Orbital physics in ruthenates: first-principles studies

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Abstract. In this review, we concentrate on the orbital physics in ruthenates. Two issues will be addressed. One is related to the spin/orbital ordering in Ca$_{2-x}$Sr$_x$RuO$_4$. Based on detailed first-principles calculations, we will discuss the crucial role of orbital degree of freedom and its relationship to structure distortions and magnetic properties. The orbital-dependent magnetic phase control in Ca$_{2-x}$Sr$_x$RuO$_4$ will be illustrated. The second issue is concerned with the electronic state and quantum transport in the presence of the spin order, namely the anomalous Hall effect (AHE) in ferromagnetic Ca$_{1-x}$Sr$_x$RuO$_3$. By detailed first-principles calculations and comparison with experimental result, we provide firm evidence for the intrinsic mechanism of AHE due to the existence of Berry phase in the presence of spin–orbital coupling, which is entirely topological.
1. Introduction

The role of the orbital degrees of freedom in transition metal oxides is one of the key issues in the physics of strongly correlated electronic systems. In particular, the interplay among the charge, spin and orbital degrees of freedom plays an essential role in determining the transport, optical, thermal and magnetic properties of those systems. In this paper, we give a comprehensive review on the various aspects of Ru oxides with a focus on the orbital degrees of freedom. There are several reasons to choose this family of compounds: (i) there are four electrons in the t_{2g} orbitals of the 4d level for Ru^{3+} and orbital degrees of freedom are active; (ii) the relativistic spin–orbit coupling (SOC) is reasonably large (∼0.3 eV for atomic value), which may lead to various nontrivial effects in solids; and (iii) the electron correlation is moderately large leading to the various orderings, while the first-principles band calculations give a solid foundation to the understanding of these materials.

In this paper, we discuss (1) the spin and orbital orderings in Ca_{2−x}Sr_{x}RuO_{4} and their relation to the structure of the crystal and (2) the anomalous Hall effect (AHE) in ferromagnetic Ca_{1−x}Sr_{x}RuO_{3} from the viewpoint of the magnetic monopole in momentum space. The first point is concerned with the question: what determines the spin/orbital order? There are basically two possible candidates for the key factors, one being the electron–lattice coupling including Jahn–Teller (JT) distortion and lattice structure and the other being the electron–electron interaction, and it is one of the main subjects of our study to identify the most dominant one. This is especially important when one goes beyond the ground state and discusses various physical properties by constructing the model Hamiltonian. Often one may start with the strong-correlation model chosen by one’s taste, but a solid base is needed to specify the model for each material. For this purpose, we employ the unbiased first-principles band calculation taking into account the precise structure of the material obtained from experiments. Ca_{2−x}Sr_{x}RuO_{4} has attracted intense interest because of the rich phase diagram including the p-wave superconductor Sr_{2}RuO_{4} and the antiferromagnetic (AF) Mott insulator Ca_{2}RuO_{4} at the two ends [1]–[13]. Therefore by changing the concentration x, it is expected that the strength of the electron correlation will change. At the intermediate point x = 0.5, a novel crossover has been observed from the nonmagnetic (x > 0.5) to nearly ferromagnetic metallic (x < 0.5) states. This has motivated several theorists to consider the role of the orbital degrees of freedom in the Mott transition [5], [8]–[13]. In particular, Anisimov et al [9] proposed the orbital-selective...
Mott transition where the $yz/zx$-bands of Ru-4d become Mott insulating while the $xy$-band remains itinerant. This is a fundamentally important problem in the physics of transition metal oxides in general and needs further scrutiny. Here, it is noted that it is too naive to model this system just by changing $U/t$. For example, in a real system $\text{Ca}_2-x\text{Sr}_x\text{RuO}_4$, the rotation, tilting and flattening of the octahedron play crucial roles as will be shown below by our first-principles band calculation.

The second topic of this paper is concerned with the electronic state and quantum transport in the presence of spin order. AHE is a phenomenon which occurs when the Hall resistivity $\rho_H$ contains the anomalous contribution associated with the magnetization in addition to the usual one proportional to the external magnetic field. This effect has been known for many years experimentally, but its origin is still controversial. Namely, the electric distribution is determined by the balance between acceleration due to the external electric field and the relaxation due to impurity scatterings, etc, which is not taken into account in the first theory proposed by Karplus–Luttinger [14] based on band theory. In contrast to this intrinsic mechanism, extrinsic mechanisms such as skew scattering and side-jump have been advocated [15, 16]. The main reason why this issue has not been settled is the absence of a reliable calculation to be compared with the reliable experiments in the clean sample. $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ is an ideal system for this purpose since (i) the residual resistivity is relatively small ($<50 \mu\Omega \text{cm}$), (ii) it is a typical itinerant ferromagnet with $T_c \approx 100$ K, and (iii) the relativistic spin–orbit interaction is expected to be effective. We have recently carried out a detailed band calculation on $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ and obtained the transverse conductivity $\sigma_{xy}$ based on the band mechanism of Karplus–Luttinger. We obtained a good agreement with the experiments, which provides the first evidence for the intrinsic mechanism of the AHE [17]. Here, the quantum interference of the Bloch waves in the ferromagnetic state is crucial, which is modified by the relativistic spin–orbit interaction in an essential way. This leads to nontrivial quantum topological properties which are represented by the gauge field (Berry phase) in the momentum space. Hence, the effect is non-perturbative, i.e., the perturbative expansion with respect to the spin–orbit interaction as assumed in Karplus–Luttinger is not allowed. The singularity due to the band crossing, i.e., the magnetic monopole, plays the crucial role here, which is evidenced by the non-monotonic temperature dependence of the AHE as will be discussed in section 4. The plan of the paper is as follows. We describe our method in section 1. In section 2, we study the spin and orbital orderings in $\text{Ca}_2-x\text{Sr}_x\text{RuO}_4$. Firstly, we describe the magnetic instability induced by the rotation, tilting and flattening of the octahedron in the general framework. Then, using the experimentally observed structural data, we discuss the orbital state in the real system $\text{Ca}_2-x\text{Sr}_x\text{RuO}_4$. In section 3, the theory of AHE based on the quantum topology of the Bloch wavefunction is described for $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$.

2. Method

The results presented here are based on the first-principles calculations [18]. We used the plane-wave basis pseudo-potential method. The $2p$ states of oxygen and $4d$ states of Ru are treated by the Vanderbilt ultra-soft pseudo-potential (USPP) [19], while the norm-conserving scheme [20] is used for other states. The USPP is useful not only for efficient calculations of transition metal oxides but also for implementing the LDA + $U$ [21] method to treat the effects of strong correlation. In the LDA + $U$ method, the strong Coulomb interaction is explicitly taken into account in the subspace of localized orbitals through a Hartree-like scheme. For calculations of
the conductivity tensor, we need to evaluate the matrix elements of the momentum operator. For this purpose, we use the converged Kohn–Sham eigenfunction but with the core-compensation term added [22]. For all the calculations, we use a cut-off energy of 30 Ryd for the wavefunction expansion. The $k$-point sampling of the Brillouin zone was well checked to provide enough precision to the calculated total energies.

3. Orbital physics in Ca$_{2-x}$Sr$_x$RuO$_4$

The main purpose of this section is to understand the complicated magnetic phase diagram of Ca$_{2-x}$Sr$_x$RuO$_4$ in terms of the orbital physics. Since the substitution in Ca$_{2-x}$Sr$_x$RuO$_4$ is isovalent, which does not change the number of valence electrons, the dominant effects of substitution should be the structural modifications due to the reduced ionic size of Ca compared with Sr (ionic radii being 1.00 and 1.13 Å for Ca$^{2+}$ and Sr$^{2+}$, respectively). Therefore, in section 3.1, we will concentrate on the crucial role of lattice distortions. We will study how and why the magnetism of Ca$_{2-x}$Sr$_x$RuO$_4$ is affected by the structure distortions. For this purpose, we employ the LDA for all the doping ranges to avoid any ambiguity introduced by the $U$ term in the LDA + $U$ method. Furthermore, we use Sr$_2$RuO$_4$ instead of Ca$_{2-x}$Sr$_x$RuO$_4$ by neglecting the alloying effect of the (CaSr) random potential, but take into account the structural distortions artificially by modifying the structure of Sr$_2$RuO$_4$. Then in section 3.2, we will study orbital physics related to the structure distortions by using the experimental atomic positions, and the effect of $U$ especially for the Ca-rich side will also be considered.

3.1. Crucial role of lattice distortions

Three main types of structural distortions are identified from experiments [4], namely, RuO$_6$ octahedron rotation around the $c$-axis, RuO$_6$ tilting around an axis parallel to the edge of the octahedron basal plane and the flattening of RuO$_6$ along the $c$-axis. We can introduce the rotation and tilting by keeping the Ru–O lengths, and the flattening by keeping the RuO$_6$ volume unchanged. For each fixed structure, three different magnetic states (non-magnetic (NM), ferromagnetic (FM) and staggered AF) are calculated. Then a magnetic phase diagram (as shown in figure 1) can be constructed by searching the lowest energy state among three calculated states. Here, we use $\phi$ and $\theta$ to denote the rotation and tilting angle respectively, and the degree of flattening of RuO$_6$ octahedron can be defined as $\lambda = d_c/d_{ab}$ with $d_c$ ($d_{ab}$) denoting the Ru–O bond length along the $c$-axis (in the $ab$ plane). The apical oxygen and the oxygen in the $ab$ plane are called O(2) and O(1) respectively. From right to left of the phase diagram, first the RuO$_6$ starts to rotate along the $c$-axis by up to 12°, and then with the 12° rotation being fixed, the RuO$_6$ starts to tilt up to 12°.

Structural analysis by neutron scattering [4] allows us to make a one-to-one correspondence between the structural changes, i.e., the horizontal axis of our phase diagram, and the doping level $x$ in Ca$_{2-x}$Sr$_x$RuO$_4$. For $x = 2.0$ (Sr$_2$RuO$_4$), the system has $I4/mmm$ symmetry with $\phi = \theta = 0°$, corresponding to the right end of our phase diagram. With reduction of $x$, RuO$_6$ starts to rotate and the symmetry is reduced to $I4_1/a$ until $x = 0.5$ (Ca$_{1.5}$Sr$_{0.5}$RuO$_4$), where $\phi = 12.78°$ and $\theta = 0°$ at 10 K. With further reduction of $x$, RuO$_6$ starts to tilt and the symmetry is further reduced to Pbca until $x = 0.0$ (Ca$_2$RuO$_4$), where $\phi = 11.93°$ and $\theta \sim 12°$ at low temperature, corresponding to the left end of our phase diagram. It was also pointed out by

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Figure 1. The calculated magnetic phase diagram of Sr$_2$RuO$_4$ with structural distortions. When the tilting of RuO$_6$ octahedron is conducted, RuO$_6$ rotation is fixed at 12° (see the text for a detailed description). The solid bold lines are calculated phase boundaries, while the triangles linked by dashed line correspond to experimental data from [8].

The experiment [4] that, from $x = 2.0$ to $x = 0.5$, the degree of flattening $\lambda$ remains almost constant ($\sim 1.07$), while from $x = 0.5$ to $x = 0.0$, the rotation angle $\phi$ is almost unchanged ($\sim 12°$). Three representative experimental points are shown in our phase diagram by triangles. Now, the basic tendency suggested by our phase diagram is that the RuO$_6$ rotation will drive the system from a NM state to a FM state, while the subsequent tilting plus the flattening of RuO$_6$ will push the system to an AF region. This general tendency is quite consistent with the experimental results.

The results presented above suggest that the rich experimental phase diagram can be simply understood in terms of the close coupling between structural distortions and magnetism. In all the calculations, we used LDA, which tends to overestimate the FM stability. Experimentally, no FM long-range order has been observed for $x = 0.5$, while the significant enhancement of susceptibility down to 2 K clearly suggested the existence of strong FM correlation (at least for short range) [3]. Actually, recent experiments down to 0.3 K suggested the existence of a weak FM component (cluster glass) at this doping [6]. This suggests that some magnetic orders may be energetically in near-degeneracy with the FM state. At present, we do not have any clear idea about what magnetic orders they may be and the problem is left for future studies. Another important aspect in our phase diagram is that the flattening of RuO$_6$ is important not only for the AF state but also for the FM state. This suggests that, simply by uniaxial pressure, Sr$_2$RuO$_4$ can be driven from the NM state to a FM state. To understand the close correlation between the structural distortions and the magnetic properties suggested by our above results, we should study the orbital states in this compound. This will be discussed in section 3.2.
3.2. Orbital-dependent phase control

To analyse the detailed orbital characters, we perform the calculations in a different manner from those in section 3.1. Firstly, we used the experimental structures rather than the artificial structures constructed above. Secondly, we included the alloy effect of (Ca, Sr) by using the virtual crystal approximation, which should be valid in this case because Ca and Sr are isoelectronic and their valence levels are far above the Fermi level. Thirdly, we use LDA + \( U \) for the insulating Ca-rich side \((x < 0.2)\). The reasons for this are three-fold: (1) although our above calculations using LDA can correctly predict the tendency to AF state for the Ca-rich side, the insulating gap is underestimated by LDA. To reproduce the gap, we use LDA + \( U \) with \( U_{\text{eff}} = 2.5 \text{ eV} \); (2) the inclusion of \( U \) will enhance the gap, but will not affect the orbital characters qualitatively as will be shown below; and (3) the effect of \( U \) for the metallic region \((x > 0.2)\) is small, because of the screening by the conduction electrons. We schematically present our main conclusions for the orbital characters in figure 2, while the detailed actual information is given in figure 3.

There are four electrons in the Ru 4d–t\(_{2g}\) orbitals. The three Ru t\(_{2g}\) orbitals \((xy, yz, zx)\) hybridize strongly with O-2p states, but only weakly with each other in tetragonal Sr\(_2\)RuO\(_4\). Therefore each orbital plays distinct roles. We start with the case of Sr\(_2\)RuO\(_4\). The partial density of states (PDOS) shown in figure 2(c) indicates that the \(xy\) orbitals, which form a two-dimensional square lattice, contribute dominantly to the well-known van Hove singularity (VHS) just above the Fermi level. The \(\gamma\) Fermi surface has the character of \(xy\). It is mostly responsible for FM spin fluctuation due to the high DOS around the Fermi level. On the other hand, \(yz\) and \(zx\) orbitals contribute to the \(\alpha\) and \(\beta\) Fermi surfaces and produce the incommensurate spin fluctuation coming from the strong nesting effect due to the quasi-one-dimensional nature of those states.

Now, let us turn to Ca\(_2\)RuO\(_4\) at 10 K. Our calculations predict the AF ground state with an energy gain of about 28.2 meV with respect to the FM state. Let us concentrate on the orbital characters first, then we will discuss the mechanism for the stabilization of AF state in terms of orbital ordering. The PDOS in figure 2(a) suggests that the present situation may correspond to the localized spin picture of \(S \cong 1\), where the \(xy\) states are fully occupied and the \(yz/zx\) orbitals are half-filled. In reality, as the Ru 4d orbitals are extended, inter-site hybridization modifies the

**Figure 2.** Schematic plots for the orbital states (PDOS of each orbital) in three characteristic doping points: (a) for Ca\(_2\)RuO\(_4\); (b) for Ca\(_{0.5}\)Sr\(_{1.5}\)RuO\(_4\); and (c) for Sr\(_2\)RuO\(_4\).
Figure 3. The calculated (a) orbital occupation numbers and (b) magnetic moments for the ground state of Ca$_{2-x}$Sr$_x$RuO$_4$ with different doping $x$. $M_{xy}$ ($M_{yz/zx}$) denotes the magnetic moment associated with the $xy$ ($yz/zx$) orbital and $M_{\text{Ru total}} = M_{xy} + 2M_{yz/zx}$. The absolute value of magnetic moments from oxygens are shown in (c) (see text for further explanation). The panel (d) shows the total energy difference between the FM and AF states. The AF side ($x = 0.0, 0.1$) is connected with the FM side ($x = 0.2, 0.5$) by dashed lines. (From [8].)

picture quantitatively. For example, the occupation numbers (in LDA + $U$) are given as follows: $n_{xy}^\uparrow = 0.86$, $n_{yz/zx}^\uparrow = 0.87$, $n_{xy}^\downarrow = 0.79$ and $n_{yz/zx}^\downarrow = 0.28$, with up and down arrows indicating the spins (see figure 3(a)). The cooperative occupation of the $xy$ orbital for all Ru sites forms the ferro-orbital ordering. These occupation numbers give 1.25 $\mu_B$ as the magnetic moment of a Ru atom $M_{\text{Ru total}}$, which agrees well with the experimental value of 1.3 $\mu_B$ [4]. As for the spin polarization of oxygen, the in-plane oxygen atoms have no net polarization due to symmetry while the apical oxygen atoms are strongly polarized (about 0.1 $\mu_B$) due to the strong p–d hybridization because the $yz/zx$ orbitals which extend towards apical oxygen contribute dominantly to the Ru spin polarization. The corresponding values in LDA for the above orbital population are $n_{xy}^\uparrow = 0.80$, $n_{yz/zx}^\uparrow = 0.82$, $n_{xy}^\downarrow = 0.71$ and $n_{yz/zx}^\downarrow = 0.40$. Therefore, the basic feature of the orbital population remains the same in LDA, although the orbital polarization and the spin polarization are reduced compared with those in LDA + $U$. For example, LDA gives 0.93 $\mu_B$ as $M_{\text{Ru total}}$. The reduction in these polarizations is due to the stronger inter-site hybridization caused by the vanishing band gap in LDA. Therefore, we believe that the results obtained by LDA + $U$ which adjusts the effective Coulomb repulsion $U_{\text{eff}}$ to reproduce the band gap should be quantitatively more reliable than those by LDA. The present results for the electronic structure are consistent with previous calculations [9].
As for the orbital character, there are three factors mainly contributing to the stabilization of the \(xy\) orbital:

1. The energy level splitting due to the 2D crystal field in the layered structures (in contrast to its three-dimensional (3D) counterpart, where the \(t_{2g}\) (or \(e_g\)) states are degenerate). Our calculations suggested that even for the hypothetical tetragonal \(\text{Ca}_2\text{RuO}_4\) without JT distortion (i.e., three Ru–O bonds having equal length), the \(xy\) orbital is lower in energy than the \(yz\) and \(zx\) orbitals by about 0.2 eV. As a first approximation, the origin of this energy level splitting is attributed to the following geometrical aspect in the second neighbour configurations: in \(\text{Ca}_2\text{RuO}_4\), Ru–O–Ru in the \(ab\) plane is replaced with Ru–O–Ca along the \(c\)-axis. Two factors coming from this geometrical aspect contribute to the energy level splitting. Firstly, the electrostatic potential due to the reduced positive charge of the second neighbour \(\text{Ca}^{2+}\) along the \(c\)-axis will raise the energies of those orbitals extending along the \(c\)-axis, like the \(yz\) and \(zx\) (or \(3z^2 - r^2\)) states. Secondly, due to the absence of Ru–O bond at one side of the apical oxygen along the \(c\)-axis, the remaining Ru–O bonds are strengthened. This will further push up \(yz\) and \(zx\) states, which are the anti-bonding parts of the 2p–4d hybridization.

2. The compressive JT distortion. The \(xy\) state is further lowered by about 0.06 eV due to the 2% shrinkage of the apical Ru–O bond length observed for \(\text{Ca}_2\text{RuO}_4\) at 10 K.

3. The orbital-dependent hybridization. In the AF state, the inter-site hybridization between the occupied orbitals and the unoccupied ones, which is the origin of the super-exchange, will push up the unoccupied \(yz/zx\) states, and again enhance the splitting between \(xy\) and \(yz/zx\) in minority spin by about 0.07 eV from our calculations. This effect does not exist in the FM state.

As a result, \(n_{xy}^-\) reads 0.79, 0.72 and 0.67 for the cases corresponding to \((x = 0.0, 11\, \text{K}, \text{AF}); (x = 0.1, 10\, \text{K}, \text{AF}: \text{JT distortion is nearly vanishing}); and (x = 0.0, 11\, \text{K}, \text{FM}), respectively. It is clear that the \(xy\) occupation is dominantly determined by the energy-level splitting due to the 2D structure, which is comparable with the typical band width of \(t_{2g}\) states. The existence of such a 2D crystal-field is common for all the layered perovskites, while it has not been considered seriously so far.

We also performed self-consistent calculations by including the SOC using the relativistic fully separable pseudo-potentials [23] in the framework of non-collinear magnetism. We found that the obtained orbital occupations are almost identical to those for the case without SOC, in the AF ground state of \(\text{Ca}_2\text{RuO}_4\). This is consistent with the above discussions in the sense that the crystal field is strong enough to quench the orbital moment and stabilizes the real-orbital \(xy\). Using our calculated orbital pictures, the experimental anisotropic optical conductivity and the x-ray-absorption spectroscopy can be well explained [8]. This presents firm evidence for the \(xy\) ferro-orbital ordering for \(x = 0.0\).

Having this orbital ordering pattern in mind, it is natural to understand the stabilization of the AF state. This is mostly due to the strong super-exchange interaction between the occupied majority-spin and unoccupied minority-spin \(yz/zx\) orbitals. The \(xy\) orbital will not contribute to any exchange interactions due to the nearly full occupation.

Now going from \(x = 0.0\) to 0.1, we see quantitative change of the electronic states (figure 3), while the ordering pattern does not change qualitatively. The elongation of the Ru–O bond along the \(c\)-axis [4] (going from \(x = 0.0\) to 0.1) tends to suppress the occupation of the \(xy\) orbital, and to destroy the AF order. As a result, we see from figure 3 the following: (1) the energy gain of AF
state with respect to the FM state reduces, being consistent with the reduced Néel temperature $T_N$ observed experimentally; (2) the reduction of ordered moments; (3) electron transfer in the minority spin channel from the $xy$ orbital ($n_{xy}^\uparrow$) to the $yz/zx$ orbitals ($n_{yz/zx}^\downarrow$); and (4) redistribution of magnetization from the $yz/zx$ orbitals ($M_{yz/zx}$) to the $xy$ orbital ($M_{xy}$).

However, for $x = 0.5$, where RuO$_6$ is quite elongated and has only strong rotation around the $c$-axis without tilting, the situation is completely different (figure 3). These structural modifications produce basically two important changes in the electronic structure compared with the case of Ca$_2$RuO$_4$: (1) reduction in $n_{xy}^\downarrow$ due to the elongation and (2) broadening of the $yz/zx$ bands due to the absence of tilting. Nevertheless, the existence of RuO$_6$ rotation keeps the $xy$ band narrow. The RuO$_6$ rotation couples mostly with the $xy$ orbital but not with the $yz/zx$ orbitals because the pd$\pi$ type hybridization between the O(1)-2p and the $xy$ states will be significantly reduced by the RuO$_6$ rotation, but those between the O-2p and the $yz/zx$ states are not affected so much. The direct results of this reduced pd $\pi$ type hybridization between the O(1)-2p and the $xy$ states are, first the narrowing of $xy$ band width and second the downward shift of $xy$ band (about 0.4 eV narrowing and 0.1 eV downward shift of $xy$ band for 12° of rotation). As the latter brings the VHS closer to the Fermi level, both results will enhance the DOS at the Fermi level (for the NM state). The enhanced DOS at the Fermi level by rotation will lead to the Stoner-type FM instability. Since this instability mostly comes from the $xy$ state, we observe from the FM solution (figure 2(b)) that the $xy$ states are strongly spin polarized, opening a pseudo-gap, and contributing to the magnetization dominantly (figure 3). On the other hand, $yz/zx$ bands are quite broad and are located around the Fermi level with much reduced spin polarization compared with the case of $x = 0.0$. (Note the difference between rotation and tilting. Once tilting is additionally introduced such as the Ca-rich side, all of the $t_{2g}$ bands will become narrower. This together with flattening enhances the AF instability.) In contrast to the $S \cong 1$ picture with the magnetic moment supported by the $yz/zx$ orbitals for the $x = 0.0$ case (Ca$_2$RuO$_4$), the present case may correspond to the $S \cong 1/2$ picture where the $xy$ orbital contributes to the magnetic moment. This picture accounts well for the observations by the Curie–Weiss fitting with $S = 1/2$ of susceptibility [3] and the polarized neutron [7] showing the $xy$ character for the spatial distribution of the field-induced magnetic moment. The large spin polarization for the in-plane oxygen atoms and the negligibly small one for the apical oxygen atoms (figure 3(c)) are the results coming from the $xy$ orbital origin of the Ru magnetic moment and are consistent with the experiment [7].

In contrast to the present study, the proposal in [9], which claims the contribution of $yz/zx$ states to the magnetization, was obtained by neglecting the RuO$_6$ rotation, which is an important ingredient for obtaining our orbital-dependent picture. In [9], an elaborate LDA + DMFT (dynamical mean-field theory) scheme was used, but a high symmetry structure was assumed for Sr$_2$RuO$_4$. Then the effects of doping are simulated by increasing the size of $U$, instead of changing the band-width. However, we pointed out in our calculation that the strong RuO$_6$ rotation will reduce the band-width of $xy$ significantly, but not that of the $yz, zx$ bands. This difference produces the main source of the discrepancy discussed above.

Finally, we discuss only briefly the case for the critical point $x = 0.2$. In this case, 10 K is already above the metal–insulator transition temperature [4], and the system crystallizes in the $L$–Pbca phase with a long apical Ru–O bond, suggesting the adjacency to the metallic side ($x = 0.5$). However, in contrast to the case of $x = 0.5$, the tilting of RuO$_6$ still exists to reduce the width of $yz/zx$ bands as well at $x = 0.2$. This aspect tends to stabilize the insulating AF state. If we adopt LDA, the former aspect is emphasized to make the case of $x = 0.2$ very similar to the case of $x = 0.5$. On the other hand, the LDA + $U$ method with $U_{\text{eff}} = 2.5$ eV emphasizes the
latter aspect to bring the AF state very close to the FM state with the energy difference given by $E_{\text{FM}} - E_{\text{AF}} = -3$ meV. Note, however, that a similar LDA + $U$ calculation for $x = 0.5$ enhances the stability of the FM state with respect to the AF state and doubles the energy difference in figure 3(d). These calculations, though not conclusive, clearly suggest that the system with $x = 0.2$ may be in the critical situation.

4. AHE in Ca$_{1-x}$Sr$_x$RuO$_3$

AHE is a phenomenon where the transverse resistivity $\rho_{xy}$ in ferromagnets contains the contribution due to the magnetization $M$ in addition to the usual Hall effect. The conventional expression for $\rho_{xy}$ is

$$\rho_{xy} = R_0 B + 4\pi R_s M,$$

(1)

where $B$ is the magnetic field, $R_0$ is the usual Hall coefficient and $R_s$ is the anomalous Hall coefficient. This expression implicitly assumes that the additional contribution is proportional to the magnetization. This is supported by all the conventional theories proposed thus far [14] since they are based on the perturbative expansion in the SOC $\lambda$ and the magnetization $M$, i.e., $R_s \propto \lambda$.

However this expectation is invalidated by the experimental data presented below, showing the non-monotonic temperature dependence including even a sign change.

From the wavefunction of the Bloch state $\psi_n(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_n(\vec{r})$ with $n$ denoting the band index and $u_n(\vec{k})$ being the periodic part, one can construct the Berry phase connection $a_{n\mu}(\vec{k})$ as

$$a_{n\mu}(\vec{k}) = i \left( u_n(\vec{k}) \frac{\partial}{\partial k_{\mu}} u_{n}(\vec{k}) \right).$$

(2)

It is important to note that this quantity, formally behaving as a vector potential, is related to the transverse conductivity $\sigma_{xy}$ as [24]

$$\sigma_{xy} = \sum_{n, \vec{k}} n_F(\varepsilon_n(\vec{k})) b_{z}(\vec{k}),$$

(3)

where $b_{nz}(\vec{k}) = \partial_{k_z} a_{ny}(\vec{k}) - \partial_{k_y} a_{nx}(\vec{k})$ is the $z$-component of the gauge field made from $a_{n\mu}(\vec{k})$, and $n_F(x) = 1/(e^{\beta(x-\mu)} + 1)$ ($\beta$ is the inverse temperature and $\mu$ is the chemical potential) is the Fermi distribution function.

In the real system, $b_z(\vec{k})$ has strong $\vec{k}$-dependences. The enhancement of the gauge field $b_z(\vec{k})$ occurs when more than two bands are energetically close, which corresponds to the monopole$^5$ and shows its fingerprint in AHE and Kerr rotation as described below [25]. Consider the general case where two-band Hamiltonian matrix $H(\vec{k})$ at $\vec{k}$ can be written as $H(\vec{k}) = \sum_{\mu=0,1,2,3} f_{\mu}(\vec{k}) \sigma_{\mu}$, where $\sigma_{1,2,3}$ are the Pauli matrices and $\sigma_0$ is the unit matrix. Then we can consider the mapping from $\vec{k}$ to the vector $f(\vec{k}) = (f_1(\vec{k}), f_2(\vec{k}), f_3(\vec{k})) = f(\vec{k})(\cos \varphi \sin \theta \hat{\imath}, \sin \varphi \sin \theta \hat{j}, \cos \theta \hat{k})$ as shown in figure 4(a). Then $H(\vec{k})$ can be easily diagonalized to obtain the two eigenvalues

$^5$ It has been recognized in the original paper by Berry [25] that the degeneracy point in the parameter space acts as a magnetic monopole where the gauge field is enhanced.
Figure 4. Geometrical meaning of the contribution $\sigma_{xy}^{2\text{-bands}}$ when the two bands are nearly degenerate (see text for details). (b) Calculated flux distribution in $\vec{k}$-space for a $t_{2g}$ band as a function of $(k_x, k_y)$ with $k_z$ being fixed at 0 for SrRuO$_3$. The sharp peak around $k_x = k_y = 0$ and the ridges along $k_x = \pm k_y$ are due to the near degeneracy of $yz$ and $zx$ bands for symmetry reasons. (From [17].)

$$\epsilon_{\pm}(\vec{k}) = f_0(\vec{k}) \pm f(\vec{k}).$$

Calculating equation (3) in this case, we obtain the contribution to $\sigma_{xy}$ from these two bands as

$$\sigma_{xy}^{2\text{-bands}} = \frac{e^2}{8\pi\hbar} \int d^3\vec{k} [n_F(\epsilon_-(\vec{k})) - n_F(\epsilon_+(\vec{k}))] \left( \frac{\partial \varphi_{\vec{f}}}{\partial k_x} \frac{\partial \varphi_{\vec{f}}}{\partial k_y} - \frac{\partial \varphi_{\vec{f}}}{\partial k_y} \frac{\partial \varphi_{\vec{f}}}{\partial k_x} \right) \sin \theta_{\vec{f}}$$

$$= \frac{e^2}{8\pi\hbar} \int dk_z d\Omega_{\vec{f}} [n_F(\epsilon_-(\vec{k})) - n_F(\epsilon_+(\vec{k}))],$$

where $d\Omega_{\vec{f}} = [\partial(\theta_{\vec{f}}, \varphi_{\vec{f}})/\partial(k_x, k_y)] \sin \theta_{\vec{f}} dk_x dk_y = d\varphi_{\vec{f}} \sin \theta_{\vec{f}} d\theta_{\vec{f}}$ is the $\vec{f}$-space solid angle, which is the integral of the gauge field

$$\vec{b}(\vec{f}) = \pm \frac{\vec{f}}{2|\vec{f}|^3}$$

due to the monopole at $\vec{f} = 0$ over the infinitesimal surface in $\vec{f}$-space corresponding to the small square $dk_x dk_y$ in $\vec{k}$-space (figure 4(a)). Therefore $\sigma_{xy}^{2\text{-bands}}$ again has the geometrical meaning in $\vec{f}$ space. This gauge field strongly depends on $\vec{k}$ in the (near) degenerate case, i.e., when $\vec{f}(\vec{k})$ is near the monopole.
There are two cases for the (near) degenerate bands. One is the accidental degeneracy [26, 27], where the three equations \( f_1(\vec{k}) = f_2(\vec{k}) = f_3(\vec{k}) = 0 \) are satisfied at \( \vec{k} = \vec{k}_0 \). Near this accidental band crossing, one can expand as \( f_a(\vec{k}) = \sum_b a_{ab}(k_k - k_{0b}) \) where \( a, b = 1, 2, 3 \). In this case, the \( f \)-space can be identified with the \( \vec{k} \)-space, and the gauge field distribution in \( k \)-space around \( \vec{k} = \vec{k}_0 \) is similar to equation (5) replacing \( f \) by \( k - k_0 \). Although there occurs no singularity in \( \sigma_{xy} \) at \( \mu = \varepsilon_{\pm}(\vec{k}_0) \) due to the cancellation between the positive and negative \( k_z - k_{z0} \), the nonlinear dependence of \( f_a(\vec{k}) \) gives rise to the strong \( \mu \)-dependence of \( \sigma_{xy} \) slightly away from this energy. The other class of (near) degeneracy is due to the symmetry, where the \( k \)-group has the irreducible representation with the dimensions more than two. As an example, one can consider the simplest tight-binding model of \( t_{2g} \) orbitals of \( \gamma_z \) and \( \gamma_x \) on the cubic perovskite structure, which is relevant to the SrRuO\(_3\) discussed below. In this case the \( H(\vec{k}) \) for these two bands with up-spin is given by \( f_0(\vec{k}) = -2t_1 \cos k_z - t_1(\cos k_x + \cos k_y) \), \( f_1(\vec{k}) = 2t_2 \sin k_x \sin k_y \), \( f_2(\vec{k}) = -\lambda M \), \( f_3(\vec{k}) = -t_1(\cos k_x - \cos k_y) \), where \( t_1 \) and \( t_2 \) are the effective intra- and inter-orbital transfer integrals respectively. When \( \lambda M = 0 \), there occurs the degeneracy along the line \( \vec{k} = (0, 0, k_z) \). Furthermore, when \( t_2 = 0 \), there occurs the degeneracy along the plane \( k_x = \pm k_y \). Considering the case \( t_1 \ll t_2 \ll \lambda M \), which is relevant to SrRuO\(_3\), the gauge field \( b_\alpha(\vec{k}) \) with \( k_z = 0 \) has the largest peak at \( k_x = k_y = 0 \) and is enhanced along the lines \( k_x = \pm k_y \), which is actually seen in the realistic calculation for SrRuO\(_3\) shown in figure 4(b). In this case, there occurs no cancellation of \( b_{\alpha z}(\vec{k}) \) from the integral over \( k_z \).

Although the discussion above is applicable to any (near) degeneracy, the (singular) gauge field from different band crossings in \( f \)-space cancel out in the presence of the time-reversal symmetry and/or the absence of the SOC. The former prohibits the finite \( \sigma_{xy} \). In the absence of SOC, up-spin and down-spin bands are decoupled, and each of them can be represented by the Hamiltonian matrix without the time-reversal symmetry breaking. In ferromagnets with the SOC, the singular behaviour of \( \sigma_{xy} \) by changing some parameters such as the chemical potential and the magnetization is the fingerprint of the monopoles in \( \vec{k} \)- and/or \( \vec{f} \)-space, which we will discuss below.

SrRuO\(_3\) with the perovskite structure is an itinerant (metallic) ferromagnet. There are four \( t_{2g} \) electrons with the low spin configurations. The 4d orbitals are relatively extended and the bandwidth is large compared with the Coulombic interaction. High-quality single crystal thin film is available nowadays with the residual resistivity of the order of 10 \( \mu \)\()Omega\). Another important aspect is that the relativistic SOC is large in 4d electrons because of the heavy mass (of the order of 0.3 eV in Ru). These aspects make this system an ideal candidate to observe the AHE due to the \( \vec{k} \)-space gauge field as described above.

The calculated DOS is not so different for the cases with and without SOC (figure 5(a)), while the \( \sigma_{xy} \) is very sensitive to the Bloch wavefunctions and depends on the Fermi level position and the spin-splitting significantly (figures 5 and 7). The sharp and spiky structures of \( \sigma_{xy} \) as functions of the Fermi-level position obtained by using a very small broadening parameter for the lifetime \( \delta (= 70 \text{ meV}) \) is just the natural result of singular behaviour of monopoles. On shifting the Fermi level, not only the absolute value but even the sign of \( \sigma_{xy} \) change. For the case without any shift of Fermi level, we obtain the value of \( \sigma_{xy} = -60 \text{ \Omega}^{-1} \text{ cm}^{-1} \), which has the same sign as and is comparable with the experimental value. From the \( \omega \) dependence of optical conductivity (figure 6), the high energy part (\( > 0.2 \text{ eV} \)) can be well reproduced by our calculation. The strong transition around 3.0 eV is mostly due to the charge transfer from O-2p to Ru-4d. The low energy part (\( < 0.2 \text{ eV} \)) of \( \sigma_{xy} \) is not measured due to technical difficulty, but it is clear that a sharp

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Figure 5. The calculated (a) density of states and (b) $\sigma_{xy}$ as functions of Fermi-level position for the orthorhombic single crystal SrRuO$_3$ [28]. (From [17].)

structure should be there because the d.c. limit $\text{Re}(\sigma_{xy}) \approx -100 \text{ cm}^{-1}$ has the opposite sign. This is reproduced correctly by the first-principles calculations, providing more evidence for the existence of magnetic monopoles.

As a result of $\mathbf{k}$-space integration over occupied monopoles, the calculated $\sigma_{xy}$ is non-monotonic as a function of magnetization as shown in figure 7. Here, we attribute the temperature ($T$) dependence of $\sigma_{xy}$ to that of the magnetization $M(T)$. As the reduction of spin-splitting, $\sigma_{xy}$, after the initial increase, decreases sharply and then increases and changes sign becoming positive, and finally goes down again, capturing the basic features of the experimental results. Another consequence of magnetic monopoles as a source of AHE is the strong structure dependence. The calculated $\sigma_{xy}$ for the fictitious cubic structure shows a strong deviation from that obtained for the orthorhombic structure, and it changes the sign to be positive at low temperature (large $M$). Therefore, the rather small orthorhombic distortion is important to obtain the experimentally observed behaviour of $\sigma_{xy}$.

5. Summary

We have presented a comprehensive review in this paper for the orbital physics in ruthenates. We first demonstrated that the complicated magnetic phase diagram of Ca$_{2-x}$Sr$_x$RuO$_4$ can be well understood in terms of orbital characters, which is strongly related to the structure distortions.
Figure 6. The calculated (left panels) and measured (right panels) diagonal ($\sigma_{xx}$) and transverse ($\sigma_{xy}$) optical conductivity of SrRuO$_3$. The measurements were made for SrRuO$_3$ single crystal film on STO substrate at 10 K, while the calculations were performed for both the orthorhombic single crystal structure [28] and the hypothetical cubic structure by keeping the average Ru–O bond length. (From [17].)

We point out that, before pursuing the strong-correlation model, the detailed crystal structures should be considered seriously. For example, in systems with orbital degree of freedom, each orbital plays a distinct role, and should be treated at a different level. Second, we explain the intrinsic mechanism of AHE in ferromagnets using Ca$_{1-x}$Sr$_x$RuO$_3$ as the sample system. We provide firm evidence for the existence of magnetic monopole in $\vec{k}$-space, which is defined in terms of the Berry connection of the Bloch wavefunction. This will stimulate and urge the reconsideration of the electronic states in magnetic materials from a very fundamental viewpoint.
Figure 7. (a) The experimentally observed temperature dependence of the magnetization $M$, the resistivity $\rho_{xx}$ and the Hall resistivity $\rho_{xy}$ of the single crystal and thin film of SrRuO$_3$. (b) The anomalous Hall conductivity $\sigma_{xy}$ as a function of the magnetization $M$ extracted from (a), and the first-principles calculation. In our calculations, the change of the magnetization is taken into account by the rigid splitting of up and down spin bands. Since $\sigma_{xy}$ should vanish with reduced $M$ at high temperatures, the calculated $\sigma_{xy}$ is multiplied by the additional $M/M_0$ ($M_0 = 1.5\mu_B$) factor phenomenologically, which does not change its behaviour except at the very vicinity of $T_c$. (From [17].)
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