Transition from Orbital Liquid to Jahn-Teller Insulator in Orthorhombic Perovskites RTiO$_3$

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(Received 25 April 2008; published 21 August 2008)

Following the same strategy used for RVO$_3$, thermal conductivity measurements have been made on a series of single-crystal perovskites RTiO$_3$ ($R =$ La, Nd, ..., Yb). Results reveal explicitly a transition from an orbital liquid to an orbitally ordered phase at a magnetic transition temperature, which is common for both the antiferromagnetic and ferromagnetic phases in the phase diagram of RTiO$_3$. This spin/orbital transition is consistent with the mode softening at T_N in antiferromagnetic LaTiO$_3$ and is supported by an anomalous critical behavior at T_c in ferromagnetic YTiO$_3$.

DOI: 10.1103/PhysRevLett.101.087205 PACS numbers: 75.30.Et, 75.40.−s

A spin order-disorder transition in a Mott insulator does not alter the exchange interaction given by a static orbital ordering. In this classic situation, the magnetic transition takes place at a temperature that is close to the prediction by fitting the magnetic susceptibility $\chi(T)$ of the paramagnetic (PM) phase to a Curie-Weiss (CW) law. The transition observed in the perovskite LaVO$_3$ does not belong to this class of magnetic transition [1]. Fitting $\chi^{-1}(T)$ of the PM phase with a CW law gives an anomalously large Weiss constant θ. In this t^2e^0 system, the orbital-lattice interaction is relatively weak and the octahedral-site distortion in the PM phase is negligible, which releases an orbital degree of freedom to the spin-orbital system coupled through the superexchange interaction. The degenerate spin-orbital system is so fragile that the orbital dynamic is sensitive to the local structural bias. The solution for the frustrated LaVO$_3$ perovskite is a phase transition at T_N where both orbital and spin become ordered in a way compatible with the intrinsic lattice distortion. Corresponding to this transition, a glassy thermal conductivity $\kappa(T)$ of the PM phase converts to an essentially phonon $\kappa(T)$ as temperature decreases from T_N, which verifies clearly the argument [2] that an orbitally ordered phase should be "transparent" for thermal phonons and orbital fluctuations would enhance the phonon scattering. The t^1e^0 system of RTiO$_3$ shares a similar evolution of local site distortion as a function of rare-earth-metal atom ionic radius (IR) that is intrinsic to the orthorhombic perovskite oxides [3]. However, the antiferromagnetic (AFM) spin-spin interaction changes to a ferromagnetic (FM) interaction as IR reduces [4]. Whether the magnetic interaction is determined by a classic orbital ordering or is induced by quantum orbital fluctuations remains unclear in this perovskite family. In an orbital-ordering model, Mizokawa and Fujimori [5] explained the magnetic interaction in RTiO$_3$ by using a spin- and orbital-unrestricted Hartree-Fock approximation and orbital functions that are a combination of two of xy, yz, and zx orbitals. Mochizuki and Imada [6] modified this orbital-ordering model by introducing the intersite t-e hybridization which contributes 1D FM coupling in addition to the FM interaction along the other directions due to the orbital ordering. These orbital-ordering models, however, are challenged by the spin-wave dispersion curve obtained on FM YTiO$_3$. The dispersion curve can be well explained with a uniform 3D FM coupling due to orbital quantum fluctuations [7]. In AFM LaTiO$_{3+\delta}$, Keimer *et al.* [8] postulated strong orbital fluctuations in the magnetically ordered phase based on their neutron-scattering results. Moreover, experimental results [9–13] of probing either the site distortion or the local electron density do not provide a consistent picture of how orbitals are ordered for a given RTiO$_3$. Ordering the occupied t orbital does not create a site distortion that is clearly larger than the intrinsic site distortion seen in RFeO$_3$ [3]. On the other hand, anomalies at T_N of lattice parameters [14], thermal expansion [15] and Raman shift [16] point indirectly to an orbital ordering occurring below T_N in LaTiO$_3$. Here we report the same approach as we have used in the RVO$_3$ family [17] to probe the orbital status by a systematic measurement of $\kappa(T)$ on crystals from AFM LaTiO$_3$ to ferromagnetic YbTiO$_3$. We have also evaluated critical exponents of the FM transition of YTiO$_3$ by isothermal magnetization $M(H)$ and specific-heat $C_p(T)$ measurements.

Single-crystal samples were grown with an image furnace in mixed H$_2$ and Ar atmosphere. A mixture of R_2O$_3$, TiO$_2$, and Ti was used as starting material. Pressed rods of starting materials were used directly for the crystal growth. The crystal quality was checked by Laue back diffraction and the oxygen stoichiometry was verified by a thermoelectric power measurement. The δ in RTiO$_{3+\delta}$ is about 0.001 for La, Gd, Dy, Tm, and Yb; it is about 0.02 for the other rare-earth-metal atoms. The $\kappa(T)$ measurements have been carried out in a homemade setup with the steady-state method. All measurements of magnetization and $C_p(T)$ have been performed in a magnetic property measurement system and a physical property measurement system (Quantum Design).

As shown in Fig. 1(a), all crystals, regardless of an AFM or FM phase in the phase diagram, exhibit a glassy $\kappa(T)$ in

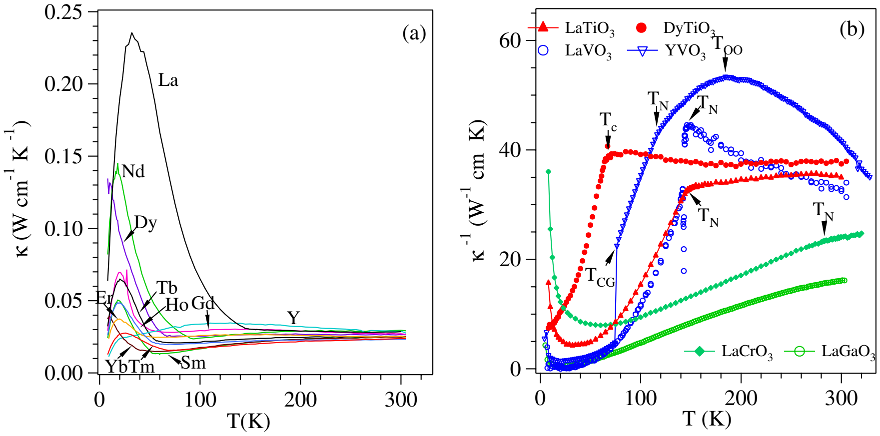

FIG. 1 (color online). (a) Temperature dependence of κ of RTiO$_3$ ($R =$ La, Nd, ..., Yb) crystals. (b) Temperature dependence of inverse κ of several RMO$_3$ perovskites.

the PM phase in terms of both its magnitude and temperature dependence. It is also common to these crystals that a minimum κ occurs at T_N or T_c. A similar $\kappa(T)$ of the PM phase and its behavior on crossing T_N have been observed in the hexagonal RMnO$_3$ ($R =$ Y, Ho–Lu). The glassy $\kappa(T)$ of the RMnO$_3$ compounds has been attributed to the geometrically frustrated spin-spin interaction and the rattling of the oxygen within the triangle of Mn^{3+} ions [18]. Neither of these causes is applicable to the perovskite RTiO$_3$. Spin ordering generally influences $\kappa(T)$ by introducing a critical scattering that manifests itself as a small dent in the vicinity of T_c or T_N on top of the dominant lattice contribution as, for example, in the AFM insulator CoF$_2$ [19] and the FM semiconductor EuO [20]. The critical scattering effect may be enhanced slightly in a geometrically frustrated system such as the hexagonal RMnO$_3$ [18,21], but this effect is insufficient to justify the overall glassy $\kappa(T)$ found in the PM phase of RTiO$_3$. Magnons as heat carriers certainly contribute to a recovery of $\kappa(T)$ at the spin ordering temperature. This contribution, which can have a giant effect on $\kappa(T)$ in a quasi-1D system, is, however, significantly smaller in a 3D structure such as ferromagnetic EuO and AFM LaCrO$_3$. The presence of magnons also creates additional scattering of phonons. The message from the results of Fig. 1 is clear: (a) classic orbital ordering is *not* established in the PM phase of RTiO$_3$, (b) there is a significant change at T_c or T_N in the lattice dynamics due to orbital ordering.

Before deriving the implication of the orbital status for the magnetic interactions, we made a comprehensive comparison of the $\kappa(T)$ of several perovskites $R^{3+}M^{3+}$O$_3$ that include the orbitally degenerate systems of RTiO$_3$ (t^1e^0) and RVO$_3$ (t^2e^0) as well as orbitally nondegenerate AFM LaCrO$_3$ (t^3e^0), and the diamagnetic LaGaO$_3$ (t^6e^4). LaGaO$_3$ in Fig. 1(b) demonstrates a typical phonon $\kappa^{-1}(T)$ for an orthorhombic perovskite oxide since it has neither spin nor orbital degeneracy. LaCrO$_3$, which is the only ceramic sample in this study, shows a slightly large, but an essentially phononlike, $\kappa^{-1}(T)$ as that of LaGaO$_3$. Type-G spin ordering at $T_N = 289$ K induces a small slope change in $\kappa^{-1}(T)$ of LaCrO$_3$. In contrast, the magnitude of $\kappa^{-1}(T)$ for the orbitally degenerate antiferromagnets jumps to a significantly higher value relative to that of LaGaO$_3$ at room temperature, and $\kappa^{-1}(T)$ of the group shows a glassy behavior. The glassy RVO$_3$ perovskites convert to a phase showing ideal phonon $\kappa(T)$ at low temperature. However, LaVO$_3$ and YVO$_3$ choose totally different paths to approach the final state as temperature decreases. LaVO$_3$ undergoes a major change in the vicinity of T_N. The orbital degree of freedom is suppressed dramatically at $T < T_N$ and $\kappa(T)$ approaches the phonon $\kappa(T)$ in low temperature. However, the orbital ordering at $T_{\mathrm{OO}} > T_N$ does not restore the phonon $\kappa(T)$ in YVO$_3$. The orbital quantum fluctuations are still significant in this orbitally ordered phase in the interval $T_{\mathrm{CG}} < T < T_{\mathrm{OO}}$; these fluctuations are further reduced at the spin ordering temperature T_N and are eliminated completely through the first-order, spin/orbital flipping transition at T_{CG}. In comparison with RVO$_3$, the $\kappa(T)$ of all the RTiO$_3$ perovskites is restored abruptly at T_N or T_c. Whether $\kappa^{-1}(T)$ at $T < T_c$ or T_N can reach to that of LaGaO$_3$ as temperature decreases depends on the crystal quality. The $C_p(T)$ study made by Fritsch *at al.* [22] posits only a serious doubt on an orbital liquid proposed for the magnetically ordered phase [23]. Our results of $\kappa(T)$ rule out the possibility that orbitals remain fluctuating at $T < T_N$ or T_c. The argument [23] that not much spin-fluctuation energy can be gained by any pattern of static orbital orderings certainly needs to be reconsidered. On the other hand, the glassy $\kappa(T)$ indicates unambiguously an orbital-liquid phase in the PM phase of RTiO$_3$.

After clarifying the existence of orbital fluctuations in the PM phase of RTiO$_3$ and demonstrating an abrupt change of lattice dynamics at T_N or T_C due to an orbital-ordering transition, we come to a point to ask whether an AFM spin-spin interaction in the RTiO$_3$ perovskites with large IR and a FM interaction with smaller IR deduced from PM susceptibility can be resolved from a spin-orbital system with a full orbital degree of freedom. The orbital-liquid models predict a meltdown of the spin ordered state

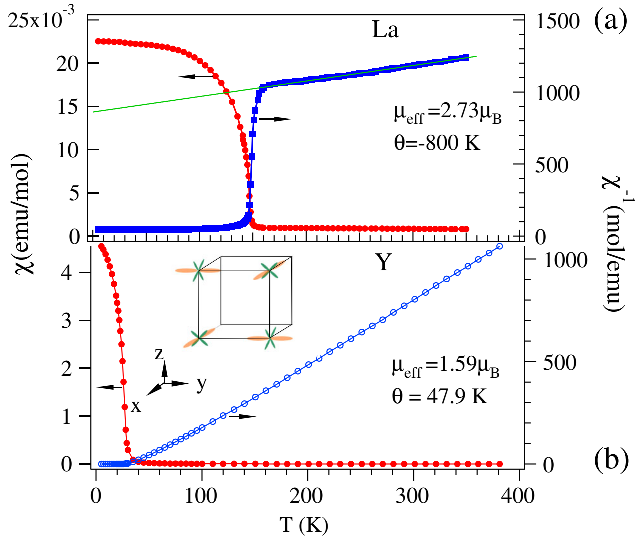

FIG. 2 (color online). Temperature dependence of magnetic susceptibility χ and inverse χ of $LaTiO_3$ and $YTiO_3$. Inset is a schematic drawing of the orbital ordering in a unit cell of $YTiO_3$.

in the e-orbital system [24] whereas an AFM coupling can be obtained in the t-orbital system [23]. An AFM coupling can indeed be inferred from $\chi^{-1}(T)$ in the PM phase of $LaTiO_3$. However, a Weiss constant obtained by fitting it to a CW law as shown in Fig. 2 is unphysical and $\mu_{\mathrm{eff}} = 2.73\mu_B$ is larger than that of one localized spin. The spin ordering in $LaTiO_3$ appears to be not induced by the magnetic coupling parameter J through a mean-field model. Instead, restoring the phononlike $\kappa(T)$ at T_N is likely due to a Jahn-Teller transition below which spins and orbits are ordered simultaneously. This scenario is consistent with results of Raman spectra [16] and the temperature dependence of lattice parameters [14]. The anomalous $T_N/|\theta|$ ratio of $LaTiO_3$ may signal a temperature dependent Weiss constant resulting from changing orbital fluctuations in the PM phase.

On the other hand, the Weiss constant from fitting $\chi^{-1}(T)$ of the PM phase of $YTiO_3$ is close to T_c as in a normal ferromagnet. It is therefore interesting to ask whether the increasing intrinsic structural distortion as IR decreases could introduce such a dramatic change of magnetic coupling from that of $LaTiO_3$. Although orbital fluctuations in the PM phase of both $LaTiO_3$ and $YTiO_3$ are responsible for a glassy $\kappa(T)$, the structural bias effect clearly confines the orbital fluctuations in a way compatible with the intrinsic site distortion [3], i.e., alternating long O-M-O and short O-M-O bonds within the a-b plane in $YTiO_3$ and a bond angle $\alpha < 90°$ in $LaTiO_3$ [14]. Moreover, the octahedral-site distortion can introduce an intrasite e-t hybridization proposed for RVO_3 [25]. A tentative static orbital ordering is illustrated schematically as an inset of Fig. 2(b). The long O-Ti-O bonding direction accommodates the small percentage of e orbital occupation, which gives a FM-coupling component in the ab plane. The yz and zx arrangement of the large percentage of t orbital ordering along the c axis gives rise to a FM interaction along this direction. In this case, the dominant magnetic exchange interaction is built through the time-independent orbital overlap integrals while the confined quantum zero-point fluctuations remain. Spin ordering due to the time-independent overlap integrals lowers the symmetry of the spin-orbital system, which eliminates quantum orbital fluctuations at $T < T_c$. We have further tested this unusual magnetic transition by its critical behavior.

The $\chi^{-1}(T)$ of $YTiO_3$ of Fig. 2(b) deviates from a CW law in an interval (T-T_c), which signals large critical spin fluctuations in the PM phase. We have measured the isothermal $M(H)$ from 21 to 32 K with a 0.5 K step and specific heat in order to evaluate the critical behavior of the FM transition. The plot M^2 versus H/M for each temperature on crossing T_c does not give parallel linear lines as expected from a mean-field theory. However, a modified Arrott plot with Heisenberg critical exponents does show nearly parallel linear lines. M_s was obtained by a polynomial curve fitting the isothermal $M^{1/\beta}$ versus

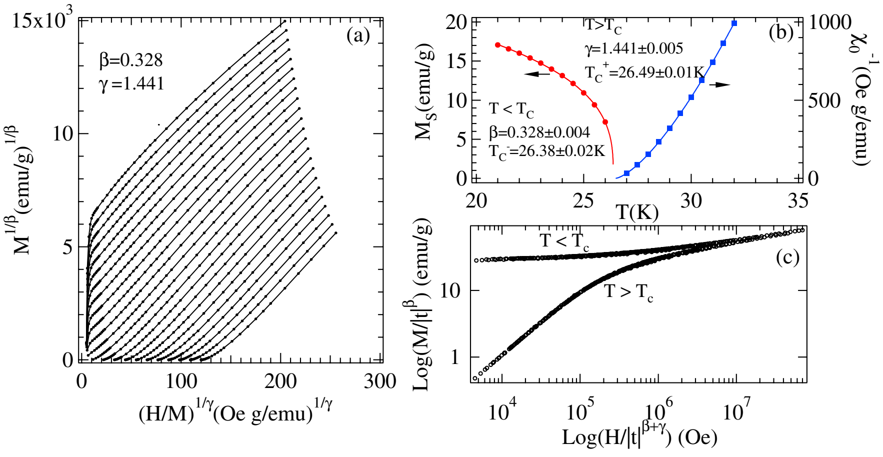

FIG. 3 (color online). (a) The modified Arrott plot $M(H)$ with critical exponents determined through the iteration starting with Heisenberg model. (b) Temperature dependence of M_s and χ_0^{-1} with power law fittings. (c) A scaling plot of the $M(H)$ obtained at $21 \leq T \leq 32$ K with the γ and β obtained from the power law fitting in (b), where $t = |(T - T_c)|/T_c$.

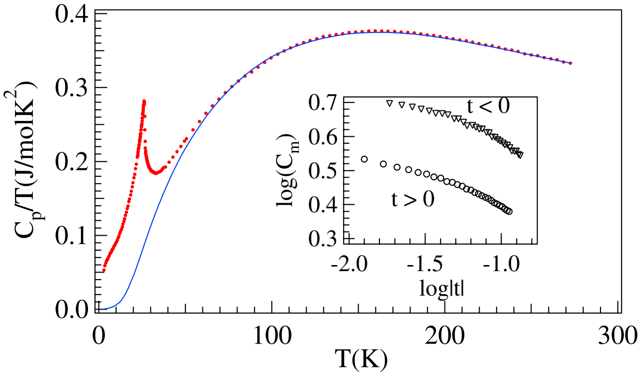

FIG. 4 (color online). (a) Temperature dependence of specific heat C_p/T. The lattice contribution is simulated by using the method described in Ref. [27]. The C_p of $LaGaO_3$ was used to obtained the temperature dependence of Debye temperature θ_D. Inset: The magnetic contribution C_m versus scaling temperature t.

$(H/M)^{1/\gamma}$ at $T < T_c$ and χ_0^{-1} was taken where the line crosses with $M = 0$ in a modified Arrott plot. M_s versus T and χ_0^{-1} versus T were fit with the power law $M_s(T) \sim B|t|^{\beta}$ and $\chi_0(T) \sim C|t|^{-\gamma}$, respectively, which gives critical exponents $\beta = 0.328$ and $\gamma = 1.441$. The final results are plotted in Figs. 3(a) and 3(b). A narrow difference of the scaling plot in Fig. 3(c) at $T > T_c$ and $T < T_c$ with the critical exponents obtained indicates that our analysis is reliable. The critical exponents from magnetic properties suggest that $YTiO_3$ is a normal Heisenberg ferromagnet like EuO [26].

C_p reflects the thermodynamics from both magnetism C_m and lattice C_L. All critical exponents at T_c of a Heisenberg ferromagnet should fall into a universality class that fulfills a relationship $\gamma + 2\beta - \alpha = 2$ and an $\alpha \approx 0.11$ in the power law $C_m^+(T) \sim (A/\alpha)|t|^{-\alpha}$, $t > 0$, and $C^-(T) \sim (A'/\alpha')|t|^{-\alpha'}$, $t < 0$, where $t = (T - T_c)/T_c$. The C_p of $YTiO_3$ in Fig. 4 shows a second-order transition. The explicit temperature dependence of the magnetic contribution C_m can be obtained only after the lattice contribution is subtracted from C_p precisely. By using three common methods to simulate the lattice contribution, however, we obtained a C_m that does not give a linear line on the $\log C_m$ versus $\log|t|$ plot of Fig. 4. Instead of speculating that the magnetic transition in $YTiO_3$ falls into a different universality class, we believe that a curved $\log C_m$ versus $\log|t|$ plot signals an anomalous lattice contribution associated with a major lattice reorganization due to orbital ordering in the vicinity of T_c.

In conclusion, $\kappa(T)$ measurements on a series of single-crystal samples provide an explicit answer to the issue of orbital order versus an orbital-liquid phase of the perovskites $RTiO_3$ that is currently controversial. Strong scattering from orbital fluctuations causes a glassy $\kappa(T)$ in the paramagnetic phase. A phononlike $\kappa(T)$ is restored below T_N or T_c, which indicates an orbital ordering in the magnetically ordered phase. In the AFM phase of the $RTiO_3$ family with larger IR, the magnetic coupling in the orbital-liquid phase is too weak to give a long-range spin ordering; spins order where orbitals become ordered at a Jahn-Teller transition. For the $RTiO_3$ family with smaller IR, the structural bias effect confines to a great extent the orbital fluctuations so as to create a time-independent overlap integral responsible for the FM transition. In this case, spin ordering helps to eliminate orbital fluctuations at $T < T_c$.

We thank the Robert A. Welch Foundation and NSF for financial support. J. S. Z. thanks H. D. Zhou for his help in the early stage of the crystal growth.

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