Hybridization, superexchange, and competing magnetoelastic interactions in TiOBr

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A crystalline sample of TiOBr is probed at room temperature by a combination of electron spectroscopies and the results are compared to theoretical embedded-cluster calculations. Resonant photoemission of the valence band confirms that the lowest binding energy feature arises from the singly occupied Ti 3d orbital. The polarization dependence of this orbital in nonresonant photoemission is consistent with the expected dominant \( d_{x^2−y^2} \) character. The analysis of the Ti L\(_{2,3}\) x-ray absorption spectra confirms the complete splitting of the Ti 3d shell. X-ray absorption and resonant photoemission at the O 1s edge provide direct evidence for hybridization between the transition metal orbitals and the O 2p levels, which leads to superexchange interactions between the Ti ions. The existence of a mixing of O and Ti states and of strong superexchange interactions is supported by calculations of the ground-state electronic and magnetic properties. The calculated superexchange interchain interaction is one fifth in strength of the total magnetic coupling along the chain, and is antiferromagnetic in character. This O-mediated interchain interaction is frustrated in the room temperature phase of TiOBr and thus couples strongly to distortions of the soft lattice. The competition between the interchain magnetoelastic coupling and the spin-Peierls interaction might be at the origin of the complex TiOBr phase diagram.

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I. INTRODUCTION

Titanium oxyhalides (chemical formula TiOX with X =Cl, Br) have attracted much attention in the past few years due to their quasi-one-dimensional (1D) magnetic character¹ and because they represent the electron analog (3d\(^3\)) of the cuprate oxides (3d\(^9\)). The TiOX crystal structure consists of buckled TiO bilayers stacked along the crystallographic c axis and separated from one another by two halogen planes. Each bilayer contains alternating Ti and O arrays oriented parallel to the b axis.²,³ The nominal valence charges are X\(^−\), O\(^2−\), and Ti\(^{3+}\) (electronic configuration 3d\(^1\)). The halogens are expected to have almost pure ionic character, while the ionic bonding inside the TiO bilayers is expected to have a partial covalent character.

TiOBr and TiOCl have a strikingly similar phase diagram. At high temperature they crystallize in the FeOCl structure type,⁴,⁵ with each Ti ion surrounded by a heavily distorted \( O_4X_2 \) octahedron. While band theory predicts a metallic ground state, TiOX is an insulator. It is believed that the ligand field of \( C_{3v} \) symmetry lifts completely the degeneracy of the Ti 3d shell, and that the ground state orbital, which is filled by only one electron, has lobes pointing along b and c.⁴ Due to the large Coulomb repulsion at the Ti site, the d electron in the ground state acts to a large degree as a localized spin.

Direct overlap of adjacent d orbitals only occurs along b, and the resulting 1D exchange interaction leads at room temperature to the formation of antiferromagnetic spin chains.⁵ As the temperature is lowered, TiOX displays a second order transition to an incommensurate phase at \( T_{c1} \), followed, at a lower critical temperature \( T_{c2} \), by a first order transition to a spin Peierls phase with doubling of the unit cell along b. The transition temperatures are \( T_{c1} = 27 \) K (67 K) and \( T_{c2} = 47 \) K (91 K) for TiOBr (TiOCl).⁶,⁷ The phase diagram of TiOX is at odds with the conventional spin-Peierls scenario where only one (second order) transition is expected.

The origin of the unconventional spin-Peierls behavior of TiOX is debated. Early studies speculated that orbital fluctuations might play a role in the high temperature phase, suggesting that phonon-induced orbital fluctuations might be present at high temperatures.⁸–¹⁰ This scenario has been, however, refuted by other studies. Density functional calculations⁴ in the local density approximation with a Hubbard-like correction (LDA+U) as well as a more recent cluster computation¹¹ gave an energy separation of 0.3 eV between the ground state orbital and the first excited Ti 3d state, which is too high for mixed- orbital ordering to occur. The lack of a dynamical Jahn-Teller admixture of higher lying \( d \) levels in the ground state has been confirmed experimentally.¹²–¹⁴ The microscopic mechanism responsible for the complex phase diagram of TiOX is not fully understood.¹³,¹⁵ A detailed knowledge of the ground state above \( T_{c2} \) is helpful to clarify this issue.

II. METHODS

To investigate the electronic structure of TiOBr we performed photoemission (PES), resonant photoemission, and x-ray absorption (XAS) spectroscopy measurements, accompanied by \textit{ab initio} embedded-cluster calculations of the electronic structure and of the relevant magnetic interactions in the room-temperature phase.

A c-oriented TiOBr crystal was grown by chemical vapor transport³,¹⁶ and its crystallinity checked by x-ray diffraction. Experiments were performed at the surface branch of beam-
line I-511 (Ref. 17) of the MAXlab-II synchrotron radiation facility. The sample was introduced in the entry lock of the experimental chamber and cleaved there in an inert nitrogen atmosphere. The loadlock was then pumped down and the sample was transferred to the experimental chamber (base pressure $1 \times 10^{-10}$ mbar). The light polarization could be varied from parallel to normal with respect to the sample surface without modifying the photoelectron detection geometry, which could be chosen to be normal with respect to the sample ($7^\circ$ from the surface normal) or grazing ($70^\circ$ from the surface normal). The analyzer acceptance angle was $\pm 6^\circ$.

The XAS spectra were acquired by varying the photon energy across the Ti $L_{2,3}$ and O K absorption edges and measuring the induced Auger decay or the total electron yield. Resonant photoemission of the valence band states was performed at the same photon energies. The experimental resolution was better than 0.1 eV for both PES and XAS. Special precautions were taken to avoid charging effects during the measurements, which easily occurred due to the strongly insulating character of TiOBr. The sample was glued with silver paste onto a metallic substrate to ensure the best possible grounding. All measurements were performed at room temperature, and the photon flux was lowered until neither binding energy shifts nor broadening of the photoemission features could be detected in the valence band spectrum.

The theoretical study was performed using the embedded cluster approach. To approximate the $N$-electron wave function, the restricted active space self-consistent field (RASSCF) method was used. This method allows a treatment of electron correlation in which a restricted number of electrons is correlated whereas all other electrons are considered to be in doubly occupied orbitals (inactive space). This restricted space is divided in three orbital-specific spaces starting from RAS1 for which orbitals contain a chosen maximum number of holes and ending with RAS3 where we consider orbitals containing a maximum number of electrons. The RAS2 orbital space contains all electrons that are not in RAS1, RAS3, or inactive orbitals. The configuration interaction (CI) expansion of the wave function includes all possible distributions of the electrons within the restrictions mentioned above. Using only the RAS2 space (i.e., if the RAS1 and RAS3 contain no orbitals) yields a conventional complete active space self-consistent field (CASSCF) calculation. In a RASSCF or CASSCF calculation not only the CI expansion coefficients, but also the orbitals are optimized. Often a common set of orbitals is optimized for a weighted average of a number of similar, closely lying states.

The ground state electronic structure of an embedded [TiO$_2$Br$_2$]$_2^-$ cluster was first investigated using only the RAS2 space containing one electron in five orbitals (corresponding to a CAS(1,5)SCF calculation). The cluster was surrounded by eight Ti$^{3+}$ ions represented by total ion potentials in order to account for the electrostatic interaction between the cluster atoms and the shell of first neighbor atoms, and further embedded in a field of point charges fitted to reproduce the Madelung field due to the rest of the crystal. The crystal lattice is taken from Ref. 2. The orbitals in the cluster region were derived from a $(21s15p10d6f4g)$ primitive basis set for the titanium and a $(14s9p4d3f)$ primitive basis set for the oxygen ions. Following the atomic natural orbital (ANO) contraction of Widmark and coworkers, we used a (14s9p4d3f) basis for Ti and a (4s3p) basis for O. These are the so-called ANO-L bases as implemented in the MOLCAS quantum chemistry package. For the Br atoms, an effective core potential (ECP) with a valence basis set from Dolg was employed. To obtain the ground state electron distribution a small active space consisting of five orbitals of mainly Ti 3$d$ character is sufficient, as dynamical electron correlation effects are expected to be small for the charge distribution of this state with one single 3$d$ electron.

Theoretical modeling of the O 1$s$ and Ti 2$p$ XAS spectra was performed. To simulate a hole in one of the four oxygen 1$s$ orbitals of a TiO$_2$Br$_2$ cluster, the nuclear charge of that atom was increased from 8 to 9. In addition, an electron was added to the cluster and the energies of the 3$d^2$ manifold were obtained from CAS(2,5)SCF calculations. This simple procedure was repeated for each oxygen ligand in order to gain an insight in the origin of the lowest-energy peaks in an O 1$s$ XAS spectrum. For each oxygen hole the final state wave functions were obtained from two average RASSCF calculations (one for the spin-singlet and one for the spin-triplet states of the 3$d^2$ manifold). A more advanced method is required to simulate the Ti 2$p$ spectrum because in this case it is necessary to include relativistic effects, in particular the spin-orbit coupling. Initial (2$p^6$ 3$d^1$) and final (2$p^5$ 3$d^2$) states without spin-orbit coupling effects were initially obtained from RASSCF calculations using the same embedded cluster and basis sets as for the computation of the ground state. The RAS2 space used for this computation contains ten orbitals (5 Ti $3d^4$+5 Ti $3d'$), where the five $3d'$ orbitals are added to allow for a proper treatment of dynamic electronic correlation. For the computation of the final states the three Ti 2$p$ orbitals were constrained to be in the RAS3 space, with a maximum of five electrons. Due to the large number of final-state wave functions to be computed (75 for $S=M_s=1/2$ states and 30 for $S=3/2$ states), these were obtained from four average RASSCF calculations, one for each irreducible representation of the C$_{2v}$ point group. The resulting initial and final state wave functions were then used as input for a RASSCF state interaction (RASSI) computation performed in order to include the spin-orbit coupling and to compute the absorption intensity for the ensuing 270 final absorption lines. The calculated spectrum was broadened with a Gaussian and a Lorentzian function to mimic the instrumental resolution and lifetime broadening. A full width at half maximum of 0.1 eV was used for the Gaussian function to reproduce the experimental resolution. The Lorentzian width was set to 0.2 eV, which is a typical value of lifetime broadening for 2$p$ core levels in 3$d$ transition metal oxides.

The magnetic interactions were computed within the density functional theory (DFT) broken-symmetry approach using the scheme proposed by Yamaguchi and the B3LYP exchange-correlation potential with a 6-311G* Gaussian basis set. For the computation of each magnetic interaction, a cluster containing the two interacting Ti ions and their O and Br first neighbors was considered. The next shell of Ti$^{3+}$ ions was simulated by Al$^{3+}$ ECP potentials and the resulting cluster embedded in a distribution of point charges.

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III. RESULTS AND DISCUSSION

A. Photoemission and resonant photoemission spectra

Figure 1(a) shows the overview photoemission spectra measured in both emission geometries with 650 eV photon energy and light polarization parallel to the sample surface. The absence of extra peaks other than Br, Ti, and O features establishes that the sample is pure and that the surface is free of adsorbates. Comparison between the two geometries indicates that the crystal is Br terminated, which is expected since the covalently bonded TiO bilayers interact via van der Waals forces, so that cleavage occurs between adjacent halogen planes. The final state spin-orbit splitting of the Ti 2p core level is 6 eV, as visible in the inset of Fig. 1(a).

The PES intensity in the valence band region, shown in Fig. 1(b) for the two light polarizations, derives from O 2p, Br 4p, and Ti 3d states. The lowest binding energy feature has mainly Ti character (see below). A preliminary DFT study of the orbital-projected density of states in TiOBr shows that the spectral feature at 8 eV binding energy has mostly O 2p character, while the components at intermediate binding energies have a dominant Br 4p character. Similar results were obtained in recent DFT calculations using the generalized gradient approximation including the on-site Hubbard U. Our valence band spectra display the same structure as the angle-resolved spectra measured on TiOCl and TiOBr. The Ti-derived feature at lowest binding energy is well-separated from the rest of the spectrum in both systems, though the separation is smaller in the TiOBr case due to the larger unit cell, and has a similar width in both cases (roughly 2.5 eV).

Figure 2 shows the resonant valence band photoemission spectra acquired at various photon energies across the Ti 2p and O 1s absorption edges. In the spectra acquired at the Ti 2p edge [Fig. 2(a)] a large resonant enhancement of the Ti feature is observed. As a function of the photon energy the intensity of the feature closest to EF displays two maxima which are 6 eV apart. These correspond to the resonant process involving the two possible spin-orbit states of the Ti 2p core hole. It can be seen in Fig. 2(a) that also the intensity of the other valence band features is slightly enhanced across the two thresholds, signaling a partial Ti character of these states as well. The enhancement of the lowest binding energy feature is by far the most important, which confirms that this feature derives mainly from Ti states.
The mainly Ti 3d-derived feature displayed a resonant enhancement also when the excitation light was varied across the O 1s edge [Fig. 2(b)], though the magnitude of the enhancement was smaller than for the Ti 2p edge. The observation of such a resonance indicates that there is a significant admixture of O 2p character to the mainly Ti 3d-derived band, as will be discussed in more detail in relation to the x-ray absorption spectra. In the resonant photoemission at the O K edge also the states above 3 eV binding energy are enhanced, especially those at highest binding energy, which is in agreement with their dominant oxygen character. A small peak appears above the Ti 3d states for photon energies right above each absorption edge. The binding energy of the features scales linearly with the photon energy, which shows that they originate from the Auger decay of the Ti 2p and O 1s core hole, respectively.

As visible in Fig. 1(b), the intensity ratio between the Ti 3d states and the O- and Br-derived density of states is higher when the light polarization is parallel to c. This reflects the fact that the ground state orbital has mainly \( d_{2z^2-r^2} \) character (we use the convention of Ref. 13 for which \( x | a, y | b, \) and \( z | c \)). In normal emission the directions of the detected photoelectrons form a cone around the c axis. Due to polarization selection rules, electrons occupying an orbital of even parity with respect to a plane containing the crystallographic direction c (such as the \( d_{2z^2-r^2} \) orbital) can be photoemitted in that direction only if the polarization of the incident light is parallel to c. The nonzero signal recorded with light polarization perpendicular to c is here mainly due to the geometry of the experiment: the sample had to be tilted slightly (less than 10°) toward the impinging light (the light incidence cannot be perfectly grazing), which implied a similar deviation of the detection direction from the c axis. A nonvanishing Ti 3d signal with light polarization along a was observed also in TiOCl and attributed there to a possible sample misalignment and/or the effect of symmetry-breaking phonons.

We note that the Br- and O-derived features also display a dependence on polarization [Fig. 1(b)]. The shoulder at 4 eV binding energy visible in the spectrum with light polarization in the ab plane, mainly Br-derived, is absent in the spectrum taken with the other light polarization. This polarization dependence is in line with the large dispersion of the O and Br valence band states observed in the angle-resolved PES study on TiOBr.

B. Electronic structure calculations of the ground state and excited 3d\(^1\) states

Our CASSCF cluster study of the valence electronic structure confirms the results of Ref. 11 in that the ground state has one electron in a Ti 3d\(_{2z^2-r^2}\) orbital with some O 2p character mixed in. The ground-state singly occupied orbital is shown in Fig. 3. The largest lobes are observed around the central (Ti) atom, confirming the dominant Ti 3d character. The contribution to the ground state of oxygen orbitals from the nearest-neighbor O atoms lying close to the bc plane containing the central Ti atom (labeled O3 and O4 in Fig. 3) is clearly visible. We have also computed the energies of the higher-lying (excited) 3d\(^1\) orbitals. Four low-lying excited 3d\(^1\) states exist, with energies 0.34, 0.70, 1.62, and 2.21 eV above the ground state. These values are similar to those found in our previous study. The geometry of these excited states is the same in both TiOCl and TiOBr. Ir-active orbital excitations were observed at 0.5–0.8 eV (1.3–1.6 eV) with E parallel to a (b) in transmittance experiments on TiOBr. The energy windows of these features correspond to the energies of the computed 3d\(^1\) excited states at 0.70 and 1.61 eV. The interpretation of the ir transmittance dips in TiOBr is the same as for the corresponding TiOCl spectra.

Although the 3d degeneracy is completely lifted, one can distinguish in the computed 3d\(^1\) levels three lower-lying \( t_{2g} \)-derived and two higher-lying \( e_g \)-derived states, separated by an effective crystal field energy splitting of about 1.6 eV. In all five 3d\(^1\) states (ground state and excited states), the singly occupied orbital shows some hybridization with O 2p orbitals. The effect is strongest for the \( e_g \)-like orbitals.

C. XAS spectra and calculations for 3d\(^2\) excited states with a core hole

The O K-edge XAS spectrum of TiOBr is shown in Fig. 4 for the two light polarizations. Since x-ray absorption is an element-and-orbital-selective probe, the detection of absorption at the O 1s edge is direct evidence for hybridization between the Ti 3d and O 2p orbitals, as the O 3s states lie above the vacuum level, i.e., too high in energy to be observed. On the contrary, we did not measure any absorption at the Br 3s or 3p core level thresholds, which confirms the ionic character of the Br species in the compound.

As in many other transition metal oxides, the absorption features at the O K edge derive from the mixing of the O 1s states with the \( d \) (lower energy) and \( s-p \) (higher energy) orbitals of the transition metal. The signal intensity at the absorption threshold is related to the degree of covalency in the compound, which we have already seen to be non-negligible (Fig. 2). In a quasi-octahedral environment, the low energy region of the O 1s XAS spectrum usually consists of two peaks, usually associated with the 3d \( t_{2g} - e_g \) crystal field...
TABLE I. Energy differences (in eV) between the lowest-energy spin-triplet $^3T_{2g}$ and the higher-lying triplet and singlet configurations, calculated using CAS(2,5)SCF on the 3$d^2$ manifold of a TiO$_x$Br$_2$ cluster with a simulated O1s hole. The table summarizes the results obtained for the four possible positions of the core hole. Due to the local symmetry, the oxygen ligands are two by two equivalent and each level shown is twofold degenerate.

<table>
<thead>
<tr>
<th>Oxygen hole site</th>
<th>O1, O2</th>
<th>O3, O4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ triplet ($t_{2g}^2e_g^0$)</td>
<td>1.32</td>
<td>1.61</td>
</tr>
<tr>
<td>$\Delta E$ singlet ($t_{2g}^1e_g^1$)</td>
<td>0.78</td>
<td>1.28</td>
</tr>
</tbody>
</table>

configuration ($^3T_{2g}$ and $^3T_{1g}$ in O$_h$) have energies which are at least 1.3 eV higher than the lowest lying triplet excitations, whereas $t_{2g}^2$-like spin-singlet excitations have energies which are 0.8 eV higher than the corresponding triplet configurations (spin-singlet final states involving $e_g$-like orbitals have even higher energy). Absorption processes in which both electrons are in the higher orbitals in the final configuration (i.e., $t_{2g}^0e_g^2$-like final states) lie high in energy and contribute a low spectral intensity to the XAS spectrum. The total energy spread of the $t_{2g}^2e_g^0$ and $t_{2g}^1e_g^1$ configurations is 4.7 eV. Atomic correlation effects are expected to reduce this interval by about 25% to 3.5 eV, in rather good qualitative agreement with the energy spread of the first two peaks observed in the O K-edge spectra.

Based on these results we interpret the first of the two lowest O 1s XAS peaks as corresponding to $t_{2g}^2$-derived spin-triplet final states and the second peak as being due to a superposition of $t_{2g}^2e_g^0$-like spin-singlet as well as $t_{2g}^1e_g^1$-like spin-triplet final states. The calculations do not yield quantitative information on the relative intensities. Nevertheless, the results indicate that only the second peak involves occupation of an $e_g$-like orbital. In the spectrum acquired with light polarization along $c$, the relative intensity of the first absorption feature is lower than the orthogonal polarization. This might be related to the fact that the lowest unoccupied $d$ level has $d_{xy}$ symmetry, so that transitions from a $3s^2\ 3d^-t_{2g}^-1$ to a $1s^1\ 3d^-t_{2g}^-2$ state involving such an orbital are dipole-forbidden when the $E$-vector is parallel to $c$.

Figure 5(a) shows the XAS spectra recorded at the Ti 2$p$ edge. The core hole spin-orbit coupling splits the spectra into two replicas, corresponding to the $J=3/2$ (lower photon energy) and $J=1/2$ (higher photon energy) states, with an average separation close to that observed in the photoemission spectrum of the Ti 2$p$ core level [inset of Fig. 1(a)]. From statistical arguments owing to the degeneracy of the $2p_{3/2}$ and $2p_{1/2}$ subshells, a $L_3/L_2$ intensity ratio of 2:1 is expected. While this ratio is in fact observed in the Ti 2$p$ PES spectrum, it is not the case for the XAS spectrum. This is a common feature of the $L_{2,3}$ spectrum of many transition metals which originates from a many-electron effect.  

The Ti $L_{2,3}$ absorption features arise from $2p^63d^1 \rightarrow 2p^53d^2$ dipole transitions and carry indirect information on the various unoccupied 3$d$ states and on their symmetry (orientation). The interaction between the electron in the Ti 3$d$ ground state orbital and the second electron which fills
the unoccupied state in the absorption process, and the coupling between the 2p core hole and the 3d electrons combine to give rise to a rich multiplet structure. The direct Coulomb interaction is of the order of a few eV, and it is dependent on the symmetry of the empty orbital which is populated in the absorption step. The theoretical Hund’s rule energy (the so-called “pairing energy”) for two electrons sitting in different $t_{2g}$-like orbitals is of the order of 1–1.5 eV,34 and is also orbital-dependent. The spin-orbit interaction in the 3d shell and the intersite magnetic exchange are instead much smaller orbital-dependent. The spin-orbit interaction in the 3d levels by the ligand field. The difference in line shape between the two spin-orbit replicas originates as the multiplet lines involved are not equivalent due to the different spin-orbit state of the core hole. Each spin-orbit replica consists of two main groups of features in both light polarizations, of which the group at lower energy is less intense. This is reminiscent of the low-energy line shape of the O 1s XAS spectrum, which arises from hybridization with d states. The average energy separation between the two groups of features is roughly 2.5 eV and the total width of each replica is slightly above 4 eV, as found for the O 1s XAS spectra.

An interesting feature of Fig. 5(a) is the more pronounced structure observed with light polarization in the ab plane. The advantages of XAS over other optical probes are the wider energy range accessible and the less stringent selection rules. While only transitions to the second and third excited 3d$^1$ orbitals can be observed in ir transmittance experiments,13 the XAS spectra contain contributions from transitions to all five d sublevels. We stress, however, that a direct comparison between the two experiments cannot be done due to the different states probed by the two techniques. In particular, XAS involves an intermediate state with a 3d$^2$ valence configuration in the presence of a core hole, which strongly modifies the orbitals’ symmetry and energy. The absorption features between 456 and 457 eV in the spectrum with light polarization orthogonal to c, which are not present in the other polarization, might arise from transitions involving the lowest lying 3d level of $d_{xy}$ symmetry, which is unoccupied in the ground state, as discussed also for the O XAS spectra (the corresponding valence band transitions are instead not active in ir).

The theoretical simulation of the Ti 2p XAS spectrum is presented in Fig. 5(b). Despite the large number of input states for the RASSI computation, which reduces the accuracy of the calculation, a semiqualitative agreement is observed between the experimental and the theoretical results. In particular, the splitting into two groups of features with an energy separation of around 6 eV is found in the simulated spectra as well, and the line shapes of the experimental and simulated spectrum with E parallel to c are found to be quite similar, though the energies of the main features do not all correspond exactly. Note, moreover, the relatively more pronounced structure of the calculated spectra with light polarization along a, which is reflected in the larger width of the main spectral features around 464 and 458 eV photon energy in the experimental spectrum with light polarization in the ab plane. This semiqualitative agreement indicates the validity of our embedded cluster quantum calculations, and further evidences the complete crystal-field splitting of the 3d shell.

**D. Magnetic interactions**

Since our data as well as those of Refs. 12 and 13 exclude the possibility of orbital fluctuations, the existence of an intermediate phase between the room temperature (RT) antiferromagnet and the low temperature spin-Peierls phase, and the unconventional character of the transition at $T_c$, must be taken as indications that competing orders are at work in titanium oxyhalides. The direct observation of strong hybridization between the Ti and O states, confirmed by our ab initio calculations, suggests that oxygen-mediated superexchange might play an important role.

To investigate this we have computed the main magnetic couplings in the RT structure of TiOX: along the chain axis...
TABLE II. Calculated magnetic interactions in TiOX. The last column reports the values obtained from the analysis of the magnetic susceptibility in the high-temperature phase (see text for details), after Ref. 1 for TiOCl and Ref. 13 for TiOBr.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_b$ (K)</th>
<th>$J_{nn}$ (K)</th>
<th>$J_a$ (K)</th>
<th>$J_b$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiOBr</td>
<td>$-250$</td>
<td>$-47.0$</td>
<td>$12.0$</td>
<td>$-375$</td>
</tr>
<tr>
<td>TiOCl</td>
<td>$-353$</td>
<td>$-40.8$</td>
<td>$7.4$</td>
<td>$-660$</td>
</tr>
</tbody>
</table>

($J_b$), between adjacent nearest-neighbor chains ($J_{nn}$), and between nonadjacent Ti chains along a. The values of these interactions (in units of K) are listed in Table II for both TiOBr and TiOCl.

The coupling $J_b$ is the dominant interaction and is antiferromagnetic in character. The role of the interchain coupling $J_{nn}$, also antiferromagnetic, is, however, far from marginal, as its intensity is roughly 20% (12%) of the intrachain coupling $J_b$ in TiOBr (TiOCl). The exchange along a is instead much weaker, and ferromagnetic in character. The relative strength and character of these three interactions can be explained based on the nature and geometry of the singly occupied orbital. Since there is no admixture in the ground state of d states other than the $d_{z^2}$ orbital, as previously shown, and because the distance between two Ti ions in adjacent chains is too large to give rise to a significant orbital overlap, the $J_{nn}$ and $J_a$ couplings originate from O-mediated superexchange. The larger admixture of O 2p character from oxygens which are coplanar with the ground state in TiOBr compared to TiOCl, results in a lower value of the magnetic susceptibility, taking the nominal ratio of $J/J_{\text{max}} = 0.64$ typical of the Bonner-Fisher curve. Our calculated values for $J_b$ are off by a factor less than 2 with respect to the experimental ones. Similar discrepancy may be expected for the computational method used, which is known to provide only estimated values. Estimates of $J_b$ provided by previous theoretical work are in somewhat better agreement with the experimental values, but they are based on semiempirical methods which depend on the choice of free parameters (such as U). In addition, these studies do not explicitly take into account magnetic couplings other than along b.

Our method yields the correct order of magnitude of the $J_b$ coupling in both compounds, and the ratio between the calculated and experimental estimates is very similar in the two TiOX compounds. This indicates that, although the magnitudes of the various $J$’s might be off by a (small) scale factor, our $J_{nn}/J_b$ ratios are reliable estimates of the relative strengths of these interactions. Our calculations indeed confirm the larger deviation of TiOBr from a quasi-1D behavior. We base the following discussion on this result.

We argue that the frustrated $J_{nn}$ superexchange, which couples adjacent Ti chains, plays an important role for the TiOX phase diagram. The existence of an interchain interaction was suggested already in Ref. 13. Such interchain coupling was there associated to an electron-lattice mechanism, while our study clearly demonstrates that also a magnetic interchain coupling exists, of superexchange origin. Oxygen-mediated superexchange between transition metal ions is considered to be an important ingredient of the physics of many transition metal oxides, including the high-T$_c$ cuprate superconductors and notably in CuGeO$_3$, the only other example of inorganic spin-Peierls system known so far besides the titanium oxyhalides. A magnetic nature of the interaction competing with the interchain exchange is also suggested by the reported decrease in $T_c$ in the presence of a magnetic field applied along b.

It should be stressed that the transitions observed in the TiOX compounds have a magnetoelastic (rather than simply magnetic) origin, and that a proper description of the system must consider the full spin-lattice couplings. Each exchange interaction depends in a sensitive way on the interatomic distances and bond angles with the linking oxygens, and is therefore coupled to the distortion of the rather soft FeOCl-type structure. As $J_{nn}$ is frustrated in the RT phase of 1D antiferromagnetic chains, any displacement of a Ti ion away from its RT equilibrium position favors a particular superexchange path resulting in a net energy gain. Given the relatively large value of $J_{nn}$ and its frustrated character, we expect the magnetoelastic energy gain associated with such displacements to yield a rather important contribution to the free energy of the low-temperature phases. We propose that the competition between the two magnetoelastic couplings associated, respectively, with $J_b$ and $J_{nn}$ is at the origin of the complex phase diagram of TiOX and in particular of the existence of an incommensurate phase between the RT phase and the spin-Peierls ground state. The intermediate phase is characterized by the opening of a pseudogap in the magnetic spectrum, indicative of the formation of a minority of spin-singlets. The most likely scenario for this phase is the coexistence of a minority of spin singlets em-
bedded in a paramagnetic state with antiferromagnetic correlations, which is accompanied by a structural distortion incommensurate with the RT lattice. The formation of a fraction of spin-singlets is accompanied by an overall distortion of the structure, resulting, we argue, in a free energy gain on the remaining uncoupled spins due to the $J_{nn}$ superexchange. The sensitive dependence of the critical temperatures on halide substitution found experimentally may be expected in this case as the size and position of the halide ions influences the overlap between Ti and O states and thereby the magnitude of the magnetoelastic coupling.

Lower values of the transition temperatures (especially $T_{c1}$) are expected in TiOBr than in TiOCl, as the larger $J_{nn}/J_{p}$ ratio suggests also a stronger competition between the associated magnetoelastic couplings in the former compound. For the same reason a larger $T_{c2}/T_{c1}$ ratio may be expected in TiOBr. A microscopic investigation of the magnetic ordering in the intermediate phase would be necessary to settle this issue and to understand quantitatively the role played by the interchain superexchange in the TiOX system.

IV. CONCLUSIONS

A TiOBr crystalline sample was probed by photoemission and x-ray absorption spectroscopy and theoretical calculations were performed on the electronic and magnetic structure of the intermediate phase. The O 1$s$ and Ti 2$p$ XAS spectra provide direct experimental evidence for the complete lifting of degeneracy in the Ti 3$d$ shell due to the crystal field. The five Ti 3$d$-derived states may still be grouped roughly into two sets, separated by an average O$_{2p}$-like crystal field splitting of about 1.6 eV. The computed separation between the ground-state and first-excited 3$d^1$ orbital in TiOBr is found to be 0.34 eV, which is too large to give rise to $d$-orbital mixing or ordering.

On the basis of our theoretical results, the first peak in the O 1$s$ XAS spectrum is associated with excitations to high valence-spin O 1$s$ Ti 3$d$ $t_{2g}$-like final states. The second peak has contributions from the same configuration with a low valence-spin value, and from O 1$s$ Ti 3$d$ $t_{2g}$-like configurations. A large number of states and the richness of the interactions in TiOBr conspire to give rise to the rich structure observed in the Ti 2$p$ XAS spectra.

The observation of absorption at the O 1$s$ edge and the resonant enhancement of the lowest binding energy feature as the photon energy varies across the O K edge points to a significant admixture of O 2$p$ character in the Ti 3$d$ ground state. Such hybridization leads to superexchange interactions between Ti ions on different chains. On the other hand, the absence of absorption from the Br 3$s$ and 3$p$ core level thresholds confirms that no Br 4$p$-Ti 3$d$ mixing is present. Our cluster calculations indicate that the nearest-neighbor interchain interaction $J_{nn}$ is a significant 19% (12%) fraction of the intrachain exchange $J_b$ in TiOBr (TiOCl). This leads one to speculate that the TiOX phase diagram results from the competition between the spin-Peierls ordering associated with the exchange along b and the magnetoelastic coupling associated to the frustrated superexchange $J_{nn}$ between next-neighboring chains.

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23. The final states with $S=3/2$ are $3 \times 10=30$ (from the $2p$ hole and 10 from the two $3d$ electrons with parallel spins); for $S=1/2$ there are 30 states where the two $3d$ electrons have parallel spins and 45 with antiparallel spins, for a total of 75. The total number of lines in the absorption spectrum is thus $75 \times 2 + 30 \times 4 = 270$.


28. P. De Boeij (private communication).


36. The superexchange along $a$ would vanish if the bilayer were not buckled, since in this case the exchange direction would be orthogonal to the $3d$ ground state orbital. This indicates that the magnetic coupling along $a$, originates from the small tilt between the oxygen orbitals involved and stems from mutually orthogonal states at the same oxygen site, which explains its weak ferromagnetic character.


