Extended Van Hove Singularity in a Noncuprate Layered Superconductor Sr_2RuO_4

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Angle-resolved photoemission spectroscopy was performed on a ruthenate superconductor Sr_2RuO_4 ($T_c \sim 1$ K) which has the same crystal structure as La_2CuO_4, but with RuO_2 layers replacing CuO_2 layers. Sr_2RuO_4 shows an *extended* Van Hove singularity (VHS) at 20 ± 2 meV below E_F just like the cuprates, regardless of the character of the electronic states at E_F. This suggests that the *extended* VHS is a general feature of a two-dimensional correlated *d*-electron metal. The observed Fermi surface is in contrast to local-density-approximation calculations.

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In understanding the mechanism of superconductivity in high transition temperature (high-T_c) cuprate superconductors, one of the most important questions today is: Given a pairing force originating in either electron-electron or electron-phonon interactions, or of a more exotic origin, how is the T_c enhanced to the experimentally observed transition temperatures? Theoretical studies have emphasized the importance of a Van Hove singularity (VHS) arising from a saddle point in the energy-versus-momentum (k) relation, which would provide a very high density of states at the Fermi level (E_F) as a possible cause for an enhanced T_c [1]. In a more recent study, the possibility of an electronic pairing mechanism based on the logarithmic VHS has been identified [2]. While there was indirect evidence for the existence of high density of states at E_F in the cuprates from various experiments [3], only very recent high-resolution angle-resolved photoemission studies have directly observed the VHS near E_F, possessing a saddle-point topology. Specifically, $YBa_2Cu_4O_8$ (Y124) exhibits an extended saddle-point singularity derived from energy bands of the CuO_2 planes positioned at 19 meV below E_F [4], observed as a sharp peak just below E_F over a wide range in k space in angle-resolved photoemission measurements. It was suggested that such an extended singularity could yield a power law divergence in the density of states and could give a T_c of order 100 K in a weak coupling BCS scheme. Similarly, $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and Pr-substituted $Bi_2Sr_2CuO_6$ (Bi2201) show extended VHS's within 30 meV of E_F [5,6]. On the other hand, $Nd_{2-x}Ce_xCuO_4$ (NCCO), the electron doped cuprate, also shows a saddle-point singularity [7], but not of the extended type and positioned far from E_F ($\sim$350 meV). These observations are thought to be consistent with the normal state resistivity which shows a T^2 dependence in NCCO as for a normal Fermi liquid, while the proximity of the VHS to E_F in the *p*-type high-T_c cuprates has been tied to the linear dependence of the resistivity on temperature. The main purpose of this Letter is to show that (1) the extended VHS is not a preserve of the cuprates; we observe it in the low-T_c layered superconductor, Sr_2RuO_4; and (2) while the position of the VHS ($= 20 \pm 2$ meV, just like the cuprates) and the temperature dependence of crossover from T^2 to T linear in resistivity seem consistent with the calculations of Newns *et al.* [8], the proximity of a VHS close to E_F does not guarantee high T_c. The results suggest that the extended VHS is a general feature of a two-dimensional correlated metal and imply that the high T_c of the cuprates compared to the ruthenate is derived from an additional mechanism such as a different coupling constant or interlayer coupling between the two systems.

In this study, we present results of high-resolution angle-resolved ultraviolet photoemission spectroscopy (ARUPS) of Sr_2RuO_4. This material has the same crystal structures as La_2CuO_4, but with RuO_2 planes replacing the CuO_2 planes. It exhibits superconductivity at 0.93 K [9] and a highly anisotropic resistivity for the in-plane and perpendicular to the plane components, both of which follow a T^2 dependence below 25 K like a typical correlated metal [9,10]. While La_2CuO_4 is an antiferromagnetic insulator, Sr_2RuO_4 shows enhanced Pauli paramagnetism [11]. A band structure calculation based on the local-density approximation (LDA) to the density functional theory using the linear augmented plane wave method [12] has shown that the Ru $4d\varepsilon(xy, yz, zx)$-O $2p\pi$ antibonding bands cross E_F, while it is well established in the high-T_c cuprates that the Cu $3d_{x^2-y^2}$-O $2p\sigma$ antibonding band crosses the E_F. Moreover, though the electronic states at E_F derived from Ru-O antibonding bands have a relatively high density of states giving a specific heat γ value of $\sim$10 mJ/K^2 mol, this calculated value is still much less than the observed γ value (39 mJ/K^2 mol) [9]. These observations point to the inadequacy of a simple one-electron picture to account for the properties of Sr_2RuO_4.

Single crystals of Sr_2RuO_4 were prepared by the floating zone method. The samples were characterized for structure using x-ray diffraction. Magnetic susceptibility

measurements confirmed the superconductivity at about 0.9 K. ARUPS measurements were performed using a high-resolution angle-resolved photoemission spectrometer constructed at Tohoku University. Samples were cleaved in an ultrahigh vacuum of better than 4×10^{-11} Torr at 20 K. All measurements have also been done at 20 K within 4 h of every cleaving, as the surface degraded beyond 6 h of cleaving as seen by the reduction in intensity of the sharp peak observed near E_F and a concomitant formation of the well-known contamination or degradation derived feature at about 10 eV binding energy. The contamination-derived feature at 10 eV binding energy is absent only for an atomically clean surface as has been established recently even for Ru oxides [13]. Energy and angular resolutions were 50 meV and less than 2°, respectively. A restricted set of measurements was carried out for the ΓZ direction at higher energy resolution of 30 meV to accurately determine the position of the VHS. The Fermi level was referred to that of a gold film deposited on the sample substrate. The results presented here were acquired from over 15 cleavings and reproducible dispersion was obtained, confirming that the results are intrinsic.

Figure 1 shows the ARUPS spectra of Sr_2RuO_4 along the ΓX, ΓZ, and perpendicular to the ΓZ direction (denoted by XX) of the Brillouin zone, measured at 20 K using the He I resonance line ($h\nu = 21.22$ eV). For the ΓX direction [Fig. 1(a)], we observe two bands located at about 0.1 and 0.4 eV binding energy and $\theta = 0°$ which is derived from Ru 4d and O 2p antibonding states. These bands approach E_F for increasing θ, before crossing it beyond $\theta = 16°$ and 20°, respectively. This is understood by the sharp decrease in intensity at E_F beyond $\theta = 20°$ and is consistent with crossings expected as in the band structure calculation reported by Oguchi [12]. While the crossing at 16° is not clear along the ΓX direction, an independent measurement along the c direction shows a definite crossing at $\theta = 16°$ as marked out in Fig. 2 where the E_F crossings are shown as filled circles. The circles indicate the positions corresponding to the measurement points in the Brillouin zone. For the ΓZ direction, however, the same bands become sharp on approaching E_F for increasing θ and remain as dispersionless sharp peaks at a binding energy of less than 30 meV below E_F over a wide region of the Brillouin zone [see Fig. 1(b)]. On further increase of θ, the feature broadens out and moves again to a higher binding energy, showing that it does not ever cross E_F along the ΓZ direction. In order to further investigate the nature of the band dispersion near E_F around the zone boundary, we measured along several lines perpendicular to the ΓZ direction and one special direction parallel to ΓX direction. The corresponding cuts in the Brillouin zone are shown in Fig. 2 as rows of circles labeled c, d, e, f, and g. Figure 1(c) shows the result obtained along cut e. [Note that $\theta = 0°$ in Fig. 1(c) corresponds to $\theta = 22°$ in Fig. 1(b).] As can be seen in Fig. 1(c), the narrow peak near E_F at $\theta = 0°$ disperses slowly towards E_F for increasing and decreasing θ values and crosses over to unoccupied states at $\theta = \pm 9°$, as is evident from the disappearance of the narrow peak at E_F. Thus, in contrast to a flat maximum observed along the ΓZ direction, the same sharp peak shows a minimum on the ΓZ high symmetry line in a direction perpendicular to it. This behavior is also observed for several cuts perpendicular to the ΓZ direction and the results are summarized in Fig. 3 where we show a surface plot of the dispersion of the singular feature as a function of the in-plane wave vector. As is clearly seen in Fig. 3, the sharp peak near E_F in Sr_2RuO_4

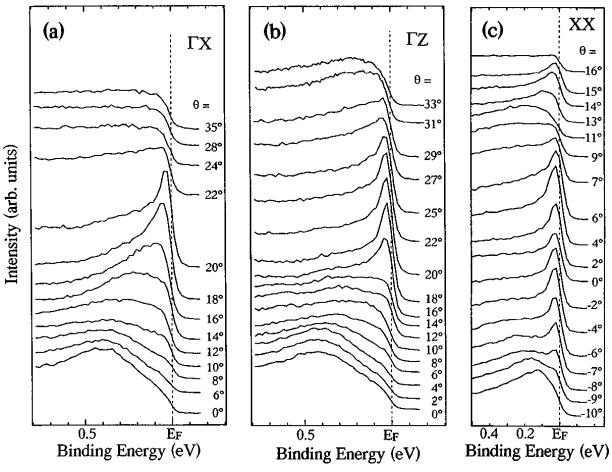

FIG. 1. ARUPS spectra of Sr_2RuO_4 in the vicinity of the Fermi level along (a) ΓX, (b) ΓZ, and (c) perpendicular to the ΓZ direction (denoted by XX) using He I photons ($h\nu = 21.22$ eV), measured at 20 K. Also see Fig. 2 for the Brillouin zone and the high-symmetry points of Sr_2RuO_4. The ΓZ direction corresponds to the Ru-O bonding direction.

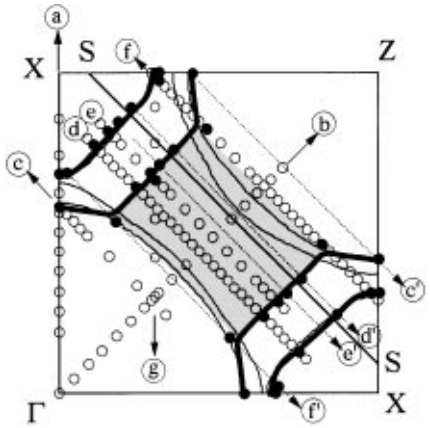

FIG. 2. Section of the calculated [12] (thin line) and observed (thick line) Fermi surface of Sr_2RuO_4 together with points in k space at which ARUPS measurements were performed (circles). Filled circles correspond to k points at which a band crossing is observed (cuts a–g) or expected to be observed (cuts c'–f') from symmetry. Shaded region corresponds to region in which the VHS lies within 30 meV of E_F.

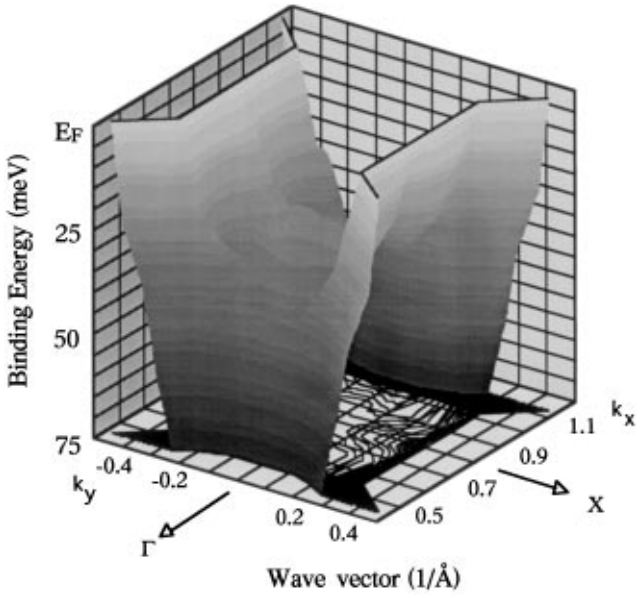

FIG. 3. A surface plot of the dispersion of the singular feature as a function of the in-plane wave vector, showing an extended saddle-point topology. A two-dimensional contour plot is shown in the k_x-k_y plane.

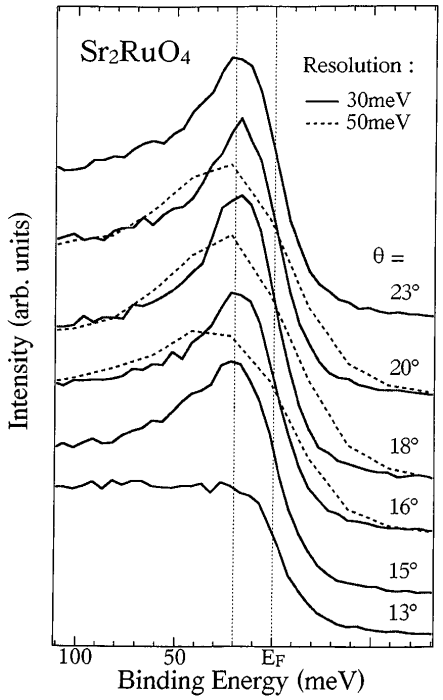

FIG. 4. ARUPS of Sr_2RuO_4 using 30 meV energy resolution (solid line) in the vicinity of E_F obtained at 20 K for several points along the ΓZ line. Broken lines are ARUPS using 50 meV resolution measured at the same k points. Note that positions of the sharp peaks of high-resolution spectra are about 20 ± 2 meV, which is closer to E_F than those of low-resolution spectra, indicating that the VHS lies at or less than 20 meV from E_F.

is a VHS possessing an "*extended*" saddle-point topology, just as is observed in the high-T_c cuprates [4–6].

In order to check the position of VHS more accurately so as to make comparisons with the VHS observed in the cuprates and to relate with the observed temperature dependence of resistivity, we performed high resolution ARUPS at several points along the ΓZ direction using 30 meV resolution. In Fig. 4, we display these results with the spectra measured at the same k points with a resolution of 50 meV (Fig. 1). The higher resolution spectra also exhibit the dispersionless sharp peak, i.e., *extended* VHS, from $\theta = 16°$ to 23°, in good agreement with the result shown in Fig. 1. But the position of the sharp peak in higher resolution spectra is 20 ± 2 meV in binding energy, closer to E_F compared to the lower resolution spectra, suggesting the position of VHS is less than or equal to 20 meV. The position of the VHS is thus exactly as is observed in the high-T_c cuprates. The existence of an extended VHS near E_F in Sr_2RuO_4 despite the different character of bands crossing E_F clarifies the following aspects in relation to the high-T_c cuprates. An extended VHS near E_F may be a necessary condition for high T_c, but is surely not a sufficient condition for the same. From a recent angle-resolved photoemission study of a low-T_c ($\sim$10 K) cuprate superconductor, King *et al.* [5] conclude that there seems to be no direct relation between a high T_c and the presence of an extended VHS. As for the present case, the relation between the position of VHS and the temperature dependence of resistivity, Newns *et al.* [8] have shown that the T-linear resistivity appears only above a temperature of approximately $\frac{1}{4}$ of the energy position of VHS. The position of VHS (20 meV−230 K) then suggests that the resistivity should exhibit T^2 behavior below about 60 K and is in fair agreement with experiments which show T^2 dependence below 25 K and a crossover to T-linear resistivity by about 100 K.

Finally, we discuss the Fermi surface topology of Sr_2RuO_4. Figure 2 shows the experimentally obtained Fermi surface (thick line) compared with that obtained from LDA calculations (thin line). Filled circles along the cuts *a*, *c*, *d*, *e*, *f*, and *g* are observed Fermi surface crossings and those along c', d', e', and f' are expected crossings from symmetry. The calculated surface shows two electron pockets centered at the Γ point and a hole pocket around the X point. While the hole pocket expected around the X point is observed experimentally, the two electron pockets are not observed. Instead, we observe an additional hole pocket around the X point. Though the possibility of an electron pocket around the Γ point cannot be ruled out with the present resolution, the observed Fermi surfaces with two hole pockets are in strong contrast to the LDA calculations. Our results seem consistent with the observation that the Hall coefficient is positive from room temperature up to about 10 K

though it changes sign below 10 K [14]. However, a recent de Haas–van Alphen (dHvA) effect measurement [15] has observed three Fermi surfaces as in the LDA calculations, though the nature of the Fermi surfaces being electron or hole type cannot be addressed by dHvA measurements. A possible explanation for the different Fermi surface observed in this study is that the surface potential could change the electron count at the surface and would make the Fermi surface topology different from that in the bulk. The possibility of a change of Fermi surface topology and a VHS along the ΓZ direction, but with a rigid band shift of approximately 0.2 electron, has been suggested by Singh [16]. But even in that case, the VHS is not of the extended type. Another explanation is that strong correlations change the band structure substantially, as is also supported from transport and magnetic measurements as well as a recent valence band resonant photoemission study [17] across the 4*p*-4*d* threshold which has identified the presence of a correlation induced satellite of the *d* band.

In conclusion, the similar nature of the extended VHS in Sr_2RuO_4 and the high-T_c cuprates regardless of the origin of the electronic states at E_F imply that the extended VHS is a general and characteristic feature of the electronic structure of two-dimensional correlated *d*-electron systems. On the other hand, the large difference of the superconducting transition temperature between Sr_2RuO_4 and the cuprates requests a reexamination of the VHS scenario and its relation to superconducting properties. The observed Fermi surface is in contrast to the LDA calculations. Further work on Sr_2RuO_4, in particular, neutron-scattering and/or nuclear-magnetic resonance studies to check for short-range antiferromagnetic correlations as the possible origin for the VHS [18], would be well worthwhile in understanding the phenomena of high-T_c superconductivity.

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[1] P. Horsch and H. Rietschel, Z. Phys. B **27**, 153 (1977); J. E. Hirsch and D. J. Scalapino, Phys. Rev. Lett. **56**, 2732 (1986); J. Labbe and J. Bok, Europhys. Lett. **3**, 1225 (1987); P. A. Lee and N. Read, Phys. Rev. Lett. **58**, 2691 (1987); J. Friedel, J. Phys. Condens. Matter **1**, 7757 (1989); R. S. Markiewicz, Int. J. Mod. Phys. B **5**, 2037 (1991).
[2] D. M. Newns, H. R. Krishnamurthy, P. C. Pattnaik, C. C. Tsuei, and C. L. Kane, Phys. Rev. Lett. **69**, 1264 (1992).
[3] C. C. Tsuei, D. M. Newns, C. C. Chi, and P. C. Pattnaik, Phys. Rev. Lett. **65**, 2724 (1990), and references therein.
[4] K. Gofron *et al.*, J. Phys. Chem. Solids **54**, 1193 (1993); A. A. Abrikosov, J. C. Campuzano, and K. Gofron, Physica (Amsterdam) **214C**, 73 (1993); K. Gofron *et al.*, Phys. Rev. Lett. **73**, 3302 (1994).
[5] D. S. Dessau *et al.*, Phys. Rev. Lett. **71**, 2781 (1993); D. M. King *et al.*, Phys. Rev. Lett. **73**, 3298 (1994).
[6] Jian Ma *et al.*, Phys. Rev. B **51**, 3832 (1995).
[7] D. M. King *et al.*, Phys. Rev. Lett. **70**, 3159 (1993).
[8] D. M. Newns, H. R. Krishnamurthy, P. C. Pattnaik, C. C. Tsuei, C. C. Chi, and C. L. Kane, Physica (Amsterdam) **186B**, 801 (1993).
[9] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1995).
[10] F. Lichtenberg, A. Catana, J. Mannhart, and D. G. Schlom, Appl. Phys. Lett. **60**, 1138 (1992).
[11] J. J. Neumeier *et al.*, Phys. Rev. B **50**, 17 910 (1994); R. J. Cava *et al.*, Phys. Rev. B **49**, 11 890 (1994).
[12] T. Oguchi, Phys. Rev. B **51**, 1385 (1995).
[13] A. Gulino, R. G. Egdell, P. D. Battle, and S. H. Kim, Phys. Rev. B **51**, 6827 (1995); P. A. Cox, R. G. Egdell, J. B. Goodenough, A. Hamnett, and C. C. Naish, J. Phys. C **16**, 6221 (1983).
[14] N. Shirakawa *et al.*, J. Phys. Soc. Jpn. **64**, 1072 (1995).
[15] A. P. Mackenzie *et al.* (private communication).
[16] David J. Singh, Phys Rev. B **52**, 1358 (1995).
[17] T. Yokoya *et al.*, Phys. Rev. B (to be published).
[18] E. Dagotto, A. Nazarenko, and A. Moreo, Phys. Rev. Lett. **74**, 310 (1995).