Observation of an "Extended" Van Hove Singularity in $YBa_2Cu_4O_8$ by Ultrahigh Energy Resolution Angle-Resolved Photoemission

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(Received 4 March 1994)

We characterize the nature of the Van Hove singularity near the Fermi energy (E_F) in $YBa_2Cu_4O_8$ using ultrahigh energy resolution (10 meV) angle-resolved photoemission spectroscopy, together with corresponding first-principles spectra intensity computations. The singularity, related to CuO_2 planes, is located about 19 meV below E_F at the Y point in the Brillouin zone and arises from a band which is nearly dispersionless along the Γ to Y direction. Such an "extended" saddle point would render the band structure quasi-1D and yield a power law divergence in the density of states, allowing the occurrence of T_c's of order 100 K even in a weak coupling BCS scheme.

PACS numbers: 74.72.Bk, 74.25.Jb, 79.60.Bm

Ever since the discovery of high-T_c superconductivity, one of the most intensely debated questions has been: What is the reason for the critical temperature in the new materials to be much higher than in the earlier superconductors such as Hg, Pb, Nb, and the A15's? Many mechanisms have been proposed to explain these high transition temperatures, some exotic and others of a more conventional nature [1]. Of interest to this Letter is the so-called Van Hove scenario [2–9], in which the occurrence of high-T_c's is tied to the presence of Van Hove singularities in the density of states (DOS) close to the Fermi energy. So far, there has only been indirect evidence for the existence of such peaks in the DOS, for example, from the discontinuity of the specific heat at T_c [6], studies of the isotope effect [7], of the thermopower [8], and of the quasiparticle lifetime broadening [9].

In this Letter, for the first time, we give direct evidence for the presence of a Van Hove singularity in $YBa_2Cu_4O_8$ near the Fermi energy. The nature of the singularity is characterized by determining its location in the Brillouin zone and the dispersion of the associated spectral density peak by ultrahigh resolution angle-resolved photoemission spectroscopy (ARPES). Here we show data at an energy resolution better than 10 meV. Most of the previously published synchrotron-based work has involved resolutions of 25–30 meV. Since the Van Hove singularity lies very close to the Fermi energy, a high energy resolution is essential for these measurements. The experimental spectra are compared with corresponding first-principles ARPES intensity calculations, and it is clearly established that the measured spectral feature arises from bulk energy bands of the crystal related to the CuO_2 planes. The conclusions are therefore generally relevant to the cuprate superconductors, particularly since we have found similar behavior in $YBa_2Cu_3O_{7-\delta}$, $Bi_2CaSr_2Cu_2O_8$, and $Tl_2Ba_2CuO_6$ [10].

The common Van Hove scenario assumes that the diverging DOS arises from a saddle point in the underlying 2D CuO_2 plane bands (i.e., a minimum along one direction and a maximum along the perpendicular direction). Our results provide a new twist to this picture in that the bands are measured to be nearly flat (within 1 meV) in one direction, so that the situation may be described as a family of simple saddle points (critical line), or an *extended saddle point,* with profound consequences for the normal and superconducting properties of the material.

Van Hove [11] showed that in a two-dimensional system a simple saddle point yields a logarithmic divergence in the DOS. However, for an extended saddle point, the DOS singularity would diverge as the much stronger $(E - E_c)^{-1/2}$, where E_c is the critical point energy [12,13]. It is then straightforward to show that when the distance between the Fermi energy and the saddle point energy is less than T_c, the phonon energy scale is replaced by an electronic energy scale in a weak coupling BCS scheme. In this case, the transition temperature scales as $T_c \sim w\lambda^2$ [12], where w denotes the band width and λ the usual coupling constant. For a reasonable value of w of order 1 eV, a coupling constant of 0.1 would already yield $T_c \sim 100$ K. Thus any coupling mechanism, even phonons, could easily explain the occurrence of high T_c's.

The specific system investigated in this study is $YBa_2Cu_4O_8$ (Y124), which is closely related to the more familiar $YBa_2Cu_3O_{6.9}$ (Y123). The crystal structure of Y124 is the same as that of Y123, except that the former contains two CuO_2 chains per unit cell. The Brillouin zones (BZ) in the two cases are also similar, with the Γ-Y line being parallel to the direction of the CuO chains.

 0031-9007/94/73(24)/3302(4)$06.00

The symmetry points at the zone boundary are $X(\pi, 0)$, $Y(0, \pi)$, and $S(\pi, \pi)$. The crystals of Y124 are, however, naturally untwinned and more stable compared to Y123, making Y124 attractive from an experimental viewpoint. We have compared the detailed spectra in Y124 with the corresponding results for Y123 in a number of cases and find the results to be quite similar, indicating that our conclusions are relevant for Y123.

The measurements were carried out at the Aladdin synchrotron. The high energy resolution was obtained using a commercial spectrometer, but with improved shielding and electronics and a 4 m normal-incidence monochrometer. The measurements employed untwinned Y124 single crystals with T_c of 82 K and transition widths of 1 K as determined by a SQUID magnetometer. The crystals were cleaved at 12 K in a vacuum better than 4×10^{-11} Torr and the ARPES spectra taken below T_c in order to avoid difficulties of oxygen loss and sample degradation. A number of experiments were carried out above T_c but did not show the presence of a superconducting energy gap, consistent with previous studies, even though peak shifts bigger than 1 meV are detectable by our instrument [14]. The specimens were oriented to an accuracy better than 1° by Laue diffraction and the orientation further confirmed in the experimental chamber via the observed symmetry of sharp photoemission features around high symmetry points.

In order to carry out first-principles computations of ARPES intensities in structures of the complexity of the high-T_c superconductors, we have generalized the one-step Green's function based photoemission approach which considers a semi-infinite solid of nonoverlapping muffin-tin potentials separated from the bulk by a potential step [15]. Our specific muffin-tin potentials are obtained via the semi-relativistic self-consistent Korringa-Kohn-Rostoker Green's-function (KKR) band structure methodology [16] and yield the bulk band structures and Fermi surfaces of Y124 and Y123 in reasonable accord with the well-known results [17]. Given the close similarity of the electronic structures and ARPES spectra of Y124 and Y123, the present computations on Y124 follow along the lines of our earlier study of Y123 [15], where an excellent accord was obtained between the computed and measured shape, polarization, and k dependence of the calculated and measured spectral peaks associated with the CuO_2 plane bands. Accordingly, we have assumed the surface to possess an ideal BaO/CuO_2 termination (i.e., the topmost layer is BaO, followed by the CuO_2 layer) and have chosen the imaginary part of the self-energy parameter to reflect an energy dependent broadening of initial and final states representative of the experimental spectra.

Figure 1 shows ARPES measurements in two perpendicular directions centered on the Y symmetry point. The spectra in Fig. 1(a) clearly show an intense peak, nearly dispersionless along the Γ-Y-Γ_1 direction (Γ_1 is in the second BZ). The peak position remains fairly constant for a region of $k_\parallel$ values centered on Y extending to

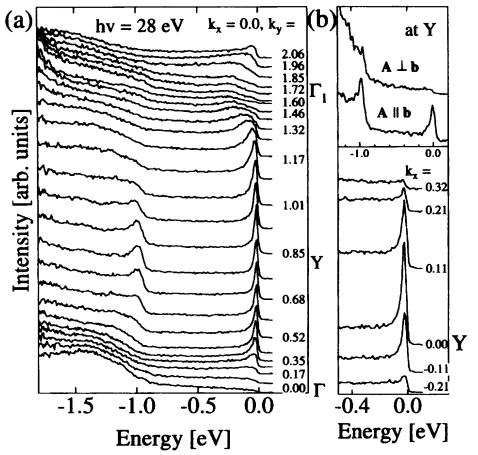


FIG. 1. Experimental ARPES spectra from untwinned $YBa_2Cu_4O_8$ along (a) Γ-Y and (b) Y-S directions. Note the large peak in the spectra very close to E_F in the vicinity of the Y point. The spectra are labeled with momenta at E_F in units of $Å^{-1}$. The inset in (b) shows that the band is excited only when the light is polarized along the **b** axis, having *even* symmetry with respect to the mirror plane containing the **b** and **c** axes (Γ-Y plane).

about $\frac{1}{3}$ of the Γ-Y-Γ_1 distance [18]. When moving from Y toward S [Fig. 1(b)], the band loses intensity as it crosses the Fermi level. This can be seen more clearly if we expand the energy scale by 1 order of magnitude, as shown in Figs. 2 and 3. Figure 2 shows the measured and computed spectra for $k_\parallel$ values varying along the same direction as in Fig. 1(a). The experimental spectra [Fig. 2(a)] show the peak lying 19 meV below the Fermi energy at the Y point. The characteristic features of the measured and computed spectral peak are very similar, in that both become more intense around the Y point, with the intensity remaining quite high as we move away from Y towards either Γ or Γ_1, but decreasing rapidly and broadening as the feature disperses to higher binding energies. The theoretical peak, however, displays more dispersion than the experiment, consistent with the notion that the associated band in the real material becomes flatter, presumably due to electron-electron correlations beyond the local density approximation used in the present calculations. Figure 3(a) shows that as we vary $k_\parallel$ in a perpendicular direction to that of Fig. 2(a) from the Y point (to the BZ corner S, as opposed to Γ), the spectral peak rapidly moves above the Fermi energy. As noted above, a convincing demonstration of this behavior is crucially dependent on the ultrahigh energy resolution achieved in this experiment. As in Fig. 2 above, the dispersion of the theoretical peak in Fig. 3(b) is greater than that of the experimental feature, presumably also due to electron-electron correlations.

The peak in the theoretical spectra of Figs. 2(b) and 3(b) originates in a bulk band related to the CuO_2 planes. We have established this via additional computations which show that, unlike the case of surface related features, this feature is insensitive to changes in the position of the

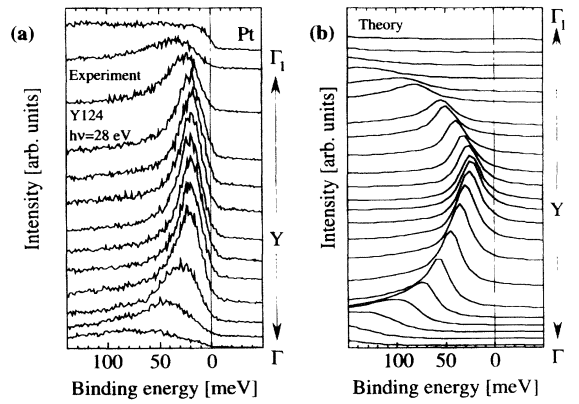


FIG. 2. (a) Same as Fig. 1, except with the energy scale expanded by 1 order of magnitude. The data show the peak at the minimum binding energy of 19 meV at Y. The emission angles vary by 2°. The Pt edge at the top shows the ultrahigh energy resolution (10 meV) of the spectrometer. This figure emphasizes spectra shapes. The quantitative E-k values obtained from these spectra are given in Fig. 4. (b) Corresponding first-principles computed intensities at $\frac{1}{2}$ the momentum interval (= 1°) used in (a) in order to clearly delineate the $k_{\|}$ dependence of the spectral shape.

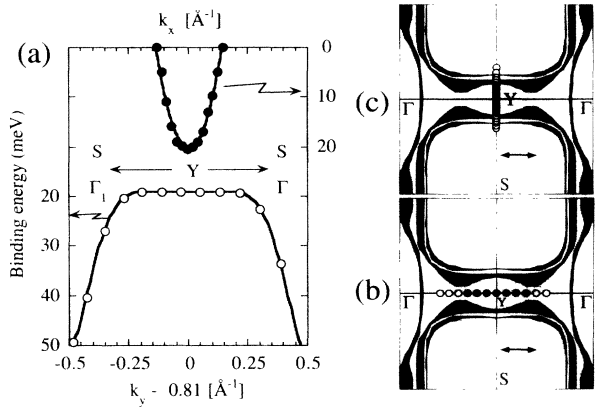


FIG. 4. (a) Band dispersion around Y obtained from the experimental spectra of Figs. 2(a) and 3(a). (b) Positions in momentum space where the spectra in Fig. 2(a) were taken superposed on a plot of the Fermi surface projected onto the basal plane in the zone. Filled dots represent positions where the band is flat. (c) Positions in momentum space where the spectra in Fig. 3(a) were taken. Dots are filled when the band is below the Fermi level. The arrows in (b) and (c) indicate the direction of polarization of the photons.

surface barrier and also to the z component of the incident light. We have measured the detailed dependence of the intensity on polarization and find the observed behavior to be similar to the calculation. Bearing these considerations in mind, we conclude that the experimental feature in Figs. 2(a) and 3(a) is of *bulk* origin.

Figure 4(a) summarizes the dispersion of the state around the Y point obtained from the peak positions in the spectra of Figs. 2(a) and 3(a). A surface plot resulting from additional measurements [19], in which spectra were taken along several lines parallel to Y-S but offset along the Γ-Y direction, is shown in Fig. 5. The data show a maximum around Y as one moves towards Γ by varying k_y, but a minimum when moving towards S by varying k_x, and establish unambiguously an *extended saddle point* behavior of the highest occupied CuO_2 band around the Y point in Y124.

Additional information concerning the k_z dispersion is provided by changing the photon energy at fixed $k_{\|}$. Our studies show the k_z dispersion to be small in the vicinity of the Y point, indicating that the band structure is quasi-two-dimensional. On changing the photon energy, we also find a feature at a binding energy of 115 meV at the Y point [19]. This feature also displays a saddle point behavior and may arise from the second CuO_2-related plane band. We omit a detailed discussion here since

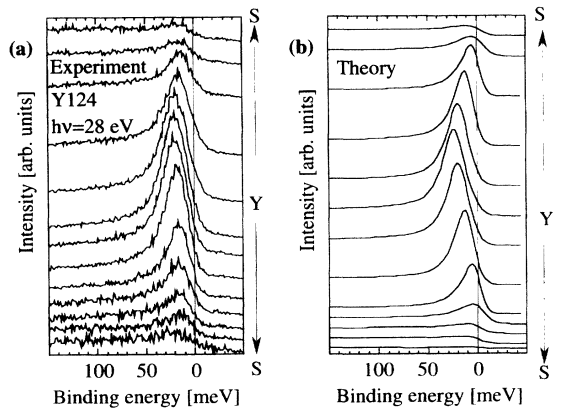


FIG. 3. Same as Fig. 2, except that here the $k_{\|}$ values are varied from Y towards the S point in a direction perpendicular to that of Fig. 2, showing the spectral feature dispersing towards E_F. Experimental and theoretical spectra are at the same momentum intervals (the emission angles vary by 1°).

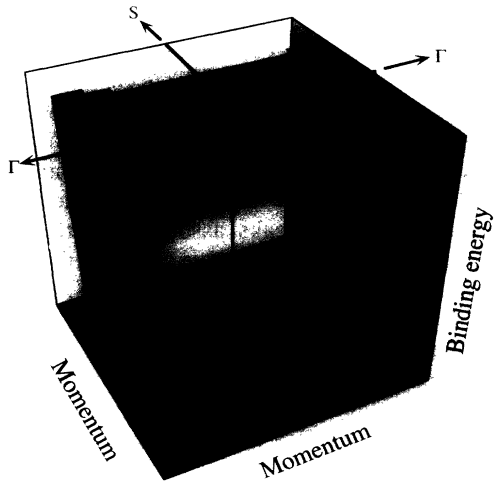


FIG. 5. A surface plot of the measured band dispersion around the Y point. The k_x and k_y axes cover an interval of 1 Å^{-1} centered on the Y point. The binding energy axis spans 0 to 60 meV.

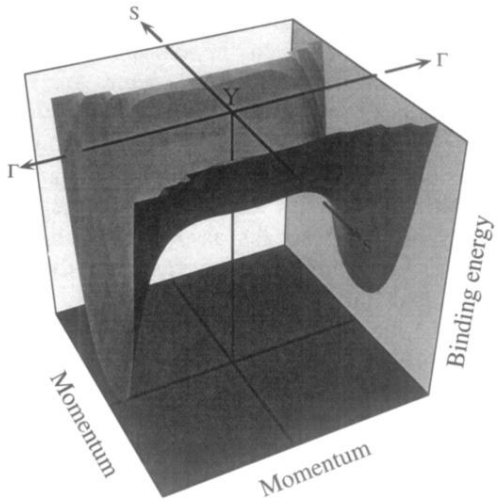
this second saddle point lies at a much higher binding energy compared to the feature in Fig. 1, making it less interesting from the viewpoint of superconductivity. The peak nearest E_F is excited strongly at 28 eV in the first and second BZ, while both peaks are excited at 21.1 and 17 eV in the second BZ.

As already noted, the saddle point singularities appear to be present in all the cuprates studied so far. They lie at the zone boundaries, extended along the direction of the Cu-O bonds. In materials such as Y124, Y123, Tl2212 [10], and Bi2212 [20], which possess T_c's of $\sim$100 K, the saddle points lie within 20 meV of E_F. These cuprates also display linear resistivity in the normal state, temperature independent thermopower, and other "unusual" properties. On the other hand, in NdCeCuO (T_c = 23 K), the saddle point binding energy is a few hundred meV [21], too high to significantly enhance T_c, and this material has normal state resistivity exhibiting the usual T^2 dependence. These observations suggest that the binding energy of the saddle point may be a useful parameter in classifying the cuprates.

In summary, we have directly observed an extended saddle point around the Y symmetry point in $YBa_2Cu_4O_8$ and shown that it arises from bulk electronic states related to the CuO_2 planes. Such an extended Van Hove singularity can easily explain the occurrence of high transition temperatures even in a conventional weak coupling BCS scheme. If this scenario is correct, one could conceivably obtain higher T_c's by "engineering" the electronic structure so as to increase the number and extension of saddle point singularities.

We thank R. S. Markiewicz for a discussion. This work was supported by the DOE under contract No. W-31-109-ENG-38, including a subcontract to Northeastern University; NSF Grants No. DMR 8914120, DMR 8809854, and DMR 91-20000, through the Science and Technology Center for Superconductivity; and benefited from a travel grant under the US-Finland program of the NSF, an ASLA-Fullbright travel grant, and the allocation of supercomputer time on the NERSC and Pittsburgh supercomputer centers.

[1] For a recent discussion see, *Spectroscopies in Novel Superconductors,* edited by F. M. Mueller, A. Bansil, and A. J. Arko, J. Phys. Chem. Solids, Vol. 54 (1993).
[2] J. E. Hirsh and D. J. Scalapino, Phys. Rev. Lett. **56**, 2735 (1986).
[3] J. Friedel, J. Phys. Condens. Matter **1**, 7757 (1989).
[4] R. S. Markiewicz, Int. J. Mod. Phys. B **5**, 2037 (1991).
[5] D. M. Newns *et al.,* Phys. Rev. Lett. **69**, 1264 (1992).
[6] C. C. Tsuei *et al.,* Phys. Rev. Lett. **69**, 2134 (1992).
[7] C. C. Tsuei *et al.,* Phys. Rev. Lett. **65**, 2724 (1990); C. C. Tsuei *et al.,* Phys. Rev. Lett. **68**, 1091 (1992).
[8] D. M. Newns *et al.* (to be published).
[9] P. C. Pattnaik *et al.,* Phys. Rev. B **45**, 5714 (1992).
[10] K. Gofron *et al.* (to be published).
[11] L. Van Hove, Phys. Rev. **89**, 1189 (1953).
[12] A. A. Abrikosov, J. C. Campuzano, and K. Gofron, Physica (Amsterdam) **214C**, 73 (1993).
[13] The experiment with finite resolution can, of course, only establish that the effective mass in the vicinity of the Y point is substantially greater than that near the Γ point. Under this assumption, Ref. [12] shows that the DOS peak will possess a power law divergence $(E - E_c)^{-1/2}$, even though the band dispersion is not absolutely flat. More generally, extended saddle points will possess higher power law divergences, which are nonetheless qualitatively different from logarithmic ones.
[14] A number of representative spectra taken above T_c indicate, however, that the present results are not affected significantly by the superconducting transition.
[15] A. Bansil *et al.,* J. Phys. Chem. Solids **53**, 1541 (1992); **54**, 1185 (1993); M. Lindroos et al., Physica (Amsterdam) **212C**, 347 (1993).
[16] Specifically, the muffin-tin potentials are the same as used previously in our work on the Y123 (see Ref. [15]), except that we have placed these on the base centered Y124 lattice. For the BaO/CuO_2 terminated surface used here we expect this to be a reasonable approximation, the Cu-O chain region where the Y123 and Y124 structures differ being six layers deep below the surface.
[17] D. Koelling *et al.* (unpublished); J. Yu *et al.,* Phys. Lett. **A 122**, 203 (1987); W. E. Pickett, R. E. Cohen, and H. Krakauer, Phys. Rev. B **42**, 8764 (1990); O. K. Andersen *et al.,* Physica (Amsterdam) **185C**, 147 (1991); J. Yu, K. T. Park, and A. J. Freeman, Physica (Amsterdam) **172C**, 467 (1991).
[18] The existence of a narrow feature in the ARPES spectra of Y123 has previously been reported by Tobin *et al.* [Phys. Rev. B **45**, 5563 (1992)], and Manzke *et al.* [Surf. Sci. **269**, 1066 (1992)]. However, the dispersion of the feature and in particular its interpretation in terms of an extended Van Hove scenario has not been considered before.
[19] K. J. Gofron, Ph.D. thesis, University of Illinois at Chicago 1993 (unpublished); K. Gofron *et al.,* J. Phys. Chem. Solids **54**, 1193 (1993).
[20] D. S. Dessau *et al.,* Phys. Rev. Lett. **71**, 2781 (1993).
[21] D. M. King *et al.,* Phys. Rev. Lett. **70**, 3159 (1993).



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