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Electronic structure of magnetic Sr_2RuO_4

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Ab initio electronic structure calculations on Sr_2RuO_4, based on density functional theory within the generalized gradient approximation are reported. Contrary to calculations within the local density approximation, ferromagnetism is predicted. The results could have consequences for the interpretation of experiments which probe the Fermi surface and for the understanding of the unconventional superconductivity in Sr_2RuO_4. [S0163-1829(99)00415-4]

I. INTRODUCTION

The ruthenate Sr_2RuO_4 has attracted considerable interest since the discovery of superconductivity at temperatures below 1 K.[1] It is isostructural to the first high-T_c superconductor $La_{2-x}Ba_xCuO_4$, which has a critical temperature $T_c \approx 30$ K.[2] Sr_2RuO_4 is the only layered perovskite superconductor which does not contain copper.

The resistivity of Sr_2RuO_4 has a T^2 dependence at low temperatures, which indicates that the normal state is a Fermi liquid.[1] The large coefficient γ_0 in the specific heat and the enhanced magnetic susceptibility, as compared with RuO_2, could be signs of the presence of electronic correlations in the Fermi liquid.[3]

The variation of T_c with the coefficient γ_0 among different samples,[4] the influence of nonmagnetic impurities on T_c (Ref. 5), and the behavior of the nuclear spin-lattice relaxation rate $1/T_1$ in nuclear quadrupole resonance (NQR) measurements[6] show that the pairing state in Sr_2RuO_4 is of an unconventional nature. It has been suggested that the superconducting state of Sr_2RuO_4 is a realization of spin triplet pairing.[7] Triplet superconductivity could be induced by ferromagnetic fluctuations.[8]

The magnetic susceptibility of Sr_2RuO_4 is quite temperature independent.[3] The rather large dependence of the susceptibility on the temperature, reported in earlier papers,[9,10] was presumably due to the presence of ferromagnetic $SrRuO_3$ impurities. The magnetic properties of the iridium-doped compounds $Sr_2Ir_{1-x}Ru_xO_4$ (Ref. 11) and of the Ruddelsdon-Popper-type series $Sr_{n+1}Ru_nO_{3n+1}$, which are ferromagnetic metals for all $n \geq 2$,[12] show, however, that Sr_2RuO_4 is on the edge of ferromagnetism.

Electronic structure calculations, based on density functional theory (DFT) within the local density approximation (LDA), showed a nonmagnetic electronic structure,[13,14] while it was pointed out that no ferromagnetic instability could be found.[14] These calculations resulted in a Fermi surface which was consistent with de Haas–van Alphen (dHvA) measurements.[15] Angle-resolved photoemission spectroscopy (ARPES) experiments showed, however, a different Fermi surface.[16,17] The differences were ascribed to the fact that the photoemission experiments probed the surface while the dHvA results are more representative for the bulk.[18]

We report electronic structure calculations on Sr_2RuO_4, calculated within the scope of DFT as well, but with gradient corrections to the exchange correlation energy included. In contrast with LDA calculations, the ground state is magnetic. The results could have consequences for the interpretation of Fermi surface experiments and for models which describe spin triplet superconductivity.

II. METHOD

Self-consistent calculations are performed with the full potential linearized augmented plane wave (LAPW) method.[19] Exchange and correlation were treated within the generalized gradient approximation (GGA).[20] For comparison, calculations within the LDA approach were performed as well. The valence band states were treated in a scalar relativistic approximation, while the core states were calculated relativistically. The experimental equilibrium crystal structure was used.[21] The electronic structures of nonmagnetic (NM) and ferromagnetic (FM) Sr_2RuO_4 as well as two antiferromagnetic (AF) phases were calculated. The basis set contained more than 1100 plane waves in the NM and FM calculations and was extended with local orbitals for a better description of semicore states. Since the unit cell of the antiferromagnetic phases was twice as large as the primitive unit cell, the number of plane waves was doubled in these cases. The sphere radii used in the calculations were 2.2, 1.6, 2.02, and 2.15 atomic units for the Sr, Ru, O(1) (in-plane oxygen), and O(2) (apical oxygen) spheres, respectively. The Brillouin zone (BZ) integration was performed using the modified tetrahedron method on a special mesh of 240 k points in the irreducible part of the BZ of the primitive unit cell. Such a high number of k points was necessary in order to reliably calculate the energy difference between the NM and FM phases, due to slow convergence of the NM phase with respect to the number of k points. The k-point density was twice as small in the calculations with a doubled unit cell. This was possible since the energy difference between the different magnetic phases converged much faster with respect to the number of k points than the energy difference between the FM and NM phases.

III. RESULTS

The electronic structure of Sr_2RuO_4, calculated within the LDA approach, is in full agreement with previously reported

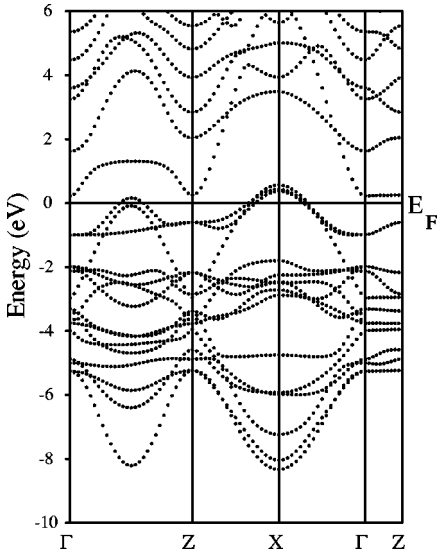

FIG. 1. Band structure of the majority spin channel of ferromagnetic Sr_2RuO_4.

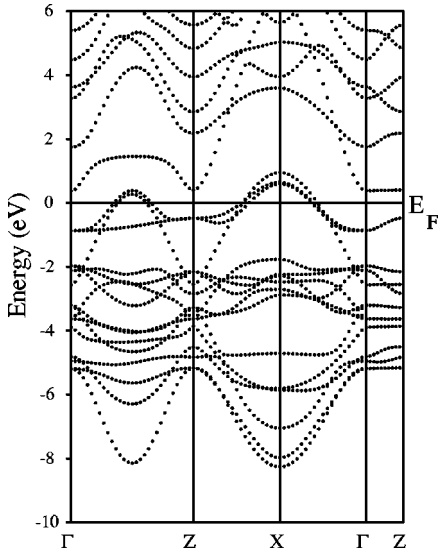

FIG. 2. Band structure of the minority spin channel of ferromagnetic Sr_2RuO_4.

calculations. In summary, the band structure is strongly anisotropic due to the layered crystal structure. The wave functions near the Fermi energy are formed by strongly hybridized Ru $4d(t_{2g})$ and in-plane oxygen $2p$ states. The Fermi surface consists of two electronlike, almost cylindrical sheets centered at the Γ point and one holelike sheet centered at X. A van Hove singularity (VHS) is present just above the Fermi energy. We refer to the papers by Oguchi[13] and Singh[14] for a complete discussion on the LDA band structure.

The electronic structure of nonmagnetic Sr_2RuO_4, calculated within GGA, shows only minor differences with the LDA results. The valence band width is approximately 0.1 eV smaller, the first VHS above the Fermi energy lies 0.01 eV closer to the Fermi energy, while the lengths of the Fermi wave vectors k_F are the same within 1%. The topology of the electronic bands and the Fermi surface is identical. The small differences in the electronic structure can be attributed to a slightly stronger localization of electrons.

However, the nonmagnetic phase of Sr_2RuO_4 is not the ground state within the GGA approximation. Whereas LDA shows no sign of magnetism, with gradient corrections included a ferromagnetic phase is found with a total energy which is 4 meV/Ru ion lower than the NM total energy.

The band structure of FM Sr_2RuO_4 is shown in Figs. 1 and 2. Figure 3 shows the total and sphere projected electronic density of states (DOS). The electronic structure shows a small exchange shift between the majority and minority electron energies. The exchange shift, being somewhat dependent on the energy and on the k vector, is approximately 0.2–0.4 eV in the region near the Fermi energy. As a result, the unit cell bears a net magnetic moment of $0.5\mu_B$. Due to the strong Ru-O hybridization at the Fermi energy, the magnetic moment is distributed among the Ru ($0.25\mu_B$/ion) and O(1) ($0.07\mu_B$/ion) spheres, as well as in the interstitial space.

The DOS at the Fermi energy is 1.87 states/eV for the majority spin direction and 1.44 states/eV for the minority channel, adding up to 3.31 states/eV per cell. This is 25% smaller than the nonmagnetic DOS at the Fermi energy.

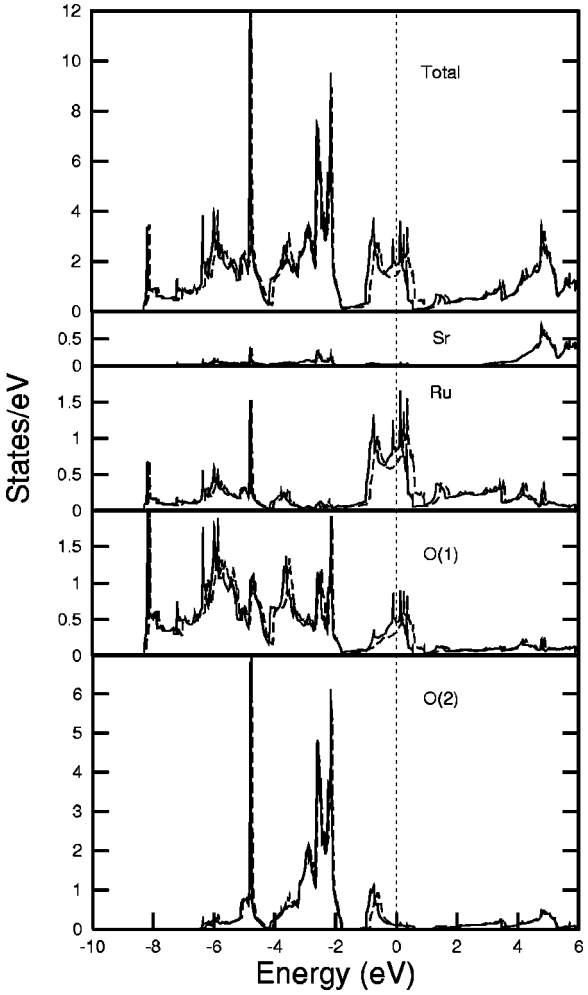

FIG. 3. Total and sphere projected density of states of ferromagnetic Sr_2RuO_4. The solid (dashed) lines denote the density of states of the majority (minority) spin direction.

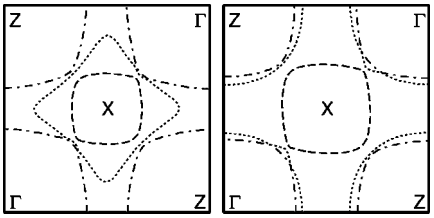

FIG. 4. Fermi surface of ferromagnetic Sr_2RuO_4. The left (right) figure shows the Fermi surface of the majority (minority) spin direction.

An important feature of the electronic structure is the position of the VHS which lies just above the Fermi energy according to the nonmagnetic calculations. Due to the exchange shift the VHS is spin split and is now positioned at 0.27 eV above the Fermi energy for the minority spin direction. However, in the majority channel the VHS is pulled down to 0.09 eV *below* the Fermi energy.

Another consequence of the spin-split electronic structure is the different Fermi surface of the two different spin directions (Fig. 4). The Fermi surface has a quasi-two-dimensional character due to the small dispersion in the *c* direction. Therefore, only the Fermi surface in the basal plane is shown. The Fermi surface of the majority spin direction consists of one almost cylindrical electronlike sheet, centered at the Γ point, and two holelike sheets centered at the *X* point. The minority spin direction shows a Fermi surface with two electronlike sheets and one holelike one. The topology of the minority Fermi surface is similar to the calculated NM Fermi surface. Table I shows the effective masses, the number of electrons and the dHvA frequencies associated with the Fermi surface sheets.

Besides a FM phase, a magnetic phase with a zero net magnetic moment was found. In this antiferromagnetic phase, the magnetic moments on the Ru ions within a basal plane were ferromagnetically ordered, while the magnetic moments of successive RuO_2 planes were antiparallel aligned. The total energy of the AF phase was even lower than the FM phase, although the energy difference was very small (≈ 0.1 meV/Ru ion), again reflecting the small interactions in the *c* direction.

The band structure of the AF phase is very similar to the FM band structure, which can be understood by the two-dimensional character of the electronic structure. Due to the small interactions in the stacking direction the AF band structure is basically a superposition of the majority and minority band structures of the FM phase. As a consequence, many features of the electronic structure are the same. As in the FM phase, the AF electronic structure shows a VHS just below (now 0.11 eV) the Fermi energy. The sphere projected densities of states are similar, except for a reversal of the spin up and spin down densities at every other plane. The magnetic moments within the atomic spheres are the same within $0.01\mu_B$. The Fermi surface consists of three electronlike and three holelike sheets per spin direction.

We also searched for a magnetic solution with magnetic moments of nearest neighbor Ru ions antiparallel aligned. By keeping these moments antiparallel during the self-consistency cycle the calculation always converged to the NM solution.

TABLE I. Calculated Fermi surface properties: effective mass, number of electrons, and dHvA frequency associated with each sheet (see Fig. 4).

Sheet	h/e	$m^*(m_e)$	Electrons	F (kT)
Majority				
1	*e*	2.3	0.57	16.0
2	*h*	−2.7	0.75	6.9
3	*h*	−0.9	0.90	2.8
Minority				
1	*e*	1.6	0.44	12.2
2	*e*	1.7	0.49	13.6
3	*h*	−1.1	0.84	4.6

IV. DISCUSSION

The application of GGA should be considered with caution. GGA is often, but not necessarily always, a better approximation than LDA. This should be kept in mind when discussing the results. GGA consistently yields larger Stoner factors for magnetic materials than LDA, due to the slightly more localized wave functions it produces. Since Sr_2RuO_4 is already close to a Stoner instability within LDA, it is not completely unexpected that GGA results in a magnetic ground state. Further, it is remarkable that antiferromagnetism wins over ferromagnetism, with a very small energy difference. This could be due to a weak superexchange interaction, which is overestimated in LDA and GGA.[22]

The results show that the ground state exhibits ferromagnetic ordering within basal RuO_2 planes. However, the ground state, as probed experimentally, is a superconductor rather than a ferromagnetic metal. Both ferromagnetism and superconductivity are symmetry-breaking phenomena which lower the density of states at the Fermi energy. There is a competition between ferromagnetism and superconductivity at very low temperatures, leading to a superconductive ground state, which *ab initio* electronic structure methods are not able to predict. Nevertheless, it is noteworthy that nonmagnetic Sr_2RuO_4 is not the ground state according to the calculations.

Although the ground state is superconducting rather than ferromagnetic, magnetism could be important for the nature of the superconductivity. The calculations show that the first VHS above the Fermi energy is pulled down to below this energy in magnetic Sr_2RuO_4. The importance of the presence of a VHS at or near the Fermi energy is widely discussed in the context of high-T_c superconductivity. Further, ferromagnetic fluctuations are responsible for the spin triplet pairing state, while there are possible consequences of antiferromagnetic spin fluctuations for the unconventional superconductivity. It is desirable that these consequences are considered in further research on the theory of unconventional superconductivity.

The calculated band structure of FM Sr_2RuO_4 shows resemblance to the band structure as probed by ARPES experiments, especially as far as the VHS just below the Fermi energy is concerned. This leads to the question of to what extent magnetism plays a role in Sr_2RuO_4 above T_c.

First of all, it is, in principle, possible that bulk

Sr_2RuO_4 shows ferromagnetism in the temperature region just above the superconducting critical temperature of 1 K. Several experiments seem to exclude this possibility. The magnetic susceptibility is almost constant, although it shows a weak temperature-dependent behavior even in the best samples,[3] which could be due to some ferromagnetism. Further, dHvA experiments showed merely three Fermi surface sheets, while in magnetic Sr_2RuO_4 six sheets would be present due to the exchange splitting. It cannot completely be excluded that some of the sheets are missed by the dHvA measurements due to high effective masses. Nevertheless, it seems unlikely that bulk Sr_2RuO_4 is magnetic at any temperature.

Although the bulk is nonmagnetic, it is possible that the surface of Sr_2RuO_4 is magnetic at low temperatures, just above T_c. This could in principle be detected by spectroscopy experiments which probe the surface rather than the bulk. As mentioned before, ARPES experiments revealed a VHS just below the Fermi energy, just like the calculation of FM Sr_2RuO_4. These experiments showed merely three Fermi surface sheets as well. However, the Fermi surface was reconstructed from peaks in the measured spectra which were actually rather broad. In fact, the exchange shift in Sr_2RuO_4 is of the same order of magnitude as the experimental resolution in most spectroscopy experiments,[16,17,23–25] which hampers the detection of surface magnetism. It cannot be excluded that, since some of the sheets are rather closely positioned, the ARPES experiments accidentally detected one peak where there should be two or three. It is suggested that the majority sheet 1, together with the minority sheets 1,2 (see Fig. 4) were seen as one sheet, and sheets 3 of both spin directions as one sheet as well. It is remarked, however, that the position of the VHS may be a result of structural phenomena, e.g., surface reconstruction. Therefore it remains an open question whether the surface of Sr_2RuO_4 exhibits ferromagnetism. A clear sign of surface magnetism could be given by, for instance, the measurement of the nonlinear magneto-optical Kerr effect.[26]

Finally, ferromagnetic fluctuations may be present above T_c in Sr_2RuO_4. Since the characteristic time scale of dHvA experiments, which is determined by the cyclotron frequency, is much larger than the time scale in photoemission, the difference between these experiments can be understood if the ferromagnetic fluctuations appear on a time scale in between.

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