

Resonant X-Ray Scattering from Orbital Ordering in LaMnO_3

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Dipole resonant x-ray scattering from ordered Mn 3d orbitals in LaMnO_3 has been observed near the Mn K-absorption edge. The polarization of the scattered photons is rotated from σ to π' and the azimuthal angle dependence shows a characteristic twofold symmetry. A theory for the resonant scattering mechanism has been developed by considering the splitting of the Mn 4p levels due to the Mn 3d orbital ordering. The order parameter of the orbital ordering decreases above the Néel temperature ($T_N = 140$ K) and disappears at $T_O = 780$ K, concomitant with a structural phase transition. [S0031-9007(98)06638-1]

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Over the last few years, magnetic-field-induced phenomena in perovskite-type manganites, such as negative colossal magnetoresistance (CMR), have attracted a great deal of attention [1]. In these materials, the charge, spin, and orbital degrees of freedom each play important roles. However, while the charge and spin configurations have been investigated by neutron and electron diffraction techniques, it has proved difficult to observe the orbital ordering directly. Nevertheless, Murakami *et al.* [2] have recently succeeded in detecting orbital ordering in the doped layered-perovskite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, by using resonant x-ray scattering techniques with the incident photon energy tuned near the Mn K-absorption edge. In this Letter, we describe the observation of orbital ordering in the undoped, three-dimensional perovskite LaMnO_3 , using the same techniques. LaMnO_3 is of fundamental interest as the parent compound of CMR materials, and has been much studied as a result both experimentally [3,4] and theoretically [5,6]. Our results confirm the picture of orbital ordering given by Goodenough in 1955 [7]. In addition, we present a theoretical description of the resonant scattering mechanism based on the splitting of the Mn 4p levels, induced by the orbital ordering of the Mn 3d e_g states.

The electronic configuration of Mn^{3+} ions in LaMnO_3 is (t_{2g}^3, e_g^1) using Hund's rule as a first approximation. The three t_{2g} electrons are localized, while the e_g electron orbitals are strongly hybridized with the oxygen p orbitals. There is, in addition, a strong distortion of the MnO_6 octahedra [3], which has been ascribed to a cooperative Jahn-Teller effect [8]. This distortion suggests that there is a $(3z^2 - r^2)$ -type orbital ordering of the e_g electrons which is extended in the basal a - b plane. A

schematic view of the expected orbital ordering in the a - b plane is shown in Fig. 1, together with the spin configuration. Magnetically, LaMnO_3 is an A-type antiferromagnet ($T_N = 140$ K). The magnetic structure is stabilized by the ferromagnetic superexchange interaction of the e_g electrons in the plane and by the antiferromagnetic interaction

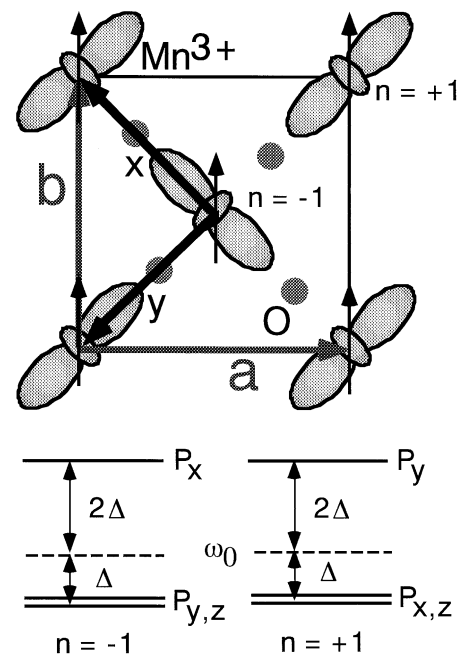


FIG. 1. Upper panel: Schematic view of the orbital and spin ordering in the a - b plane of the perovskite manganite, LaMnO_3 . The orbital ordering along the c axis is expected to repeat the same pattern. Lower panel: Schematic energy level diagram of Mn $4p_{x,y,z}$ in the orbitally ordered state.

of the t_{2g} electrons out of the plane, consistent with the extended in-plane e_g orbitals [6]. Recent magnetic neutron-scattering studies have shown two-dimensional anisotropic spin wave dispersion and critical behavior, which also suggest an extended orbital in the basal plane [4].

X-ray diffraction measurements were performed on beam line X22C at the National Synchrotron Light Source, BNL. The incident beam was focused by a bent cylindrical mirror and monochromatized by a pair of Ge(111) crystals, giving an energy resolution of about 5 eV. Polarization analysis of the scattered beam was performed using a Cu(220) analyzer crystal, which gives a scattering angle of 95.6° when the incident photon energy is set at the Mn K edge. By rotating the crystal around the scattered beam, the linearly polarized σ' (perpendicular to the diffraction plane) and π' (parallel to the diffraction plane) components can be separated, as has been described earlier (see Fig. 3 inset) [9]. A single crystal of LaMnO_3 was grown by the floating-zone method. The (1, 0, 0) surface was polished with diamond paste and fine emery paper. The polished area was approximately 5 mm^2 , and the mosaic width (FWHM) was about 0.2° . The crystal was mounted on the diffractometer in a closed cycle refrigerator or oven, as appropriate.

Orbital ordering of the e_g electrons was observed directly by exploiting the sensitivity of x-ray scattering to an anisotropic charge distribution [10]. For the basis shown in the upper panel of Fig. 1, the forbidden $(h, 0, 0)$ and $(0, k, 0)$ reflections (h, k odd) have appreciable intensities for incident photon energies near the Mn K -absorption edge as a result of the asphericity of the Mn atomic electron density present in the orbitally ordered state [11]. Figure 2 shows the energy dependence of the integrated intensity of the $(3, 0, 0)$ reflection with π' polarization together with the measured fluorescence, at $T = 10 \text{ K}$. The fluorescence data locates the Mn^{3+} K -absorption edge (E_A) at 6.552 keV. There is a striking enhancement of the intensity of the $(3, 0, 0)$ reflection at $E = 6.555 \text{ keV}$, about 3 eV above the edge, which identifies this resonance with electric dipole transitions ($1s \rightarrow 4p$). Transitions directly into the Mn $3d$ orbitals are also dipole allowed due to mixing with the finite-width oxygen $2p$ band, but occur 14 eV below the edge [12]. The observed behavior is consistent with our previous results for $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ [2].

Besides the enhancement, resonant scattering from orbital ordering is expected to exhibit several other distinctive features as characterized by the azimuthal angle (for rotations around the scattering vector) and the final polarization. We have investigated both using the experimental configuration shown in the inset in Fig. 3. The dependence of the intensity on the azimuthal angle ψ of the $(3, 0, 0)$ reflection measured at $E = 6.555 \text{ keV}$ and at room temperature is also shown in Fig. 3. The intensity has been normalized by the average intensities of the fundamental reflections $(2, 0, 0)$ and

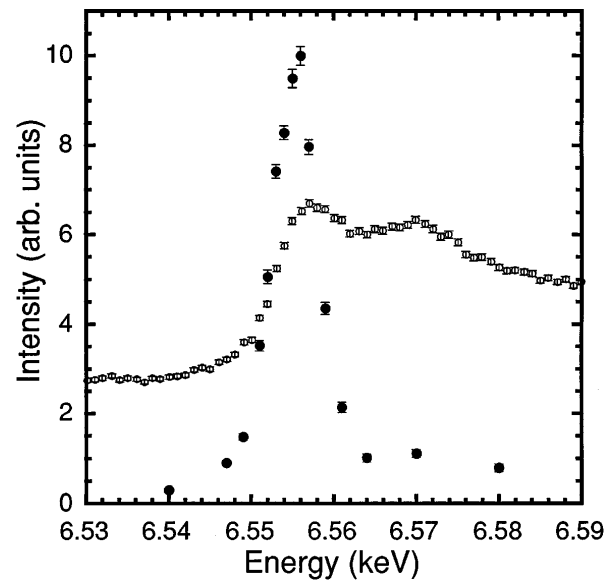


FIG. 2. Closed circles represent the energy dependence of the integrated intensity of the orbital ordering superlattice reflection $(3, 0, 0)$ with π' polarization near the manganese K absorption edge at $T = 10.0 \text{ K}$. Open circles represent measured fluorescence. Similar results were obtained at the $(1, 0, 0)$ reflection.

$(4, 0, 0)$ to correct for small variations due to the sample shape. The azimuthal angle $\psi = 0^\circ$ corresponds to the configuration in which the c axis is perpendicular to the diffraction plane. In contrast to a normal charge reflection, which is independent of the azimuthal angle, the resonant scattering exhibits a characteristic oscillation, with a twofold symmetry. The intensity approaches zero near $\psi = 0, 180^\circ$. The solid curve is the theoretically predicted behavior, $\sin^2 \psi$, described below. This result directly reflects the anisotropic electron density in the a - b plane arising from the orbital ordering.

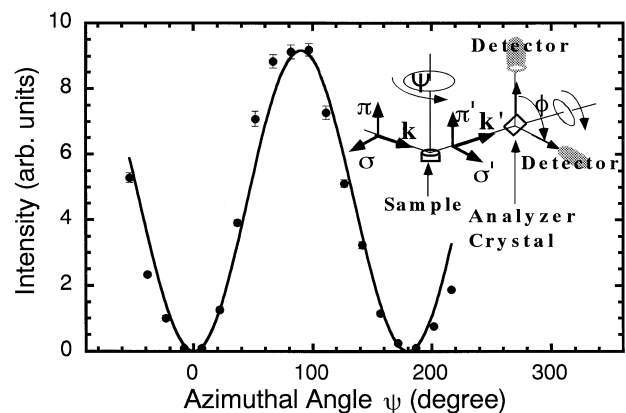


FIG. 3. Azimuthal-angle dependence of the intensity of the orbital ordering reflections $(3, 0, 0)$ normalized by the fundamental reflection $(2, 0, 0)$ and $(4, 0, 0)$ at $E = 6.555 \text{ keV}$ and at room temperature. The solid curve is the calculated intensity from Eq. (2). Inset: Schematic view of the experimental configuration and definition of the polarization directions.

Polarization analysis of the scattering revealed a predominantly σ' -polarized component at the (2, 0, 0) reflection for all azimuthal angles ψ between 20° and 140°. This is consistent with normal charge scattering and a 93% σ -polarized incident beam. In contrast, the resonant scattering from the orbital ordering measured at the (3, 0, 0) reflection was found to be predominantly π' -polarized at all azimuthal angles. Thus, the polarization of the orbital ordering scattering is completely rotated from σ to π' to within the errors of measurement ($\sim 7\% - 9\%$), which arise from the incomplete suppression of the polarization analyzer and a small π component of the incident beam.

These results can be understood on the basis of a simple model of the x-ray physics taking into account the orbital ordering. Resonant x-ray scattering is a second order process in which a core level electron is promoted to an intermediate excited state, which subsequently decays. This can lead to new scattering mechanisms, including, for example, resonant magnetic scattering. In that case, the excited electron is promoted to a partially occupied orbital and the sensitivity to the magnetic polarization arises through the exchange interaction [13,14]. In the present case, we consider a dipole transition process involving a Mn $1s$ to $4p$ transition, as required by the data. We assume that the $4p_{x,y,z}$ states are initially unoccupied, but split by their interaction with the e_g electrons in the ordered $3d$ orbitals [15]. This gives rise to a nonzero resonant scattered intensity at reflections sensitive to the difference between the orbitally ordered sublattices. We show below that the intensity of this scattering depends on the size of the splitting Δ and approximately varies as Δ^2 (see the lower panel of Fig. 1). Note that this is a different mechanism from that suggested by Fabrizio *et al.* [16] who considered quadrupolar processes.

For a difference reflection, the resonant scattered intensity I^{res} may be written [14]

$$I^{\text{res}} = \left| \sum_{\substack{m=x,y,z \\ n=\pm 1}} n \frac{\langle s | P^\alpha | p_m \rangle \langle p_m | P^\beta | s \rangle}{\omega - \omega_0 - \delta\omega_m^n + i\Gamma/2} \epsilon'^\alpha \epsilon^\beta \right|^2, \quad (1)$$

where we have chosen a coordinate system such that x and y are along the direction of the extension of the ordered e_g orbitals and z is perpendicular to the x - y plane (the upper panel of Fig. 1). $|s\rangle$ and $|p\rangle$ are the wave functions of the Mn $1s$ and $4p$ orbitals, respectively, P^α and P^β are the dipole operators, ω is the incident photon energy, and ω_0 is the energy of the unperturbed $4p_m$ levels. The incident (final) polarization of the photon is $\epsilon(\epsilon')$ and $n = \pm 1$ labels the sublattice. Γ is the lifetime of the excited state. $\langle p_m | P^\alpha | s \rangle = A\delta_{m\alpha}$, where A is a constant; $\delta\omega_m^n = -\Delta$ for $n = +1$, $m = z, x$; $\delta\omega_m^n = 2\Delta$ for $n = +1$, $m = y$; and so on.

Note that the origin of the splitting, Δ , is not specified in the model. One possible mechanism is the Coulomb interaction between the $4p$ and $3d$ orbitals, which raises (lowers) the $4p_m$ levels lying parallel (perpendicular) to

the direction of extension of the orbital by 2Δ (Δ). An alternate mechanism is provided by the motion of the oxygen atoms away from regions of high charge density in the ordered state. This lowers (raises) the energies of the $4p_m$ levels lying parallel (perpendicular) to the direction of extension of the orbital. For the purposes of this discussion all that is required is that $\Delta \neq 0$. Note also that hybridization of the Mn d or p orbitals with orbitals on the surrounding oxygens will not qualitatively change the theoretical result.

Working in a linear polarization basis, with σ (π) polarization perpendicular (parallel) to the scattering plane, it is easy to show that for σ incident polarization, the orbital ordering shown in Fig. 1 does not give rise to a σ' polarized scattered beam. That is, for any azimuthal angle ψ , $I_{\sigma\sigma'}(\psi) = 0$. In the rotated π' channel, we find

$$I_{\sigma\pi'}^{\text{res}}(\psi) \propto \frac{A^4 \sin^2 \psi \Delta^2}{[\Gamma^2 + 4(2\Delta - x)^2][\Gamma^2 + 4(\Delta + x)^2]}, \quad (2)$$

where $x = (\omega - \omega_0)$. Thus, the model predicts that the scattering is all of the $\sigma \rightarrow \pi'$ type and that it has a twofold azimuthal symmetry, with zeros coming when the incident polarization is parallel to z (c axis). This is in perfect agreement with the experimental results. It is worth adding that in the limit $\Delta \ll \Gamma$ and for photon energies off resonance, Eq. (2) becomes

$$I_{\sigma\pi'}^{\text{res}} \approx \frac{A^4 \sin^2 \psi}{(1 + 4\frac{x^2}{\Gamma^2})} \frac{\Delta^2}{\Gamma^4} \quad (3)$$

so that the line shape is a squared Lorentzian. In the present case, we expect Δ to be of order several tenths to 1 eV, while $\Gamma \sim 5$ eV. The latter is near the energy resolution of the monochromator, which prevents a definitive characterization of the line shape.

We note that there should also be nonresonant scattering from an orbitally ordered material. However, for the structure shown in Fig. 1, and for the (3, 0, 0) reflection, the charge density is symmetrically arranged about the scattering planes, and the nonresonant scattering vanishes.

Finally, the temperature dependence of the order parameter of the orbital ordering, as measured by the integrated intensity of the (3, 0, 0) reflection, is shown in Fig. 4. Interestingly, the intensity is nearly constant below the magnetic ordering temperature $T_N = 140$ K and decreases above. This suggests that the spin and orbital degrees of freedom are coupled. However, the orbital ordering persists until $T_O = 780$ K, where it goes rapidly to zero. This transition is accompanied by a dramatic increase in the intensity observed at the fundamental reflection (2, 0, 0), which we interpret in terms of an orthorhombic-to-orthorhombic structural phase transition. Such a transition has been observed in earlier studies of LaMnO_3 [17], although identifying the symmetry of the transition has been controversial. It is worth noting that very recently Rodríguez-Carvajal *et al.* [18] inferred the

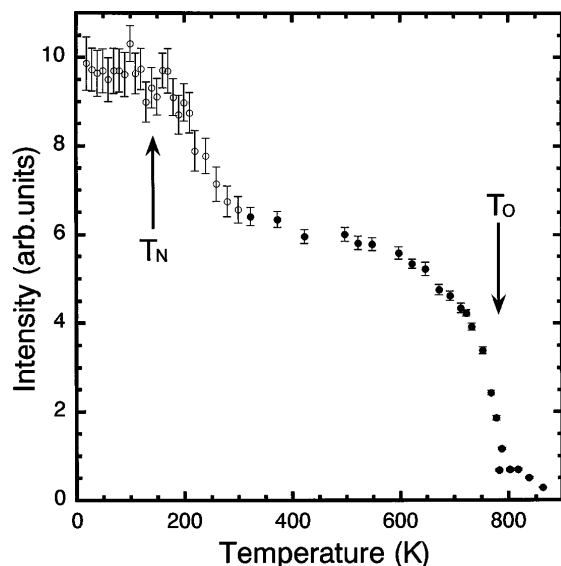


FIG. 4. Temperature dependence of the normalized intensity of the orbital ordering reflection (3,0,0) at $E = 6.555$ keV. Open symbols correspond to results obtained at an azimuthal angle $\psi = 127^\circ$ and cooling with a displacive cryostat; closed symbols were obtained for $\psi = 90^\circ$ and heating with an oven. The two data sets were scaled to be equal at $T = 300$ K.

disappearance of the orbital ordering at ~ 750 K on the basis of lattice distortions observed in neutron powder diffraction data, in which there is no change in symmetry (although the lattice becomes metrically cubic on the high-temperature side). This is consistent with our results.

In conclusion, we have presented direct evidence for orbital ordering in a three-dimensional perovskite manganite, LaMnO_3 , by using resonant x-ray scattering techniques. A theory for the scattering has been given, which is based on the splitting of the Mn $4p$ levels by the Mn $3d$ orbital ordering. Although the spin- and orbital degrees of freedom appear to be coupled, the orbital ordering does not disappear until $T_O = 780$ K, concomitant with a structural phase transition.

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