Reduction of ordered moment in strongly correlated LaTiO_{3+ δ} upon band filling

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Neutron diffraction and magnetic susceptibility experiments were performed on single crystals of the doped Mott-Hubbard insulator LaTiO_{3+δ}. The magnetic properties of the three-dimensional correlated electron system were investigated upon hole doping. The size of the ordered moment of Ti³⁺ in the canted antiferromagnetically ordered phase reaches a maximum of $0.46(2)\mu_B$ for LaTiO₃. Upon increasing the band filling, i.e., upon increasing the amount of nonstoichiometric oxygen δ from 0 to ~0.08, the ordered moment on Ti³⁺ is shown to decrease rapidly. The weak-ferromagnetic saturation moment of LaTiO_{3.07(1)}, on the verge of the insulator-to-metal transition, is reached via a series of steps in the magnetization curve. [S0163-1829(99)00318-5]

The orthorhombically distorted perovskite LaTiO₃ is a Mott-Hubbard insulator with a small charge gap ($\sim 0.2 \text{ eV}$) between the correlated Ti 3d states of the Coulomb-split lower and upper Hubbard band.¹⁻³ The nominal valence of Ti in LaTiO₃ is 3 + with $3d^1$ ($S = \frac{1}{2}$) configuration. Increasing the average valence of Ti leads to the formation of a strongly correlated metal as the gap becomes filled with carriers. This can be realized, for example, in LaTiO_{3+ δ} or $La_{1-x}A_xTiO_3$ (A is a divalent alkaline earth). A critical enhancement of the effective electron mass was found upon approaching the Mott-Hubbard insulator phase from the metallic side.^{4,5} For low carrier doping, i.e., in LaTiO_{3+ δ} with off-stoichiometric oxygen $0 \le \delta \le 0.08$ (Refs. 6–9) or $La_{1-x}A_xTiO_3$ with $0 \le x \le 0.05$ (Refs. 9 and 10), a metal-toinsulator transition occurs at low temperatures. This transition is accompanied by antiferromagnetic (AF) ordering of Ti³⁺ moments, with a weak-ferromagnetic component due to spin canting.

The dependence of the electronic and magnetic properties of LaTiO₃ on doping resembles to a certain degree the situation of the high- T_c cuprates^{11–13} and colossal magnetoresistance manganese perovskites.^{14–16} The parent compounds of cuprates and manganates are charge-transfer insulators with the gap formed between the occupied oxygen 2p states and the unoccupied Cu or Mn 3*d* states of the upper Hubbard

band. On changing the effective valence of Cu, i.e., by controlling the filling of the Cu-O related band, the cuprates exhibit a phase transition from an AF insulator to an unconventional metal through the high- T_c superconductor state. In manganese perovskites based on the AF insulator LaMnO₃, for some values of hole doping an insulator-to-metal transition occurs at a certain temperature, generally associated with the ferromagnetic Curie temperature.

For all these 3*d* electron systems the band filling control of the parent Mott insulators has been widely recognized as one of the most important aspects of the insulator-to-metal transition.^{13,17} Moreover, it is believed that magnetism strongly affects the electronic system. Therefore, a detailed knowledge of the magnetic properties of the doped Mott-Hubbard insulator LaTiO_{3+ δ} might contribute to a better understanding of the insulator-to-metal transition in strongly correlated electron systems.

In this paper, we present neutron-diffraction and magnetic-susceptibility measurements on a series of single crystals of LaTiO_{3+ δ}. We observed a significant reduction of the ordered moment size of Ti upon filling the narrow *d*-electron band of LaTiO₃, i.e., upon increasing δ from 0 to $\sim 0.07(1)$. This gives further evidence that the spin-ordered phase collapses upon approaching the Mott-Hubbard transition boundary. In the immediate vicinity of the insulator-to-

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FIG. 1. Orthorhombic *Pbnm* space group of LaTiO₃ with four distorted perovskite units in the crystallographic unit cell. Unit cell parameters at T=100 K are a=5.626 Å, b=5.590 Å, and c=7.904 Å. The positions of the Ti spins in the unit cell are labeled S_1, \ldots, S_4 . The G_zF_x magnetic structure is indicated by arrows. Note, however, that we cannot distinguish between G_xF_z and G_zF_x .

metal transition, i.e., in $\text{LaTiO}_{3.07}$, a peculiar magnetization behavior is observed. The weak-ferromagnetic saturation moment is reached via a series of steps in the magnetization curve.

All the LaTiO_{3+ δ} single crystals were prepared by floating-zone melting of sintered ceramic bars in a reducing atmosphere. The ceramics were prepared using a mixture of La₂O₃, TiO, and TiO₂ sintered at 1350 °C. Special attention was paid to the synthesis of samples with $\delta \approx 0$. The oxygen content of the crystals was measured with a thermogravimetric analyzer (SETARAM). Only crystals with a homogeneous oxygen content were used in this investigation. Neutron diffraction was performed at the thermal neutron singlecrystal diffractometer D15 at the high neutron flux reactor of the Institute Laue Langevin, Grenoble, France. The wavelength used was $\lambda = 1.17$ Å. The magnetization was measured with a commercial superconducting quantum interference device (SQUID) magnetometer (Biomagnetic Technologies, Inc.).

We have measured the intensity of 198 Bragg reflections at different temperatures of three twinned single crystals of LaTiO_{3+δ} with δ =0.000(5), δ =0.030(5), and δ =0.07(1). These crystals are located in the magnetic phase diagram where AF magnetic ordering of the Ti moments is expected. LaTiO_{3+δ} belongs to the orthorhombic space group D_{2h}^{16} -*Pbnm* with four distorted perovskite units in the crystallographic unit cell, Fig. 1. In this space group, a gain in neutron intensity *superposed* on structural Bragg peaks is ex-

TABLE I. Relative increase in neutron intensity due to magnetic ordering of $LaTiO_{3.000(5)}$ for selected reflections.

h k l	[I(5 K) - I(190 K)]/I(5 K)
100	~ 0
010	~ 0
101	0.60 ± 0.09
011	0.59 ± 0.10
111	~ 0

TABLE II. The four possible magnetic structures for the *Pbnm* space group. The symmetry operators 2z, ax, and ny relate the position and orientation of spin S_1 to S_2 , S_3 , and S_4 , respectively. The orientation of the spins along the indicated x, y, and z axis are denoted with a + or - sign.

	1	G_x	A_y	F_{z}	2		A_x	G_y	C_{z}
I	S_1	+	+	+	Ι	S_1	+	+	+
2z	S_2	_	—	+	2z	S_2	_	_	+
ax^{\dagger}	S_3	_	+	+	ax	S_3	+	_	_
ny†	S_4	+	—	+	ny	S_4	-	+	_
	3	C_x	F_y	A_{z}	4		F_{x}	C_y	G_{z}
I	S_1	+	+	+	Ι	S_1	+	+	+
$2z^{\dagger}$	S_2	+	+	—	$2z^{\dagger}$	S_2	+	+	—
ax^{\dagger}	S_3	_	+	+	ax	S_3	+	_	_

pected for AF ordering of Ti moments. For all crystals with $0 \le \delta \le 0.08$ we observed magnetic scattering at the same positions although the magnetic contribution to these Bragg peaks decreases with band filling, i.e., with increasing off-stoichiometric oxygen δ . For LaTiO_{3.000(5)}, the relative increase due to magnetic ordering of Ti moments for some principal reflections is listed in Table I.

The only four magnetic structures with zero propagation vectors that are compatible with LaTiO_{3+ δ} crystal symmetry are listed in Table II. In this table, the position of the Ti spins in the crystallographic unit cell are labeled $S_1(x,y,z)$ $=(\frac{1}{2},0,0), S_2(x,y,z)=(\frac{1}{2},0,\frac{1}{2}), S_3(x,y,z)=(0,\frac{1}{2},0), \text{ and}$ $S_4(x,y,z) = (0,\frac{1}{2},\frac{1}{2})$, see Fig. 1. The position and orientation of these spins are coupled with the symmetry operators 2z, ax, and ny, which relate the Ti spin S_1 to S_2 , S_3 , and S_4 , respectively. The two orientations of the spins along the indicated x, y, and z axis are denoted with a + or - sign. The three magnetic structures in Table II with a ferromagnetic component F can account for the weak-ferromagnetic moment previously observed in magnetization measurements.⁶⁻⁹ To distinguish among these three structures, we consider the magnetic structure factors for certain reflections listed in Table III. The significant magnetic intensity observed at the $(1 \ 0 \ 1)$ and $(0 \ 1 \ 1)$ reflection is compatible with the AF type-G structure. We have essentially zero intensity in the $(1 \ 0 \ 0)$, $(0 \ 1 \ 0)$, and $(1 \ 1 \ 1)$ reflections. This leads to the conclusion that no AF type-A and type-C

TABLE III. Magnetic structure factor for selected reflections.

h k l	Structure factor	Order type	
101	$-S_1 + S_2 + S_3 - S_4$	G	
011	$S_1 - S_2 - S_3 + S_4$	G	h+k odd, l odd
001	$S_1 - S_2 + S_3 - S_4$	A	
111	$-S_1 + S_2 - S_3 + S_4$	A	h+k even, l odd
$1 \ 0 \ 0$	$-S_1 - S_2 + S_3 + S_4$	С	
010	$S_1 + S_2 - S_3 - S_4$	С	h+k odd, l even
1 1 0	$-S_1 - S_2 - S_3 - S_4$	F	h+k even, l even
$ \begin{array}{c} 0 & 1 & 0 \\ 1 & 1 & 0 \end{array} $	$S_1 - S_2 + S_3 + S_4$ $S_1 + S_2 - S_3 - S_4$ $-S_1 - S_2 - S_3 - S_4$	C F	h+k odd, l e h+k even, l e



FIG. 2. (a) Temperature dependence of the AF ordered moment on Ti $m_{AF}(T)$ of LaTiO_{3.000(5)}, LaTiO_{3.030(5)}, and LaTiO_{3.07(1)}. The dotted lines are fits to $m_{AF} \propto (1 - T/T_N)^{\beta}$ with $\beta = 0.35(3)$ and $\beta = 0.36(4)$ for LaTiO_{3.000(5)} and LaTiO_{3.030(5)}, respectively. (b) Temperature dependence of the macroscopic weak-ferromagnetic moment $m_{WF}(T)$ measured by SQUID magnetometry.

components are present in the magnetic structure of $LaTiO_{3+\delta}$. The magnetic structure is therefore either G_xF_z or G_zF_x , Fig. 1. This means that all nearest-neighbor Ti moments are oriented antiparallel in the three-dimensional (3D) long-range ordered phase below the Néel temperature T_N , in agreement with previous neutron powder-diffraction measurements on LaTiO_{3.0}. ¹⁸ Because of the twinning of the crystals we cannot distinguish between G_xF_z and G_zF_x .

It is interesting to investigate the evolution of the ordered moment size $m_{\rm AF}$ of Ti and its temperature dependence upon band filling. Considering the observed magnetic intensities, we find for LaTiO_{3.000(5)} an ordered moment on Ti of $m_{\rm AF} = 0.46(2)\mu_B$, where μ_B is the Bohr magneton. Upon hole doping, the ordered moment decreases rapidly. For LaTiO_{3.030(5)} and LaTiO_{3.07(1)}, a moment on Ti of $0.32(2)\mu_B$ and $0.09(3)\mu_B$, respectively, is obtained. The temperature dependence of the ordered moment $m_{\rm AF}(T)$ in the three crystals is shown in Fig. 2(a). A fit with $m_{\rm AF} \propto (1 - T/T_N)^{\beta}$ in the vicinity of T_N leads to the respective critical exponents $\beta = 0.35(3)$ and $\beta = 0.36(4)$, for LaTiO_{3.030(5)} and LaTiO_{3.030(5)}, consistent with the 3D Heisenberg picture.

Generally, an ion with spin S in a 3D magnetically ordered lattice has an ordered moment of $g\mu_B S$, which yields $\sim 1\mu_B$ for $S = \frac{1}{2}$ when $g \sim 2$. The smaller ordered moment of $\sim 0.5 \mu_B$ found in LaTiO₃ is not due to quantum fluctuations. These are known to reduce significantly the ordered moment, cuprates, because of e.g., in the а reduced dimensionality.^{19,20} In fact, the ordered moment of $0.46(2)\mu_{R}/\text{Ti}$ in the 3D correlated LaTiO₃ can be explained with an unquenched orbital momentum. In the ionic picture without crystal distortion the orbital magnetization induced by spin-orbit interaction on the t_{2g} states is $1 \mu_B$. The crystal field in LaTiO₃ splits the degenerate t_{2g} orbitals and partly quenches the orbital moment. This remaining orbital momentum reduces the total magnetic moment on the Ti sites. in accordance with Hund's third rule. Roughly speaking, the result of this is a strongly reduced "effective" g factor (g ~ 1).²¹

The macroscopic weak-ferromagnetic moment found in the spin-ordered state is due to canting of the AF ordered Ti moments. The canting is driven by the GdFeO3-type distortion²² of the perovskite lattice. This rotation of the $Ti-O_6$ octahedra in the orthorhombic phase allows the antisymmetric Dzyaloshinski-Moriya superexchange term H $= \sum_{(i,i)} D_{ii} S_i \times S_i$ in the spin Hamiltonian. Figure 2(b) shows the temperature dependence of the weakferromagnetic moment $m_{\rm WF}$ for the three LaTiO_{3+ δ} crystals as measured by SQUID magnetometry. The AF ordered moment size m_{AF} , Fig. 2(a), and the weak-ferromagnetic moment $m_{\rm WF}$, Fig. 2(b), decrease by the same fraction with an increasing amount of nonstoichiometric oxygen $0 \le \delta \le 0.08$. This indicates that, within the error, the reduction of the macroscopic weak-ferromagnetic moment can be understood in terms of a decreased moment on Ti without a change in canting angle ($\sim 1.7^{\circ}$).

Figure 3 shows the dependence of the ordered moment $m_{\rm AF}$ versus Néel temperature T_N . We have included data on the weak-ferromagnetic moment $m_{\rm WF}$ of several additional LaTiO_{3+ δ} crystals with $0 \le \delta \le 0.08$, which was shown to be a good measure of m_{AF} (see above). The size of the ordered moment of Ti reaches a maximum of $0.46(2)\mu_B$ for LaTiO_{3,000(5)}. With increasing band filling, the moment decreases rapidly and long-range 3D order is suppressed for $\delta \gtrsim 0.08$, i.e., for more than ~0.16 holes/Ti. Surprisingly, $T_N(m_{\rm AF})$ does not extrapolate to zero, which prompted us to speculate about a collapse of T_N as $m_{AF} \rightarrow 0$ in the vicinity of the Mott-Hubbard transition. It is interesting to compare this behavior with the situation found in cuprates and manganates. The ordered moment size in the AF ordered phase of $YBa_2Cu_3O_{6+\delta}$ or $La_2CuO_{4+\delta}$ as determined by magnetic neutron scattering has a maximum of $m_{\rm AF} \sim 0.6 \mu_B$ for $\delta \sim 0.^{20,23}$ This limit is in agreement with the theoretical prediction for a $S = \frac{1}{2}$ 2D Heisenberg AF.¹⁹ With increasing δ ,



FIG. 3. Néel temperature T_N versus the AF ordered moment $m_{\rm AF}$ on Ti (bottom axis) for LaTiO_{3.000(5)}, LaTiO_{3.030(5)}, and LaTiO_{3.07(1)}. The weak-ferromagnetic moment $m_{\rm WF}$ for an additional series of crystals is included (top axis). The $m_{\rm WF}$ (top axis) is scaled to $m_{\rm AF}$ for LaTiO_{3.000(5)}. The dashed line is a guide to the eye.

i.e., by controlling the filling of the Cu-O related band, the ordered moment size of Cu²⁺ is reduced accompanied by a strong decrease in T_N . Contrary to the situation in LaTiO_{3+ δ}, the Néel temperature in these cuprates is found to be proportional to the ordered moment.¹² Long-range AF order in $YBa_2Cu_3O_{6+\delta}$ and $La_2CuO_{4+\delta}$ cannot develop above a critical hole concentration of ~ 0.02 holes/Cu. The AF ordered moment on Mn in LaMnO3 (AF type-A structure, 3.49 μ_B with $T_N = 140$ K) is, like for the titanates and cuprates, strongly reduced upon hole doping. Ordered moments of $2.52\mu_B$ and $0.25\mu_B$ are reported for LaMnO_{3.025} and LaMnO_{3.07}, respectively.¹⁶ In LaMnO_{3+ δ}, filling the Mn-O band leads to a decrease in AF moment and a gradual formation of ferromagnetic order, which makes it difficult to make a statement concerning the doping dependence of the Néel temperature. Note the similarity in hole doping above which AF order in LaTiO_{3+ δ} and LaMnO_{3+ δ} is suppressed. In the ionic picture, this critical doping of ~ 0.14 to 0.16 holes/site corresponds to $M^{4+}/M^{3+} \sim 1/6$, i.e., every spin (M^{3+}) has on average about one hole (M^{4+}) as its nearest neighbor. This is consistent with the model proposed by Aharony et al.,²⁴ that the effect of hole doping is not to dilute the spin system, but to introduce frustration. The holes in rare-earth oxides reside primarily on oxygen atoms. The exchange interaction between the hole on the oxygen and each of its two nearest-neighboring M (M = Ti, Mn, or Cu) holes requires that the M spins be parallel. Frustration occurs because the M-O-M superexchange interaction is antiferromagnetic. If the O-M exchange is large enough, AF order will be disrupted.

We have measured the magnetization curves m(H) of LaTiO_{3+ δ} crystals to study the behavior of the weak-ferromagnetic component to the ordered moment. The crystals have been cooled to $T < T_N$ in a μ -metal shielded environment to ensure true zero-field cooling prior to the measurement. Whereas LaTiO₃ shows the typical m(H) behavior of a weak ferromagnet, a peculiar



FIG. 4. Magnetization versus applied field m(H) of LaTiO_{3.07(1)} for temperatures indicated. The m(H) curves for T=25 K and T=40 K are offset for clarity. The sample is cooled in a μ -metal shielded environment to ensure zero-field cooling. The series of steps in m(H) are indicated by an arrow.

magnetization behavior, is found for hole-doped samples on the verge of the Mott-Hubbard transition boundary. Figure 4 shows the magnetization curves m(H) of LaTiO_{3.07(1)} for three different temperatures. Pronounced steps in the magnetization curve upon reaching the saturation moment are observed. These steps are basically equally spaced in the applied field. With increasing temperature, the separation between the steps decreases. It is interesting to note that the magnetization curve m(H) at T=5 K of the related Mott-Hubbard insulator PrTiO₃ was also shown to have a large hysteresis, with one clear step at $\mu_0 H \sim 3.5$ T.¹⁰ One might speculate that an applied field is able to switch one twin domain into another with a more favorable ferromagnetic direction, generating steps in the magnetization curve. This could also explain qualitatively its temperature dependence as being a balance between the thermal energy and the energy introduced by the field. It remains surprising, however, that the steps are regularly spaced in the applied field. Further information on the field dependence of the ferromagnetic component in the ordered state could be obtained by polarized neutronscattering experiments.

In summary, we have presented neutron diffraction and magnetic susceptibility of single crystals of the doped Mott-Hubbard insulator LaTiO_{3+δ}. The Ti³⁺ moment, 0.46(2) μ_B in LaTiO_{3.000(5)}, is shown to decrease rapidly with increasing nonstoichiometric oxygen $0 < \delta \le 0.08$. Near the insulator-to-metal transition, i.e., in LaTiO_{3.07(1)}, the weak-ferromagnetic saturation moment is reached via a series of well-defined steps in the magnetization curve.

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