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Relationship of Sr_2RuO_4 to the superconducting layered cuprates

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The properties of Sr_2RuO_4 are discussed in relation to the high-critical-temperature cuprate superconductors. The discussion is based on local-density-approximation band structure and phonon calculations. The electronic structure is highly anisotropic. Three hybridized Ru $4d$–plane O p bands cross the Fermi energy, yielding cylindrical sheets of Fermi surface. Two of these are electronlike sheets around Γ, while the third is an X-centered hole surface. The electronlike sheets change topology as the energy is raised leading to Van Hove singularities in close proximity to the Fermi energy. In general, the electronic properties are related to those of the cuprates, with the exception that Coulomb correlations are expected to be much less significant due to the larger bandwidth and smaller on-site energy. Sr_2RuO_4 is expected to be a very useful reference material for interpreting experiments on the cuprate superconductors.

INTRODUCTION

Despite intense effort over more than eight years, the fundamental origin of high-critical-temperature superconductivity in layered cuprates remains an open question. The difficulty is at least in part due to the chemical and structural complexity of the layered cuprates, which often precludes clean and readily interpreted experiments. In the absence of a generally accepted microscopic theory, the search for new materials is frequently guided by the known common features of the present high-temperature superconductors (HTS), e.g., CuO_2 planes, proximity to magnetic insulating phases, layered crystal structures, etc.

The investigation of noncuprate materials with features in common with the HTS is important, both in establishing the importance of various features of the HTS and in providing guidance in the interpretation of experiments on the HTS. As such K_2NiF_4 structure Sr_2RuO_4 although known for several decades,[1] is now being investigated in detail. Besides its possible utility as a metallic substrate for the growth of HTS,[2] Sr_2RuO_4 has many features in common with the HTS: (1) It is isostructural with the first HTS,[3] $(La_{1-x}Sr_x)_2CuO_4$; (2) it contains flat RuO_2 planes analogous to the CuO_2 planes in the HTS; (3) it is a metal that becomes insulating and magnetic through changes in doping (e.g., $Sr_2Ir_{1-x}Ru_xO_4$) (Ref. 4) and is in proximity to a variety of magnetic phases (e.g., $SrRuO_3$);[5,6] and (4) the short Ru-O distances (1.94 Å) and metallic conduction are suggestive of significant transition-metal oxygen hybridization near the Fermi energy E_F.

Very recently, it has been reported that Sr_2RuO_4 is superconducting,[7] albeit at a low temperature around 1 K. Single-crystal resistivity data[7] shows a large anisotropy, $\rho_c/\rho_{ab}=850$ at 2 K and $\rho_c/\rho_{ab}=220$ at 290 K. Remarkably, it was also reported[7] that the in-plane resistivity ρ_{ab} has a linear temperature dependence from 20 to at least 300 K, with some structure around 130 K (note that this differs from an earlier measurement,[2] suggesting sample dependence). In the HTS, a linear resistivity is frequently observed near the optimally superconducting composition. This linear characteristic has in part motivated pictures of an unconventional normal state, such as a marginal Fermi liquid,[8] nested Fermi liquid[9] or Van Hove system.[10] Here I report calculations of the electronic structure of Sr_2RuO_4 as well as some Raman phonon frequencies. The electronic structure is similar to that obtained in a recent calculation using a linearized-augmented plane-wave method by Oguchi,[11] although there are some differences, discussed below. The results show considerable similarities with the HTS materials, but also significant differences; these may be helpful in sorting out the crucial aspects of the HTS.

METHOD

The computations were performed self-consistently within the local-density approximation (LDA) using a local orbital extension[12] of the general potential linearized-augmented plane-wave (LAPW) method.[13,14] The exchange-correlation parametrization was that of Hedin and Lundqvist.[15] Core states were calculated relativistically, while valence states were treated in a scalar relativistic approximation. Well converged basis sets consisting of approximately 1150 functions were used with LAPW sphere radii of 2.10, 1.95, and 1.65 a.u. for Sr, Ru, and O, respectively. Brillouin-zone averages were performed with 63 special **k** points in the irreducible 1/16 wedge (IBZ); 207 **k** points in the IBZ were used in computing the electronic densities of states (DOS). Use of this relatively large number of **k** points was necessary in order to obtain Fermi velocities converged to two figures. The experimental **a** and **c** lattice parameters were used but the two internal structural coordinates were calculated using the force method of Yu, Singh, and Krakauer.[16] This method was also used to determine, within the harmonic approximation, the fully symmetric Raman phonon modes corresponding to these two degrees of freedom.

The **a** and **c** lattice parameters were held fixed at their experimental values.[7]

STRUCTURE, PHONONS, AND IONIC CONSIDERATIONS

Sr_2RuO_4 occurs in the body-centered tetragonal K_2NiF_4 structure as does La_2CuO_4. The Ru atom and the two plane O [O(1)] atoms are coplanar and form a two-dimensional square lattice. Assuming completely ionic character (not the case—see below), the Ru would be in a $4+$, d^4 configuration. The Ru atom is coordinated above and below by the apical O(2) atoms in the double SrO rocksalt layers; the Sr atoms lie above and below the hollow spaces in the centers of squares formed by the Ru atoms. Our calculated heights (in units of the **c** lattice parameter with the RuO_2 layers at $z=0$ and $z=0.5$) are $z_{Sr}=0.3530$ and $z_{O(2)}=0.1615$. The perfect agreement with a recent low-temperature neutron determination[17] of $z_{Sr}=0.3534$ and $z_{O(2)}=0.1613$ is fortuitous but partially coincidental since the difference is smaller than the expected errors due to use of the local-density approximation.

The in-plane Ru-O(1) distance is 1.94 Å which is less than the sum of the Ru^{4+} and O^{2-} ionic radii suggesting the possibility of significant hybridization between these two atoms. The apical O(2) height is 2.06 Å—larger than the sum of the ionic radii. The rocksalt SrO bilayer is also distorted, with a Sr-O in-plane distance of 2.74 Å and a **c**-axis distance of 2.44 Å. Thus the SrO layers are under tensile stress in the **ab** plane, while the RuO_2 layers are compressed. This implies a tendency towards buckling of the RuO_2 sheets, perhaps similar to the tilts of the octahedra in La_2CuO_4 although no low-temperature transitions from long-range ordered tetragonal symmetry[7] were observed in Sr_2RuO_4.

The relative energies of the O 1*s* core levels provide information regarding the Madelung potentials and ionic charges. Although the LDA results in significant absolute errors in the core-level positions, it can reliably predict the relative positions of the core levels. For the calculated structure, the plane O(1) 1*s* core level is shifted to 1.45 eV higher binding energy than the corresponding apical O(2) level.

The two calculated fully symmetric zone-center Raman vibrations consist of nearly uncoupled Sr and O modes. The lower frequency (Sr) mode is at 194 cm^{-1}, while the upper O(2) mode is at 616 cm^{-1}. The corresponding frequencies[18] in La_2CuO_4 are 230 and 430 cm^{-1} implying a stiffer apical Ru-O(2) bond than the Cu-O(2) bond in the La_2CuO_4.

BAND STRUCTURE AND ELECTRONIC DENSITY OF STATES

The electronic band structure is shown in Fig. 1. The corresponding total and sphere projected density of states (DOS) is shown in Fig. 2. Strong hybridization between Ru and plane O(1) states is evident both through the similar shapes of the O(1) and Ru projections of DOS below the Fermi energy (E_F) and through the strong in-plane dispersions of the energy bands. From ionic considerations the bands below E_F are expected to contain four Ru 4*d* electrons, 12 O(1) *p* electrons and 12 O(2) *p* electrons for a total of 14 bands. In fact, as in the layered cuprates the O(1) atom has significant open shell character so that this ionic picture is only approximately correct. Also like the cuprates the apical O(2) atoms are

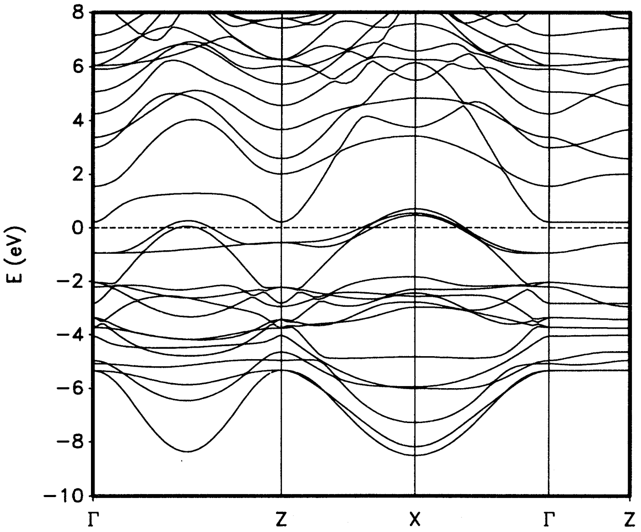

FIG. 1. Band structure of Sr_2RuO_4. The dashed horizontal line denotes the Fermi energy.

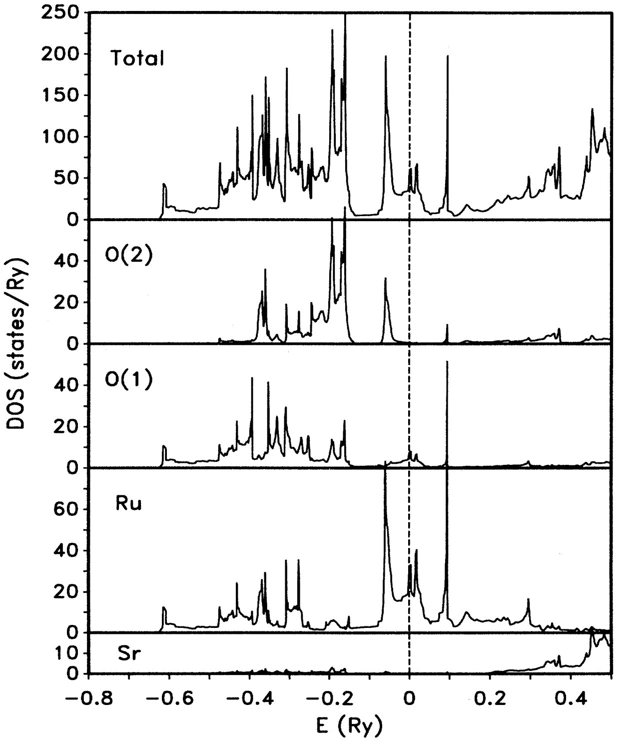

FIG. 2. Total and sphere projected electronic DOS of Sr_2RuO_4. The dashed vertical line denotes the Fermi energy. The projections are on a per atom basis.

quite ionic and have a more narrow $2p$ DOS than the O(1) atoms.

The bottom of the valence band occurs at -8.5 eV, relative to E_F and is derived from in-plane bonding combinations of Ru $4d$ and O(1) $2p$ states. The states near E_F are more strongly Ru $4d$ like, but still with some O $2p$ admixture, which is antibonding in character as found by Oguchi.[11] There are three bands crossing E_F along the Γ-X and Z-X lines; two also cross along the long Γ-Z direction; these give rise to three large cylindrical sheets of Fermi surface. E_F falls on the low-energy side of a sharp peak in the DOS. This peak occurs approximately 0.06 eV above E_F and is due to a Van Hove singularity (VHS).

A rigid band shift of approximately 0.2 electrons would position the Fermi energy at the first VHS. It would be interesting to determine the effect on the superconductivity of removing atoms from the O(2) site, if this proves possible, since removal of 0.1 O(2) atoms per cell may accomplish this shift. This VHS is due to the change in Fermi-surface topology that occurs at the band maximum of the lower of the two bands crossing E_F along the long Γ-Z direction. The upper of the two bands leads to a second VHS 0.26 eV or approximately 0.9 electrons above E_F. In the calculation of Oguchi, the two bands are closer together, and the VHS both occur at about 0.25 eV. This difference is important, since proximity to VHS can modify the transport properties, for example, providing a mechanism for a linear resistivity at low temperature, and has been much discussed in the context of the HTS. While I do not understand the reason for the difference, I note that the present calculation is considerably better converged both as regards the zone sampling and also as regards the basis set.

The DOS at E_F is $N(E_F)=56.2$ states/Ry, or 5% less than that determined by Oguchi and about twice the typical value per Cu atom for the HTS. I have searched for a possible ferromagnetic instability that can arise from high values of $N(E_F)$ but do not find one.

The band structure near and below E_F is strongly anisotropic, with very little c-axis dispersion. This is evident from the small dispersions along the short Γ-Z direction as well as the almost mirror symmetry of the bands about the center of the long Γ-Z direction. The Fermi surfaces in the basal plane (Fig. 3) show nearly square symmetry appearing almost the same when viewed from the Γ or Z points, also reflecting the very weak c-axis dispersions.

FERMIOLOGY

Fermi surfaces are shown in Fig. 3. As mentioned they consist of three cylindrical sheets. Two such sheets are large electronlike cylinders, centered at Γ and the remaining surface is a flattened holelike cylinder centered at X. The volumes enclosed are 0.28 holes for the X centered surface, 1.00 electrons for inner Γ centered surface and 1.28 electrons for the outer Γ centered surface. Thus there is one half-filled band, one band that is doped by 0.28 electrons away from half filling and a holelike band providing this doping. The HTS have one partially occupied antibonding $pd\sigma^*$ band per CuO_2 plane; this is doped away from half-filling by 0.15–0.2 holes for the highest T_c. The VHS occur when the Γ-centered surfaces touch along the long Γ-Z directions and become holelike sections centered at X. This is illustrated in Fig. 4, where the Fermi surfaces with E_F rigidly shifted to just above the first VHS.

The Fermi surface velocities $v_i=\langle v_i^2\rangle^{1/2}$ are $v_x=2.4\times10^7$ cm/s and $v_z=1.4\times10^6$ cm/s. The in-plane velocity is therefore similar to that determined by Oguchi, but the c-axis velocity is smaller yielding a larger anisotropy, v_x/v_z of approximately 17 (as opposed to 11). The difference may be due to the improved zone sampling in the present study. The Fermi velocities correspond to Drude plasma energies of $\hbar\Omega_{pxx}=\hbar\Omega_{pyy}=4.4$ eV and $\hbar\Omega_{pzz}=0.25$ eV. The values of v_x is similar to calculated in plane velocities for the HTS.[19] For example, $v_x=2.2\times10^7$ cm/s for $La_{1.85}Sr_{0.15}CuO_4$. Ω_{pxx} is, however, larger than in the single-layer cuprates due to the higher $N(E_F)$ in Sr_2RuO_4.

Bloch-Gruneisen transport theory leads to the formula,[19]

$$d\rho/dT=(8\pi^2/\hbar\Omega_p^2)k_B\lambda_{\mathrm{tr}} \tag{1}$$

valid at moderate to high temperatures where phonon scattering dominates. Here λ_{tr} is related to the conventional electron phonon coupling, λ but with different weights. If the resistivity is due to electron-phonon scattering and the scattering time is constant over the Fermi surface, a resistivity anisotropy $\rho_c/\rho_{ab}\approx300$ would result from the calculated plasma energies. Although this estimate is clearly based on a drastically oversimplified theory (note the observed temperature dependence of ρ_c) it is in the experimental range.

For a superconducting sample, Maeno *et al.*[7] obtain a roughly linear in-plane resistivity over a wide range ex-

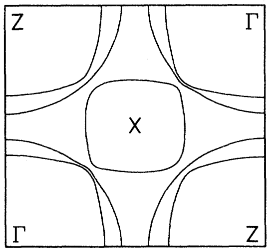

FIG. 3. Fermi surfaces of Sr_2RuO_4 in the basal plane of the body-centered-tetragonal zone.

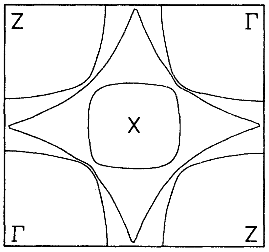

FIG. 4. Fermi surfaces with a rigid band shift close to the first VHS. Note the change in topology from Fig. 3.

tending up to 300 K, which is the highest temperature shown. For this sample, $d\rho_{ab}/dT = 6.7\times10^{-7}$ Ω cm/K; a similar value is obtained from the data of Lichtenberg *et al.* from 200 K to the highest reported temperature.[2] This results in a rather high $\lambda_{tr}\approx 3.2$, consistent with the enhancement of the low-temperature specific heat. This high λ_{tr} is of the same order as may be obtained for the HTS following the same prescription.[19] The linear coefficient of the specific heat has been measured as $\gamma = 39$ mJ/K^{2}mol for a superconducting sample.[7] The calculated $N(E_F)$ corresponds to a bare $\gamma_{\mathrm{band}} = 9.7$ mJ/K^2 yielding $\gamma/\gamma_{\mathrm{band}} = 4.0$, which is close to the above estimate of $(1+\lambda_{tr})$.

DISCUSSION

Sr_2RuO_4 is similar in many ways to the HTS, but with several differences that may or may not be important. Here I summarize the similarities and differences.

Among the similarities, (1) Sr_2RuO_4 has a layered crystal structure containing transition-metal oxide sheets with the same structure as the HTS; (2) it is near magnetic and insulating phases; (3) the electronic structure is quasi-two-dimensional; (4) there are Van Hove singularities in proximity to E_F; (5) the plane O(1) atoms are open shell and participate in the electronic structure at E_F; (6) there are near half-filled transition-metal d O(1) p antibonding bands crossing E_F; and (7) the Fermi surfaces are large and complex.

Differences include (1) $N(E_F)$ of Sr_2RuO_4 is about twice that of the HTS; (2) there are three plane derived Fermi surfaces rather than one as in the HTS and as a result the doping from half-filling does not depend on other layers in the crystal or nonstoichiometry; (3) the larger band width and the weaker effective intra-atomic Coulomb repulsion (U) expected for the 4d Ru ion relative to Cu imply that Sr_2RuO_4 is a much less strongly correlated electron system than the HTS; (4) the antibonding orbitals at E_F are derived from d_{xy}, d_{xz}, and d_{yz} combinations rather than the $d_{x^2-y^2}$ orbitals that point directly at the O(1) p_x and p_y lobes and may yield stronger electron-phonon couplings in the HTS, as discussed by Mattheiss;[20] and (5) the critical temperature is two orders of magnitude smaller than in the HTS.

The many similarities to the HTS combined with the lower critical temperatures in a system that clearly is not "strongly correlated" lends credence to the notion that studies of Sr_2RuO_4 may be very useful in unraveling experiments on the HTS.

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[1] J. J. Randall and R. Ward, J. Am. Chem. Soc. **81**, 2629 (1959).

[2] F. Lichtenberg, A. Catana, J. Mannhart, and D. G. Schlom, Appl. Phys. Lett. **60**, 1138 (1992).

[3] J. G. Bednorz and K. A. Muller, Z. Phys. B **64**, 189 (1986).

[4] R. J. Cava, B. Batlogg, K. Kiyono, H. Takagi, J. J. Krajewski, W. F. Peck, Jr., L. W. Rupp, Jr., and C. H. Chen, Phys. Rev. B **49**, 11 890 (1994).

[5] T. C. Gibb, R. Greatrex, N. N. Greenwood, D.C. Puxley, and K. G Snowdon, J. Solid State Chem. **11**, 17 (1974).

[6] J. J. Neumeier, A. L. Cornelius, and J. S. Schilling, Physica B **198**, 324 (1994).

[7] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994); see also Z. Fisk, *ibid.* **372**, 502 (1994).

[8] C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. E. Ruckenstein, Phys. Rev. Lett. **63**, 1996 (1989).

[9] A. Virosztek and J. Ruvalds, Phys. Rev. B **42**, 4064 (1990).

[10] R. S. Markiewicz, Int. J. Mod. Phys. B **5**, 2037 (1991).

[11] T. Oguchi, Phys. Rev. B **51**, 1385 (1995).

[12] D. Singh, Phys. Rev. B **43**, 6388 (1991).

[13] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[14] S. H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994), and references therein.

[15] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[16] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).

[17] J. J. Neumeier, M. F. Hundley, M. G. Smith, J. D. Thompson, H. Xie, W. Yelon, and J. S. Kim, Phys. Rev. B **50**, 17 910 (1994).

[18] L. Pintschovius, N. Pyka, W. Reichard, A. Y. Rumiantsev, N. L. Mitrofanov, A. S. Ivanov, G. Collin, and P. Bourges, Physica C **185-189**, 156 (1991).

[19] P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B **37**, 7482 (1988).

[20] L. F. Mattheiss, Phys. Rev. B **47**, 8224 (1993), and references therein.