Fermi Surface, Surface States, and Surface Reconstruction in Sr$_2$RuO$_4$

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The electronic structure of Sr$_2$RuO$_4$ is investigated by high angular resolution ARPES at several incident photon energies. We address the controversial issues of the Fermi surface (FS) topology and of the van Hove singularity at the M point, showing that a surface state and the replica of the primary FS due to $\sqrt{2} \times \sqrt{2}$ surface reconstruction are responsible for previous conflicting interpretations. The FS thus determined by ARPES is consistent with the de Haas-van Alphen results, and it provides additional information on the detailed shape of the $\alpha$, $\beta$, and $\gamma$ sheets.

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Angle resolved photoemission spectroscopy (ARPES) has proven itself to be an extremely powerful tool in studying the electronic structure of correlated electron systems. In particular, in the case of the high-temperature superconductors, it has been very successful in measuring the superconducting gap, determining the symmetry of the order parameter, and characterizing the pseudo-gap regime. On the other hand one of the fundamental issues, namely the determination of the Fermi surface (FS) topology, has been controversial, as in the case of Bi$_2$Sr$_2$CaCu$_2$O$_8$, raising doubts concerning the reliability of the ARPES results. A similar controversy has also plagued the fermiology of Sr$_2$RuO$_4$. In this context, the latter system is particularly interesting because it can also be investigated with de Haas-van Alphen (dHvA) experiments, contrary to the cuprates, thus providing a direct test for the reliability of ARPES.

Whereas dHvA analysis, in agreement with LDA bandstructure calculations, indicates two electronlike FS ($\beta$, and $\gamma$) centered at the $\Gamma$ point, and a hole pocket ($\alpha$) at the X point, early ARPES measurements suggested a different picture: one electronlike FS ($\beta$) at the $\Gamma$ point and two hole pockets ($\gamma$, and $\alpha$) at the X point. The difference comes from the detection by ARPES of an intense, weakly dispersive feature at the M point just below $E_F$, that was interpreted as an extended van Hove singularity (evHs) pushed down below $E_F$ by electron-electron correlations. With the evHs below $E_F$, rather than above (LDA bandstructure calculations place it 60 meV above $E_F$), the $\gamma$ pocket is converted from electronlike to holelike. The existence of the evHs was questioned in a later photoemission paper, where it was suggested that dHvA and ARPES results could be reconciled by assuming that the feature detected by ARPES at the M point was due to a surface state (SS). Recently, two possible explanations were proposed: first, the evHs at the M point could be only slightly above $E_F$ (e.g., 10 meV), so that considerable spectral weight would be detected just below $E_F$. Alternatively, ARPES could be probing ferromagnetic (FM) correlations reflected by the existence of two different $\gamma$-FS (hole and electronlike, respectively, for majority and minority spin direction), which escaped detection in dHvA experiments. Lastly, the surface reconstruction as detected by LEED, which has been proposed to be indicative of a FM surface, would also complicate the ARPES data. The resolution of this controversy is important not only for the physics of Sr$_2$RuO$_4$ per se, but also as a reliability test for FS’s determined by ARPES, especially on those correlated systems where photoemission is the only available probe.

In this Letter, we present a detailed investigation of the electronic structure of Sr$_2$RuO$_4$. By varying the incident photon energy and the temperature at which the samples were cleaved, we confirm the SS nature of the near-$E_F$ peak detected at the M point, and we identify an additional dispersive feature related to the ‘missing’ electronlike FS ($\gamma$). A complete understanding of the data can be achieved only by recognizing the presence of shadow bands (SB), due to the $\sqrt{2} \times \sqrt{2}$ surface reconstruction which takes place on cleaved Sr$_2$RuO$_4$ (as confirmed by LEED). Despite the surface complications, the FS as determined by ARPES is consistent with the dHvA results, and provides additional information on the detailed shape of the $\alpha$, $\beta$, and $\gamma$ sheets.

ARPES data was taken at SSRL on the normal incidence monochromator beam line equipped with a SES-200 electron analyzer in angle resolved mode. With this configuration it is possible to simultaneously measure multiple energy distribution curves (EDC’s) in an angu-
labeled following the assignments which will be given in
2D projected zone (PZ). All the features in the data are
takenine cuts in the sketch depicting 1/4 of the
experiments [4–6] are indicated together with the experi-
mental measurements [2,3], and dHvA
α and measured at 10 K. The
better than 5x10
above
respect to each other on the basis of the spectral weight
talline gold. Different cuts were then normalized with
cut were normalized against those measured on polycrys-
taline gold. The angular resolution was 0.5
◦
and
0.3
◦
along the cut, corresponding to a k resolution of 1.5% of
the Brillouin zone (BZ), with 28 eV photons. The en-
ergy resolution was 14 meV for high-symmetry cuts and photon energy dependence, and 21 meV for the FS mappings. SrRuO
single crystals were oriented by Laue
diffraction, and then cleaved in situ with a base pressure
tor. In order to compensate for the angular response of the analyzer, EDC’s in a single cut were normalized against those measured on polycrys-
talline gold. Different cuts were then normalized with respect to each other on the basis of the spectral weight above EF integrated in both momentum and energy.
In order to begin the discussion of our experimental
results, let us first give an overview of the very rich pho-
toemission spectra, introducing all the features we will focus on throughout the paper. Fig. 1 presents EDC’s along the high-symmetry directions for SrRuO
cleaved and measured at 10 K. The α, β, and γ sheets of FS expected on the basis of LDA calculations are clearly resolved in the ARPES spectra. In order to order this issue, we measured the M point region (with cuts along ΓM–Γ) varying the incident photon energy between 16 and 29 eV, in steps of 1 eV. Here, we covered the location of β and γ pockets in both first and second zone for better illustration (i.e., four EF crossings will be observed). From the EDC’s shown in Fig. 2 for 16, 22, and 28 eV, we can see that the cross sections of SS, β, and in particular γ exhibit a strong (and different) dependence on photon energy (note that by working at lower photon energies the momentum resolution increases and, in turns, the number of EDC’s becomes progressively larger in going from panel c to a). At 28 eV,
$\beta$ and $\gamma$ crossings can be individually identified in the EDC’s. Owing to the high momentum resolution we can now follow the dispersion of the $\gamma$ peaks until the leading edge midpoints are located beyond $E_F$. After that, the peaks lose weight and disappear, defining the $k_F$ vectors for the electronlike $\gamma$ pockets. Right at $k_F$ we can resolve a double structure which then reduces to the non dispersive feature (SS) located 11 meV below $E_F$. The difference between the 28 eV results and those obtained at 16 or 22 eV is striking (the latter are consistent with those previously reported at similar photon energies [7,8]). At 16 eV it is impossible to identify the $\gamma$ crossings. At 22 eV the location of the leading edge midpoints is at best suggestive of the presence of the $\gamma$ crossings.

We have showed that the $\gamma$ electron pocket had so far escaped detection in ARPES because it is indistinguishable from the SS feature at low photon energy and/or low angular resolution. In order to have a full picture of the relevant issues to be addressed, let us proceed to the discussion of the FS mapping. Fig. 3a) shows the $E_F$ intensity map obtained at 28 eV on a Sr$_2$RuO$_4$ single crystal cleaved and measured at 10 K. The actual EDC’s were taken over more than a full quadrant of the PZ with a resolution of 0.3° (1°) in the horizontal (vertical) direction. The EDC’s were then integrated over an energy window of $\pm$10 meV about the chemical potential. The resulting $\beta$ and $\gamma$ crossings are weak but yet well defined profiles (marked in yellow). They can be recognized as a replica of the primary FS, and are related to the weak SB features detected in the EDC’s along the high-symmetry lines (Fig. 1a and 1b). This result is reminiscent of the situation found in Bi$_2$Sr$_2$CaCu$_2$O$_8$ where similar shadow bands are possibly related to AF correlations, or to the presence of two formula units in the unit cell [1]. On the other hand, in Sr$_2$RuO$_4$ the origin of the SB is completely different: inspection with LEED reveals superlattice reflections corresponding to a $\sqrt{2} \times \sqrt{2}$ surface reconstruction (see Fig. 3b), which is responsible for the folding of the primary electronic structure with respect to the $(\pi,0)-(0,\pi)$ direction. This reconstruction, which was found on all the Sr$_2$RuO$_4$ samples, is absent in the cuprates. Quantitative LEED analysis of the surface structure shows a 9° rotation of the RuO$_6$ octahedra around the surface normal. This leads to the 45° rotation of the in-plane unit cell and to the enlargement of its dimensions by $\sqrt{2} \times \sqrt{2}$ over that of the bulk [12]. The reconstruction, which reveals an intrinsic instability of the cleaved surface, should be taken into account as the origin of possible artifacts in all surface sensitive measurements.

By inspecting the M point (Fig. 3b), it now becomes clear why the investigation of this $k$-space region with ARPES has been so controversial: in addition to the weakly dispersive SS feature (Fig. 1b), there are several sheets of FS (primary and ‘folded’). At this point, the obvious question is: what is the nature of the SS feature? It has been proposed that it could be a surface state [9], and in order to verify this hypothesis, we investigated its sensitivity to surface degradation by cycling the temperature between 10 and 200 K. We observed that the SS peak is suppressed much faster than all other features. Furthermore, by cleaving the crystals at 180 K and immediately cooling to 10 K we suppressed the SS, affecting the intensity of the other electronic states only weakly. A more sizable effect is observed on the SB, confirming a certain degree of surface degradation. However, this degradation was not too severe, as demonstrated by the LEED pattern taken after the measurements which still clearly shows the surface reconstruction (Fig. 3d). M-region EDC’s measured at 10 K (on a sample cleaved at 180 K), and corresponding intensity plots $I(k,\omega)$ are shown in Fig. 3f, and 3g. No signature of the SS is detected, and the identification of the Fermi vectors of $\alpha$, $\beta$, and $\gamma$ pockets is now straightforward. Performing a complete mapping on a sample cleaved at 180 K, we obtained an extremely well defined FS (Fig. 4c). With the surface slightly degraded, we expect to see less of the relative intensity coming from SB and SS (note that the intensity scales in Figs. 3f and 3g, although not displayed, are identical). At the same time, we might expect also the primary FS to be less well defined, which is precisely opposite to what is observed. The FS shown in Fig. 4c is in very good agreement with LDA calculations [3,3] and dHvA experiments [1,1]. The number of electrons contained in the FS adds up to a total of 4, in accordance
with the Luttinger theorem, within an accuracy of 1% (as a matter of fact, for the FS determined on samples cleaved at 10 K the accuracy in the electron counting reduces to 3% due to the additional intensity of folded bands and surface state). As a last remark, we can confirm that the \( \alpha \) and \( \beta \) FS present the nested topology which has been suggested [13] as the origin of the incommensurate magnetic spin fluctuations later observed [14] in inelastic neutron scattering experiments at the incommensurate wave vectors \( \mathbf{Q} \approx (\pm 2\pi/3a, \pm 2\pi/3a, 0) \).

Our results confirm the surface state nature of the SS peak detected at the M point. The comparison of Figs. 3b and 3e suggests that a surface contribution to the total intensity is responsible also for the less well defined FS observed on samples cleaved at 10 K. At this point, one might speculate that these findings are a signature of the surface ferromagnetism (FM) recently proposed for \( \text{Sr}_2\text{RuO}_4 \) [11,12]. In this case, two different FS's should be expected for the two spin directions [11], resulting in: (i) additional \( E_F \)-weight near M due to the presence of a hole-like \( \gamma \) pocket for the majority spin; (ii) overall momentum broadening of the FS contours because the \( \alpha, \beta \), and \( \gamma \) sheets for the two spin populations are slightly displaced from each other in the rest of the BZ. Moreover, due to the surface-related nature of this effect, it would have escaped detection in dHvA experiments. In this scenario, a slight degradation of the surface would significantly suppress the signal related to FM correlations, due to the introduced disorder. The resulting FS would be representative of the non-magnetic electronic structure of the bulk (Fig. 6c). The hypothesis of a FM surface seems plausible because the instability of a non magnetic surface against FM order is not only indicated by \textit{ab initio} calculations [11], but it may also be related to the lattice instability evidenced by the surface reconstruction [12]. To further test this hypothesis, we suggest spinc-polarized photoemission measurements, and both linear and nonlinear magneto-optical spectroscopy experiments [i.e., magneto-optical Kerr effect (MOKE), and magnetic second-harmonic generation (MSHG), respectively].

In summary, our investigation confirms the SS nature of the weakly dispersive feature detected at the M point (possibly a fingerprint of a FM surface). On the basis of both ARPES and LEED, we found that a \( \sqrt{2} \times \sqrt{2} \) surface reconstruction occurs in cleaved \( \text{Sr}_2\text{RuO}_4 \), resulting in the folding of the primary electronic structure. Taking these findings into account, the FS determined by ARPES is consistent with the dHvA results and provides detailed information on the shape of the \( \alpha, \beta \), and \( \gamma \) pockets.

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