Orbitally Driven Spin-Singlet Dimerization in $S = 1$ $La_4Ru_2O_{10}$

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Using x-ray absorption spectroscopy at the Ru-$L_{2,3}$ edge we reveal that the Ru^{4+} ions remain in the $S = 1$ spin state across the rare $4d$-orbital ordering transition and spin-gap formation. We find using local spin density approximation + Hubbard U band structure calculations that the crystal fields in the low-temperature phase are not strong enough to stabilize the $S = 0$ state. Instead, we identify a distinct orbital ordering with a significant anisotropy of the antiferromagnetic exchange couplings. We conclude that $La_4Ru_2O_{10}$ appears to be a novel material in which the orbital physics drives the formation of spin-singlet dimers in a quasi-two-dimensional $S = 1$ system.

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One of the most intriguing aspects of transition metal materials is the wide variety and richness of their physical properties [1]. Although conceptually clean and beautiful, theoretical simplifications in terms of a Heisenberg model or a single band Hubbard model turn out to be inadequate [2]. It now becomes more and more clear that a full identification of the relevant orbital and spin degrees of freedom of the ions involved is needed to understand, for instance, the colossal magnetoresistance behavior in the manganates [3–5], magnetization reversals, and metal-insulator transitions in early transition metal oxides [6–10], as well as the formation of spin gaps in non-one-dimensional $S = \frac{1}{2}$ systems [11–14].

Very recently Khalifah *et al.* [15] synthesized the semiconducting quasi-two-dimensional $La_4Ru_2O_{10}$ compound and discovered that this system undergoes a strong first-order structural transition at $T_s = 160$ K (see Fig. 1), accompanied by a rare $4d$-orbital ordering and spin-gap opening. Their interpretation of these phenomena was that the Ru^{4+} ion transforms from the usual $t^3_{2g\uparrow}t^1_{2g\downarrow}$ low-spin state with $S = 1$ to an $t^2_{2g\uparrow}t^2_{2g\downarrow}$ "ultralow" spin state with $S = 0$, caused by a sufficiently strong crystal-field splitting (CFS) of the Ru $4d$-t_{2g} levels due to the lattice distortion below T_s.

However, already soon after that, it was also hypothesized by Khalifah *et al.* based on unpublished standard band structure calculations that a chemical bond may be formed associated with the orbital ordering. Here we report on an x-ray absorption spectroscopy (XAS) study in which we reveal that the Ru^{4+} ions remain in the $S = 1$ spin state across T_s. This directly points to the possibility that $La_4Ru_2O_{10}$ is in fact a novel system in which the spin-gap opening is due to a singlet dimer formation in a non-one-dimensional and $S > \frac{1}{2}$ material. We find using local spin density approximation + Hubbard U (LSDA + U) band structure calculations that the distinct orbital ordering involves a significant anisotropy of the antiferro-

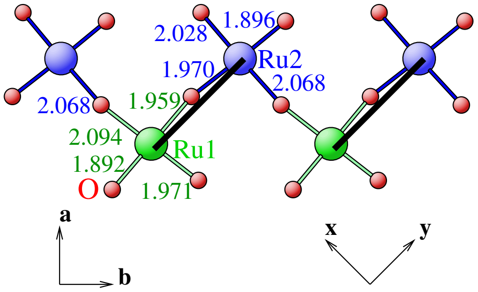

FIG. 1 (color online). The main block of the low-temperature (20 K) triclinic crystal structure of $La_4Ru_2O_{10}$ shown in the crystallographic *ab* plane: the two-dimensional Ru-O network consisting of distorted RuO_6 octahedra extends along the *c* axis (not shown, pointing into paper plane) and *b* axis with corrugation. The Ru-O bond lengths are marked in units of Å, and those out of the *ab* plane (not shown) are 2.046 and 2.057 Å for Ru1, and 2.046 and 2.082 Å for Ru2. The spin-singlet dimers are marked by black solid bars. The local orthogonal coordinate system (*xyz*) is used in our band calculations with *z* parallel to *c* and *y* (*x*) along the short (long) Ru1-Ru2 direction. The high-temperature monoclinic structure (not shown) above $T_s = 160$ K has equal Ru-Ru distances along the *x* and *y* directions: Ru1 and Ru2 are equivalent.

magnetic exchange couplings, indicating indeed the formation of Ru ($S = 1$)-Ru ($S = 1$) singlet dimers.

Floating zone crystals were grown in an NEC SC-M15HD image furnace using rods with a 1:1 or 4:5 ratio of La:Ru which had been prereacted and sintered in air at 1250 °C. A small (1–2 atm) overpressure of oxygen aided the growth, and the power was dynamically increased during the run to compensate for absorption by the copious amounts of evaporated Ru. Sizeable crystals could only be obtained using seed crystals. X-ray diffraction confirmed both the macroscopic phase purity and the universal presence of two twin domains. The XAS measurements were performed at the Taiwan NSRRC 15B beam line, equipped with a double Si(111) crystal monochromator delivering photons from 2 keV and up. The spectra were recorded using the total electron yield method in a chamber with a base pressure in the low 10^{-10} mbar range. Clean sample areas were obtained by cleaving the crystals *in situ*. The photon energy resolution at the Ru $L_{2,3}$ edges ($h\nu \approx$ 2.9 keV) was set at 0.6 eV. Strong polarization dependent O-K XAS spectra [16] verify the high sample quality.

The top curves of Fig. 2 depict the Ru-$L_{2,3}$ XAS spectra of $La_4Ru_2O_{10}$ taken at 220 K (black line) and 110 K (red line). The spectral line shapes depend strongly on the multiplet structure given by the Ru $4d$-$4d$ and $2p$-$4d$ Coulomb and exchange interactions, as well as by the local CFS and the hybridization with the O $2p$ ligands. Unique to XAS is that the dipole selection rules are very effective in determining which of the $2p^5 4d^{n+1}$ final states can be reached and with what intensity, starting from a particular $2p^6 4d^n$ initial state ($n = 4$ for Ru^{4+}) [17,18]. This makes the technique extremely sensitive to the quantum numbers of the initial state [19,20].

The essence of the Ru-$L_{2,3}$ XAS spectra in Fig. 2 is that there is only a very small change across T_s, suggesting that the local electronic and spin state of the Ru^{4+} ion in the high-temperature (HT) and low-temperature (LT) phases are quite similar. This seems surprising in view of the fact that we observed considerable modifications in the O-K XAS spectra in going from 200 K (black line) to 85 K (red line) as shown in the inset of Fig. 2 [16]. Since these O-K spectra are known to be sensitive to band structure effects [17], their modifications are fully consistent with the strong changes in the crystal structure as seen in neutron diffraction [15], confirming the good quality of our samples.

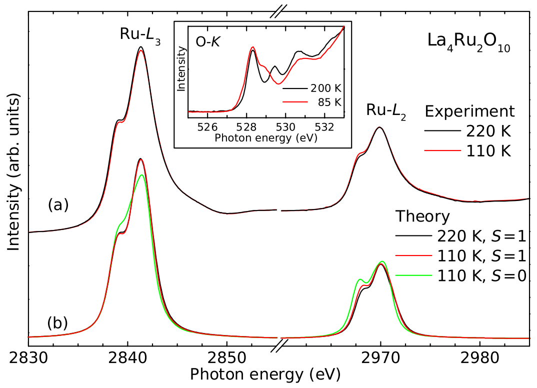

FIG. 2 (color online). (a) Experimental Ru-$L_{2,3}$ XAS spectra of $La_4Ru_2O_{10}$ measured at 220 and 110 K, i.e., above and below $T_s = 160$ K. (b) Theoretical simulations for the Ru^{4+} ion in the $S = 1$ high-temperature phase at 220 K, $S = 1$ low-temperature phase at 110 K, and $S = 0$. The inset shows O-K spectra measured at 200 and 85 K from [16].

To extract quantitative information on the CFS and spin state from the Ru spectra, we have performed simulations using the successful configuration interaction cluster model [17,18,21]. The calculations have been carried out for a RuO_6 cluster in the proper HT and LT local coordination using the XTLS 8.3 program [21]. Parameters for the multipole part of the Coulomb interactions were set standardly at 80% of the Hartree-Fock values [21], while the monopole parts (U_{dd}, U_{pd}) were taken from Ca_2RuO_4 [22,23]. The O $2p$—Ru $4d$ charge transfer energy was estimated from LDA calculations (see below), and the O $2p$-Ru $4d$ transfer integrals and their distance dependence from Harrison's relations [24]. The local CFS parameters are to be determined from the comparison between the simulations and the experimental spectra.

The bottom curves of Fig. 2 show the simulations for both the HT and LT phases. We found optimal fits (black and red lines) if the Ru-$4d$ xz orbital is set at about 100–150 meV (HT) and 200–300 meV (LT) lower in energy than the essentially degenerate (within 50 meV) yz and xy orbitals [25]. These numbers refer to total energies calculated including the CFS and covalency but without spin-orbit interaction. Important is that the cluster calculation indeed finds the $S = 1$ state for both the HT and LT phases, which is a direct consequence of the fact that in both phases the xz orbital is essentially doubly occupied while the yz and xy are each singly occupied. We also have carried out calculations for the Ru ion in the artificial $S = 0$ state by changing the CFS parameter such that the xz orbital lies above the degenerate yz and xy orbitals [25]. As shown in Fig. 2, the simulated spectrum (green curve) disagrees with the experiment. So we can rule out that the spin-gap opening is due to a local spin state transition [15].

To confirm our XAS-derived conclusions and, more importantly, to get in-depth understanding of the nature of the spin-gap state below T_s, we performed systematic LDA and LSDA + U band structure calculations [26], by using the full-potential augmented plane waves plus local orbital method [27]. We took the neutron crystal structure data at 20 K and 298 K [15]. The muffin-tin sphere radii are chosen to be 2.8, 2.0, and 1.5 Bohr for La, Ru, and O atoms, respectively. $U = 3$ eV and Hund's rule exchange $J_H =$ 0.5 eV ($U_{\text{eff}} = 2.5$ eV) are used for Ru $4d$ electrons, which are common for ruthenates [22,28,29].

Figure 3 shows the Ru $4d$ density of states (DOS) calculated using the LDA for the nonmagnetic (NM) state. The inset shows a close-up of the t_{2g} levels and a calculation of the first moments supports the XAS analysis: for

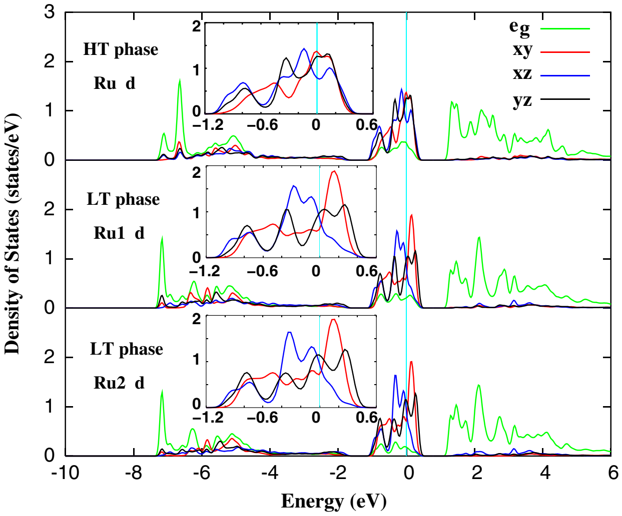

FIG. 3 (color online). LDA density of states of the Ru 4*d* orbitals in the high-temperature (HT, upper panel) and low-temperature (LT, middle and lower panels) phases. The insets show a close-up of the t_{2g} (xy, xz, and yz) states in the vicinity of the Fermi level set at 0 eV.

both the HT and LT phases, the xz orbital lies lowest and the splitting $\Delta'_{\rm CF}$ between the higher lying yz and xy orbitals is less than 50 meV. It is the magnitude of this $\Delta'_{\rm CF}$ relative to J_H which determines the spin state of the Ru^{4+} ion. To make a crude estimate: the $S = 1$ state ($xz^{\uparrow\downarrow}yz^{\uparrow}xy^{\uparrow}$) carries the Hund's stabilization energy of $3J_H$, whereas the $S = 0$ state ($xz^{\uparrow\downarrow}yz^{\uparrow\downarrow}$) has a total stabilization energy of $2J_H$ plus $\Delta'_{\rm CF}$. Assuming that 0.5 eV is a reasonable estimate for J_H, one must expect that a $\Delta'_{\rm CF}$ of 0.05 eV is far from sufficient to obtain the $S = 0$ state. Obviously this is what the XAS experiments have revealed. Moreover, our LDA calculations also find that the ferromagnetic (FM) as well as the antiferromagnetic (AF) solution are more stable than the NM one, giving further support that the $S = 0$ is unfavorable. This was also found recently by LDA calculations of Eyert *et al.* [30].

The LDA results as shown in Fig. 3 predict a metallic state for both the HT and LT phases, and this is in strong disagreement with the observed semiconducting behavior with a gap of about 0.3 eV [15]. One should note, however, that the Fermi level is located in a narrow Ru t_{2g} band with no more than 1.5 eV width. This signals that modest electron correlation effects at the Ru sites will already be able to turn this material into a Mott insulator. We therefore set out to do LSDA + U calculations for the LT phase and found that a band gap of about 0.5 eV is indeed opened in the Ru t_{2g} band as can be seen from Fig. 4(a). Within the LSDA + U mean-field approach, the lowest state of this insulator is AF and is labeled as AF_{xyz} in Table I to indicate the AF alignment with the nearest neighbors along the x, y, and z directions (Fig. 1). The Ru^{4+} spin moment inside the muffin-tin sphere is about 1.2 μ_B, confirming the XAS result that the spin state is $S = 1$ but not $S = 0$.

It is important to look now at the orbital character of the AF_{xyz} solution. Figures 4(b) and 4(c) show the orbitally resolved DOS of the AF aligned Ru1 and Ru2 ions. One can clearly see for each of the ions that the xy and yz orbitals (with the spins parallel) are singly occupied while the xz are doubly occupied. This double occupation is due to the Ru-O bonds being elongated along the x direction, see Fig. 1. We thus find an orbital ordered state which is different from the originally proposed doubly occupied xy and xz ($S = 0$) state [15].

As a result, the half-filled xy and yz orbitals are magnetically active. To explain the formation of the spin gap in the LT phase, it is crucial to identify the relevant exchange interactions in this system. We therefore have calculated other magnetic configurations: the FM and two more types of AF solutions, namely AF_{xy} and AF_{yz}. The $2 \times \mathrm{La}_4\mathrm{Ru}_2\mathrm{O}_{10}$ unit cell is used for all solutions, except for AF_{yz} where the $4 \times \mathrm{La}_4\mathrm{Ru}_2\mathrm{O}_{10}$ unit cell is taken with the doubling along the b direction (see Fig. 1). We also studied the NM solution, and confirmed that this is much higher in energy than the AF_{xyz}, by 775 meV per formula unit (Table I). The NM solution is metallic, the FM half-metallic, and all AF insulating. The Ru^{4+} spin moment is 1.2 ± 0.1 μ_B for all magnetic solutions.

The relative energies of the different magnetic states allow us to estimate the exchange constants J_x, J_y, and J_z along the x, y, and z directions (Fig. 1), respectively. With the FM being 130–150 meV higher in energy than the AF solutions, we thus have very large AF exchange interactions in this system. As listed in Table I, we find $J_x = 1.5$ meV, $J_y = 65.5$ meV, and $J_z = 4.5$ meV. The signifi-

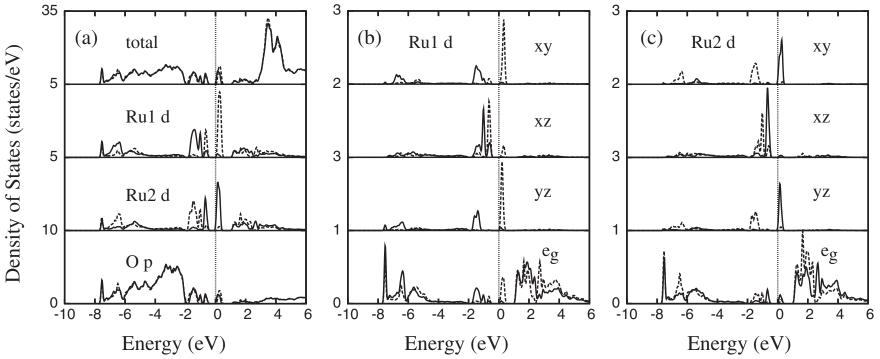

FIG. 4. Density of states (DOS) of the $\mathrm{La}_4\mathrm{Ru}_2\mathrm{O}_{10}$ in the antiferromagnetic low-temperature phase calculated using LSDA + U. (a) Total DOS per formula unit, the 4*d* states of the two inequivalent Ru^{4+} ions, and the 2*p* states of all the ten oxygens; (b) orbitally resolved 4*d* states of Ru1 and (c) of Ru2. The solid (dashed) curves denote the up- (down)-spin channels.

TABLE I. LSDA + U results for the total energy (per formula unit and relative to the lowest solution) and band gap in the low-temperature phase of $La_4Ru_2O_{10}$, calculated for the nonmagnetic (NM), ferromagnetic (FM), and three types of antiferromagnetic (AF) solutions. The exchange constants are found to be $J_x = 1.5$ meV, $J_y = 65.5$ meV, and $J_z = 4.5$ meV.

State	Exchange	Energy (meV)	Gap (eV)
NM	$\cdots$	775	$\cdots$
FM	$J_x + J_y + 2J_z$	152	$\cdots$
AF_{xyz}	$-J_x - J_y - 2J_z$	0	0.5
AF_{xy}	$-J_x - J_y + 2J_z$	18	0.3
AF_{yz}	$J_x - J_y - 2J_z$	3	0.4

cant anisotropy is related to the fact that *both* the xy and yz orbitals contribute to the exchange coupling along the y direction having the *short* Ru-O-Ru distance, while *only* the xy *or* yz orbital contributes to the x *or* z direction, respectively, having the *long* Ru-O-Ru distance. Hence we can consider the LT phase of $La_4Ru_2O_{10}$ as practically consisting of strongly coupled Ru-Ru dimers with weak interdimer coupling, or at most as two-leg ladders with $J_{\mathrm{rung}} = J_y = 65.5$ meV and $J_{\mathrm{leg}} = J_z = 4.5$ meV, with weak interladder coupling of 1.5 meV. Those rather well isolated Ru-Ru dimers or rungs will have the singlet ground state [31]. This explains naturally the appearance of a spin gap in the LT phase, which, according to our calculations, should be about 60 meV, in reasonable agreement with the measured value of 40 meV [15]. The dimer character of the spin gap seems also to agree with the results of the single-crystal neutron scattering [32].

To summarize, XAS measurements revealed that the Ru^{4+} ions in $La_4Ru_2O_{10}$ remain in the $S = 1$ spin state across the structural phase transition and spin-gap formation. LSDA + U calculations provided support for this finding and identified the distinct orbital ordering accompanying the structural transition. Crucial is that with LSDA + U we were able to estimate the intersite antiferromagnetic exchange interactions and found them to be highly anisotropic. This brought us to the conclusion that the spin-gap opening is due to the formation of Ru-Ru singlet dimers. Such a transition is rather unusual since $La_4Ru_2O_{10}$ is a two-dimensional $S = 1$ system; it is largely driven by orbital ordering which amplifies the importance of orbital physics in correlated systems.

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