Electronic Structure of MgB_2 from Angle-Resolved Photoemission Spectroscopy

H. Uchiyama,[1] K. M. Shen,[2] S. Lee,[1] A. Damascelli,[2] D. H. Lu,[2] D. L. Feng,[2] Z.-X. Shen,[2] and S. Tajima[1]

[1]*Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku, Tokyo 135-0062, Japan*

[2]*Department of Physics, Applied Physics, and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305*

(Received 4 July 2001; published 2 April 2002)

The first angle-resolved photoemission spectroscopy results from MgB_2 single crystals are reported. Along the ΓK and ΓM directions, we observed three distinct dispersive features approaching the Fermi energy. These can be assigned to the theoretically predicted σ (B $2p_{x,y}$) and π (B $2p_z$) bands. In addition, a small parabolic-like band is detected around the Γ point, which can be attributed to a surface-derived state. The overall agreement between our results and the band calculations suggests that the electronic structure of MgB_2 is of a conventional nature, thus implying that electron correlations are weak and may be of little importance to superconductivity in this system.

DOI: 10.1103/PhysRevLett.88.157002 PACS numbers: 74.70.Ad, 74.25.Jb, 79.60.Bm

The discovery of superconductivity in MgB_2, with the surprisingly high critical temperature (T_c) of 39 K [1], has garnered a tremendous amount of interest [2]. Concerning the nature of the superconducting pairing mechanism, there has been considerable speculation, particularly regarding whether superconductivity could be explained within the Bardeen-Cooper-Schrieffer framework [3]. On the one hand, on the basis of experiments performed on isotope substituted material it has been shown that the electron-phonon interaction is indeed important to the pairing in MgB_2 [4,5]; on the other hand, T_c is considerably higher than what many would have originally believed possible as a result of conventional electron-phonon interaction alone [6,7]. This has prompted the question of whether additional factors, such as electron-electron correlations [8–10], may conspire to raise the superconducting transition temperature. In order to quantitatively address this important issue, an experimental determination of the electronic structure of MgB_2 is crucial. In fact, the strength of the electronic correlations can be estimated from the renormalization of the overall electronic bandwidth, Fermi velocity, and effective mass with respect to the values predicted by band theory (in the extreme case, electronic correlations could result in the opening of a so-called Mott-Hubbard gap in systems that on the basis of the bare electron counting are expected to be metallic [11]; this corresponds to the complete breakdown of the independent particle picture which, however, is clearly not realized in MgB_2).

In this context, angle-resolved photoemission spectroscopy (ARPES) is uniquely powerful in its capability to directly probe the electronic structure of solids [12]. For instance, in the case of the copper oxides superconductors, ARPES has played a pivotal role in shaping the current understanding of their electronic structure and, in particular, in characterizing the electron-electron correlations [13,14].

In this Letter, we report the first ARPES measurements performed on the recently synthesized single crystals of MgB_2 [15]. We find a good overall agreement between the experimental data and the results of existing band structure calculations [16–20], which gives a good basis for understanding the fundamental properties of this material. Furthermore, the good agreement indicates that electron-electron correlation effects are very weak. In turn, this implies that the electronic structure of MgB_2 is of a conventional nature and electron-electron interactions are of little importance to superconductivity.

Single crystals of MgB_2 were grown in the quasiternary Mg-MgB_2-BN system under 5–6 GPa at 1600 °C. Several single crystals with typical dimensions of $0.3 \times 0.3 \times 0.1$ mm^3 were selected for this study. The single crystallinity was confirmed by four circle x-ray diffraction. Both resistivity and magnetization measurements verified that the crystals exhibit superconductivity at 38 K with a narrow transition width of 0.3 K [15]. The ARPES measurements were performed at Beamline 5-4 of the Stanford Synchrotron Radiation Laboratory with a total energy resolution of better than 40 meV and an angular resolution of $\pm 0.15°$. In this study, higher energy resolution was sacrificed in order to obtain reasonable counting statistics on the small single crystals. The samples were first aligned by Laue diffraction and then cleaved *in situ* along the *a-b* plane at a pressure better than 5×10^{-11} torr and a temperature of about 10 K. Because of the observed rapid degradation of the sample surface, all data were taken within 5 h of cleaving. Reproducible results were obtained on different cleaves.

The ARPES spectra were collected parallel to the high symmetry directions ΓM and ΓK [where $\Gamma = (0, 0, 0)$, $M = (\pi, 0, 0)$, and $K = (2/3\pi, 2/3\pi, 0)$], using a photon energy of $h\nu = 28$ eV and incident electric-field polarization perpendicular to each respective symmetry direction (see Fig. 1a). Along ΓM, the polar emission angle was changed from 0° (normal emission) to 28° in the plane defined by the surface normal and the [100] axis; along ΓK it was changed from 0° to 33° in the plane defined by the

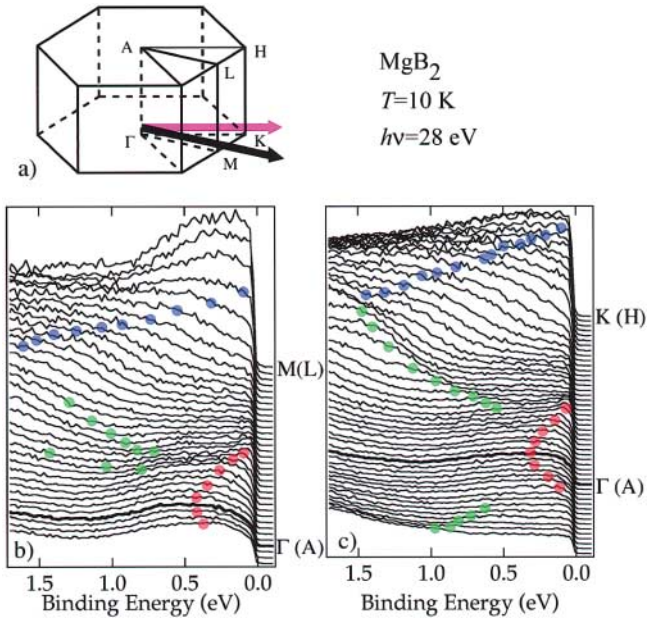

FIG. 1 (color). (b),(c) MgB_2 ARPES spectra from along the $\Gamma(A)$-$M(L)$ and $\Gamma(A)$-$K(H)$ directions, as indicated by the arrows in the Brillouin zone sketch (a). The B $2p_z$ and $2p_{x,y}$ bands are marked in blue and green, respectively, while the red dots denote the surface state centered around $\Gamma(A)$.

surface normal and the [110] axis. The normal to the sample surface was determined by a standard laser-reflection procedure, and the fine alignment of the sample with respect to the electron analyzer was verified by checking the symmetry of the detected electronic bands with respect to the normal-emission direction. Since MgB_2 is characterized by a three dimensional electronic structure and the electronic bands are predicted to show strong dispersion along the z axis [16,17], we performed photon-energy dependence measurements at normal emission in order to estimate the corresponding k_z value for each given incident photon energy [12]. The photoemission cross section was found to be maximum at $h\nu = 28$ eV in the explored range of 17–28 eV, and decreased rapidly and monotonically upon progressively lowering the photon energy. However, because of the combination of large background and low intensity it was not possible to observe a clear electronic dispersion as a function of incident photon energy at normal emission. Therefore, we could not determine experimentally the exact k_z coordinates for the ARPES data presented here.

The spectra in Figs. 1b and 1c are representative energy distribution curves (EDCs) taken along the $\Gamma(A)$-$M(L)$ and $\Gamma(A)$-$K(H)$ directions, respectively. Several dispersive bands can be observed, as emphasized by the colored dots. The positions of these markers were determined from the combined analysis of EDCs and second derivative plots, which will be described in more detail below. Although the data have been taken well below T_c, in which case a few meV superconducting gaps should be open along the normal state Fermi surface, because of the insufficient energy resolution used in the present experiment the gap has not been resolved and all the detected bands appear to reach and cross the Fermi energy. Near the $K(H)$ and $M(L)$ points, we observed a strong dispersive peak that approaches E_F, as emphasized by the blue dots. Along $\Gamma(A)$-$K(H)$ another feature, marked in green, is approaching E_F near the $\Gamma(A)$ point. Along the $\Gamma(A)$-$M(L)$ direction the corresponding feature is very weak, although subtle changes in the line shape can be discerned and are marked in green. Finally, along both the $\Gamma(A)$-$K(H)$ and $\Gamma(A)$-$M(L)$ directions, a small parabolic-like band is centered at the $\Gamma(A)$ point and reaches E_F near $(\pi/4, 0, k_z)$ and $(\pi/6, \pi/6, k_z)$, respectively.

To more effectively visualize the ARPES data in the context of band dispersions, the image plots of the second derivative of the EDCs are shown in Fig. 2a. By taking the second derivative with respect to the binding energy of the raw ARPES data shown in Figs. 1b and 1c, the relative contrast of the detected features can be enhanced, especially for those bands which are characterized by a very broad structure in the EDCs. The spurious intensity in the second derivative plots, which does not have a correspondent in the raw data and therefore does not represent any true feature, is likely due to higher sensitivity to statistical noise. The bands identified in Figs. 1b and 1c are evident in the image plots of Fig. 2a, where the overlaid colored solid lines emphasize the experimentally determined electronic bands. In particular, the two weak features in the raw data along the $\Gamma(A)$-$M(L)$ direction are much more pronounced in the second derivative image plots. Note

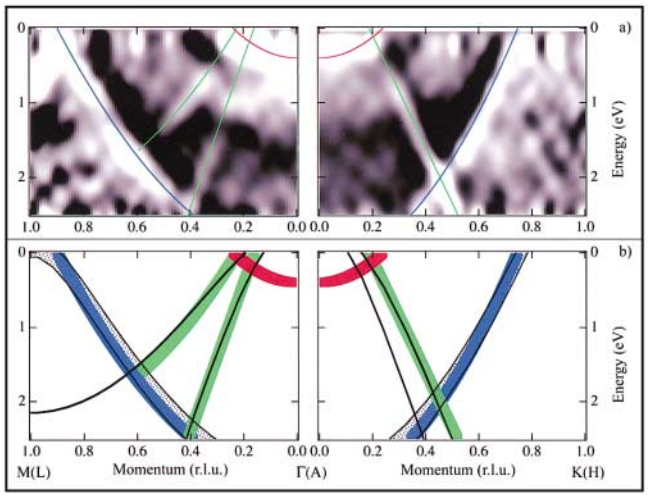

FIG. 2 (color). (a) Second-derivative plots of the energy distribution curves (EDCs) shown in Fig. 1. The data were smoothed in both energy and momentum before taking the second derivative with respect to the binding energy. Colored lines emphasize the detected electronic bands, consistently with Fig. 1. (b) Comparison between theoretical (black) and experimental (color) results. The width of the theoretical lines represents the projection of k_z values from 0 to $\pm 0.14\pi$.

that the EDCs and second derivative image plots emphasize different aspects of the data; in Fig. 1 what catches one's eye is the intensity of the EDCs, while in Fig. 2a it is the change in slope of the EDCs, independent of the relative intensity. Together with the enhancement of the photoemission intensity at the M point most probably due to matrix element effects, this is the reason for the apparent disagreement in Fig. 1b between the dispersion of the B $2p_z$ band as inferred from the EDCs and from their second derivative (blue dots).

A comparison of the features observed along ΓM and ΓK with the results of band structure calculations [16,17] for $k_z \approx 0$ is presented in Fig. 2b, which shows a remarkable agreement between experiment and theory in the whole studied energy range (i.e., up to 2.5 eV binding energy). To account for the k_z uncertainty, our results are compared to calculations projected in k_z between $k_z = 0$ and $k_z = \pm 0.14\pi$, which are represented by broad lines in Fig. 2b (it is worth emphasizing that, within the emission-angle range used in the present experiment, the percentage change in k_z is considerably smaller than in $k_\parallel$). Since the agreement is completely lost for other values of k_z, we conclude that at normal emission with 28 eV photons we are close to the plane containing the Γ point, as far as the z dispersion is concerned. Thus, our angular cuts lay close to the ΓM and ΓK lines. From Fig. 2b, we can clearly assign the feature marked in blue to the B $2p_z$ (π) band, and those marked in green to the B $2p_{x,y}$ (σ) bands. Of the two σ bands predicted along ΓK, only one is experimentally observed. However, as in the calculations where the two bands lie close in energy, the broad feature we observe may likely result from the superposition of the two. In addition, although the $2p_{x,y}$ bands along ΓM are weak in both the EDCs and the second derivative image plots, the close agreement of these features with the theoretical calculations lends strong support to our identification. We note that a similar contrast in the photoemission intensity for σ and π bands is observed also on graphite [21], which possesses an electronic structure somewhat similar to the one of MgB_2, and appears to be a consequence of matrix element effects.

Finally, we turn our attention to the electronic state centered around the Γ point and marked in red in Figs. 1, 2, and 3. From the comparison with the results of band structure calculations, one can conclude that there is no theoretically predicted *bulk* band which would correspond to this particular feature. As ARPES is an extremely surface sensitive technique, it is entirely possible that this feature originates from a *surface* electronic state. The existence of surface states, which is a consequence of the breaking of translational symmetry at the crystal surface, is a rather universal phenomenon and occurs in many simple materials such as Au, Ag, Cu, Si, and graphite [12]. Therefore, the existence of such a surface state in MgB_2 is not surprising, especially around the Γ point where there is a gap in the k_z-projected bulk band structure [16,17]. The

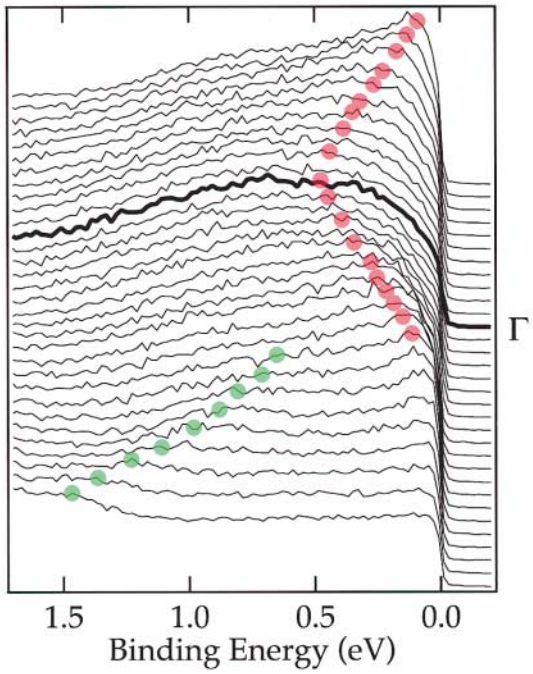

FIG. 3 (color). Enlarged view of the EDCs taken close to the Γ point, along the ΓK direction (see also Fig. 1b), which shows the surface state (red) and the B $2p_{x,y}$ band (green).

close agreement between all the other detected features and the results of band structure calculations also lends credence to our assignment of this feature to a surface state, as opposed to an unexpected bulk band. In addition, calculations for the electronic structure of the $MgB_2(0001)$ surface predicted the existence of several surface and image potential states for both B- and Mg-terminated surfaces [18–20]. In particular, there is an overall good agreement between ARPES and theoretical results for the Mg-terminated surface, as indicated by self-consistent *ab initio* calculations of the electronic structure [18,19], as well as one-step model calculations of the ARPES intensity in which the position of the surface potential is treated as a phenomenological parameter [20]. At this point, it should be noted that many measurements of the superconducting gap magnitude in MgB_2 were performed by surface-sensitive techniques such as tunneling [22–25] and angle-integrated photoemission spectroscopy [26,27]; the presence of a surface state could severely affect the interpretations of these results, especially as far as the issue of a multiple gap in the bulk electronic structure is concerned.

The close overall agreement of our experimentally determined band dispersions with the theoretical calculations seems to indicate that the effects of electron-electron correlations in this material are weak. In particular, electronic correlations would typically result in an overall renormalization or narrowing of the total electronic bandwidth as compared to the calculated value, and in an effective mass larger than the expected band mass. Clearly, as indicated by our investigation, this behavior is not observed in the

ARPES data up to binding energies as high as 2.5 eV, thus suggesting that electronic correlations in MgB_2 are fairly unimportant and that this material can be well described by conventional band theory. At low binding energies, it is in principle possible to directly estimate from the ARPES spectra the interaction, if any, of the quasiparticles with collective modes such as, for example, lattice vibrations in electron-phonon coupled systems [28]. This interaction might result in a change of the electronic velocity along the quasiparticle dispersion and/or in an additional pole structure in the EDCs at the characteristic phonon energies [28]. These effects might actually be expected in the present case, given that MgB_2 is a relatively strong-coupling superconductor in which the phonon density of states extends up to 100 meV [29]. However, no clear behavior of this kind was observed in our measurements. On the other hand, no definitive conclusion can be drawn on this issue on the basis of the present data because the signatures of an interaction between quasiparticles and collective modes could be easily masked by the broadness of the experimental line shapes. This, in turn, might be a consequence of the finite k_z dispersion and/or of a considerable disorder of the cleaved surface at the atomic scale. Further scrutiny of this issue is therefore required.

In conclusion, we have studied the electronic structure of MgB_2 by ARPES focusing, in particular, on the electronic dispersion near the Fermi level. Two σ bands and one π band were observed, as expected for the bulk electronic structure. The presence of multiple bands must be the origin of the complicated physical properties of MgB_2, such as the extremely small but remarkably temperature dependent Hall coefficient [2]. An additional band was observed around the Γ point and assigned to a surface state of the Mg-terminated cleaved surface. The close agreement between experimental and theoretical results for all detected features supports the view that MgB_2 is a conventional metal in which electronic correlations are weak and superconductivity is likely of conventional origin.

We are grateful to J. Kortus and I. I. Mazin for kindly providing their band structure calculations and useful suggestions, and to S. Drechsler and V. Servedio for showing their unpublished results. This work was supported by the New Energy and Industrial Technology Department Organization (NEDO) as Collaborative Research and Development of Fundamental Technologies for Superconductivity Applications. SSRL is operated by the DOE Office of Basic Energy Research, Division of Chemical Sciences. The office's division of Material Science provided support for this research. The Stanford work was also supported by NSF Grant No. DMR0071897 and ONR Grant No. N00014-98-1-0195.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] For a review see C. Buzea and T. Yamashita, Supercond. Science Technol. **14**, R115 (2001).
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **167**, 1175 (1957).
[4] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. **86**, 1877 (2001).
[5] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature (London) **411**, 457 (2001).
[6] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[7] P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).
[8] J. E. Hirsch, Phys. Lett. A **282**, 392 (2001).
[9] M. Imada, J. Phys. Soc. Jpn. **70**, 1218 (2001).
[10] N. Furukawa, J. Phys. Soc. Jpn. **70**, 1483 (2001).
[11] N. F. Mott, *Metal-Insulator Transition* (Taylor & Francis, London, 1990).
[12] S. Hüfner, *Photoelectron Spectroscopy* (Springer-Verlag, Berlin, 1995).
[13] Z.-X. Shen and D. S. Dessau, Phys. Rep. **253**, 1 (1995); A. Damascelli, D. H. Lu, and Z.-X. Shen, J. Electron Spectrosc. Relat. Phenom. **117–118**, 165 (2001).
[14] D. W. Lynch and C. G. Olson, *Photoemission Studies of High-Temperature Superconductors* (Cambridge University Press, Cambridge, 1999).
[15] S. Lee, H. Mori, T. Masui, Y. Eltsev, A. Yamamoto, and S. Tajima, J. Phys. Soc. Jpn. **70**, 2255 (2001).
[16] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
[17] J. M. An and W. E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
[18] V. M. Silkin, E. V. Chulkov, and P. M. Echenique, Phys. Rev. B **64**, 172512 (2001).
[19] Z. Li, J. Yang, J. G. Hou, and Q. Zhu, Phys. Rev. B **65**, 100507 (2002).
[20] V. D. P. Servedio, S.-L. Drechsler, and T. Mishonov, cond-mat/0111434.
[21] A. R. Law, M. T. Johnson, and H. P. Hughes, Phys. Rev. B **34**, 4289 (1986).
[22] G. Rubio-Bollinger, H. Suderow, and S. Vieira, Phys. Rev. Lett. **86**, 5582 (2001).
[23] G. Karapetrov, M. Iavarone, W. K. Kwok, G. W. Crabtree, and D. G. Hinks, Phys. Rev. Lett. **86**, 4374 (2001).
[24] F. Giubileo, D. Roditchev, W. Sacks, R. Lamy, D. X. Thanh, and J. Klein, Phys. Rev. Lett. **87**, 177008 (2001).
[25] P. Szabó, P. Samuely, J. Kačmarčík, T. Klein, J. Marcus, D. Fruchart, S. Miraglia, C. Marcenat, and A. G. M. Jansen, Phys. Rev. Lett. **87**, 137005 (2001).
[26] T. Takahashi, T. Sato, S. Souma, T. Muranaka, and J. Akimitsu, Phys. Rev. Lett. **86**, 4915 (2001).
[27] S. Tsuda, T. Yokoya, T. Kiss, Y. Takano, K. Togano, H. Kito, H. Ihara, and S. Shin, Phys. Rev. Lett. **87**, 177006 (2001).
[28] For a review see S. D. Kevan and E. Rotenberg, J. Electron Spectrosc. Relat. Phenom. **117–118**, 57 (2001); P. D. Johnson, A. V. Fedorov, and T. Valla, J. Electron Spectrosc. Relat. Phenom. **117–118**, 153 (2001).
[29] R. Osborn, E. A. Goremychkin, A. I. Kolesnikov, and D. G. Hinks, Phys. Rev. Lett. **87**, 017005 (2001).