rev. Lett. **86**, 4915 (2001).
[19] B. Gorshunov *et al.,* Eur. Phys. J. B **21**, 159 (2001).
[20] R. K. Kremer, B. J. Gibson, and K. Ahn, cond-mat/0102432.
[21] X. H. Chen, Y. Y. Xue, R. L. Meng, and C. W. Chu, Phys. Rev. B **64**, 172501 (2001).
[22] X. K. Chen *et al.,* Phys. Rev. Lett. **87**, 157002 (2001).
[23] C. Panagopoulos *et al.,* Phys. Rev. B **64**, 094514 (2001).
[24] S. L. Li *et al.,* Phys. Rev. B **64**, 094522 (2001).
[25] Y. Wang, T. Plackowsky, and A. Junod, Physica (Amsterdam) **355C**, 179 (2001).
[26] J. P. Joshi *et al.,* cond-mat/0103369.
[27] A. A. Zhukov *et al.,* cond-mat/0103587.
[28] Y. Takano *et al.,* Appl. Phys. Lett. **78**, 2914 (2001).
[29] T. J. Sato, K. Shibata, and Y. Takano, cond-mat/0102468.
[30] A. Chainani, T. Yokoya, T. Kiss, and S. Shin, Phys. Rev. Lett. **85**, 1966 (2000).
[31] R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. **41**, 1509 (1965).
[32] S. Haas and K. Maki, cond-mat/0104207.
[33] C.-T. Chen *et al.,* cond-mat/0104285.
[34] A. V. Pronin, A. Pimenov, A. Loidl, and S. I. Krasnosvobdtsev, cond-mat/0104291.
[35] D. J. Scalapino, in *Superconductivity,* edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, Sect. IV.
[36] We define the error bar as a 10% variation of the residual in changing values of one gap with a 0.1 meV interval, keeping another gap value constant. The smaller difference between the two gap sizes and the larger effect from the FD function make it more difficult to determine the correct gap size at higher temperatures, resulting in larger error bars. Also note that the error bar of the larger gap is bigger than that of the smaller gap due to the smaller spectral weight of the larger gap ($R = 5.2$).
[37] A. Plecenik, S. Benacka, and P. Kus, cond-mat/0104038.
[38] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).