

## Determination of the Mechanism for Resonant Scattering in $\text{LaMnO}_3$

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The resonant multiple Bragg x-ray diffraction is used to study the forbidden  $(10\bar{4})$  reflection in  $\text{LaMnO}_3$ . Using the interference between the three-beam scattering and resonant scattering we can determine the phase of the resonant scattering. This phase is shown to be consistent with a model in which the resonant scattering is caused by the influence of the Mn-O bond length distortion rather than directly by the orbital ordering on the Mn  $4p$  band structure.

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Since 1930, due to the work by Coster *et al.*, it has been realized that the sensitivity of x-ray scattering can be greatly enhanced if the energy of the incoming x ray is tuned to the absorption edge of a particular atom in the system [1]. In some situations, as it was demonstrated recently for several materials including manganites, this can also give rise to so-called forbidden reflections whose intensities are zero in the ordinary charge scattering (Thomson scattering). A particular notable example of such an experiment is the measurements performed by Murakami *et al.* [2] who used the Mn  $K$  edge to study the  $(3, 0, 0)$  reflection in  $\text{LaMnO}_3$ . Note that if all the Mn atoms were exactly equivalent, none of the  $(2h + 1, 0, 0)$  peaks would appear due to the symmetry of  $Pbnm$  space group. Nonetheless, the  $(3, 0, 0)$  peak has been observed and it was originally interpreted in terms of orbital ordering by virtue of the on-site Coulomb repulsion between an electron promoted from the  $1s$  core level into an empty  $4p$  state and another electron in the  $e_g$  orbital [2,3].

In order to see this we note that the  $\text{Mn}^{3+}$  ion is in the high spin  $d^4$  configuration in a near octahedral local coordination with one unpaired electron in the doubly degenerate  $e_g$  orbital. As was discussed by Kugel and Khomskii for the case of negligible coupling to the lattice, such degeneracy can be lifted via orbital ordering resulting in the site-dependent orientation of the quadrupole moments of  $d$  electrons [4]. The effect of the  $p$ - $d$  Coulomb repulsion ( $U_{pd}$ ) is then to lift the degeneracy of the  $4p_x$ ,  $4p_y$ , and  $4p_z$  orbitals in such a way that the orbital with lobes parallel to the occupied  $3d e_g$  orbital would be higher in energy than the other two. For example, the  $4p_x$  orbital would be higher in energy if the  $3x^2 - r^2$  orbital is occupied than if the  $3y^2 - r^2$  orbital is occupied. On the neighboring Mn sites, this splitting is, of course, reversed to account for change in the occupancy of the  $e_g$  orbitals. Since the resonant cross section is polarization and energy dependent, it is possible

to choose experimental conditions in such a way that only one type of Mn will contribute to the resonant scattering intensity. In this case the scattering will be sensitive to the asymmetry of the outermost occupied valence  $3d$  electrons and the two Mn atoms in the unit cell are distinguishable resulting in a finite intensity of the  $(2h + 1, 0, 0)$  reflections.

However, it is important to realize that for such a local atomic mechanism to be operative the  $4p$  band should be narrow. The fluorescence [2] as well as the x-ray absorption near edge structure (XANES) measurements [5] show that the total bandwidth of the Mn  $4p$  band in  $\text{LaMnO}_3$  is about 20 eV. It is, therefore, worthwhile to try to understand this effect from band structure rather than from a local atomiclike point of view. Several authors have already pointed out that the Mn  $4p$  states are extremely sensitive to the Jahn-Teller (JT) distortion of the oxygen octahedron [6–12]. Although the cooperative JT distortion and orbital ordering are not fully distinguishable experimentally, they act on  $4p$  states differently. On the contrary to the effect of  $U_{pd}$ , the elongation  $\text{MnO}_6$  octahedron actually lowers the energy of the  $4p$  orbital oriented towards the most distant oxygens, which simply follows from the change in the hopping integrals between O  $2p$  and Mn  $4p$  orbitals. This is opposite to the effect of  $U_{pd}$ . In such a case the resonant intensity is mainly controlled by the distortions in the crystal structure resulting from orbital ordering rather than directly from the orbital ordering itself. Nonetheless, it is difficult to distinguish these two mechanisms experimentally as the only difference between them is the resulting sign of the structure factor. As one can see from Fig. 1, one configuration of Mn  $4p$  orbitals in the  $ab$  plane of  $\text{LaMnO}_3$  is simply a  $90^\circ$  rotated image of the other. The only difference then is in the phase of the scattering, the determination of which is a well-known problem in conventional x-ray diffraction.

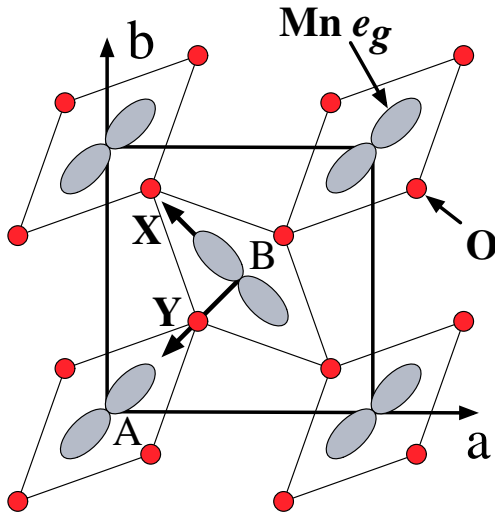


FIG. 1 (color online). An artistic concept, according to Ref. [2], of the orbital ordering and JT distortion in the (001) Mn-O plane of  $\text{LaMnO}_3$ .

In this Letter we describe a method for determining that phase by multiple Bragg scattering, a situation in which Bragg's law is satisfied for two or more  $(h, k, \ell)$  crystallographic planes. This technique has been successfully used to solve the phase problem for other situations [13]. When a crystal is rotated around the scattering vector of a particular reflection  $\mathbf{P}$ , the intensity plot vs azimuthal angle  $\Psi$  will in general exhibit sharp peaks, due to other simultaneous Bragg reflections. We note that the azimuthal dependence of the resonant scattering intensity varies only very slowly and on the scale of the width of the sharp peaks can be considered to be constant. It was found, a number of years ago [13], that those sharp peaks exhibit in general an asymmetric structure at the base of the peaks, an excess intensity on one side, and a deficient intensity on the other side. Such an asymmetry effect has been theoretically understood and recognized as a source of relative phase information [13] between the various Bragg reflections involved. The theory describing this asymmetry and the consequent line shape is very similar to the Fano effect involving excitations to a sharp peak coupled to a broad continuum, each with their own transition amplitudes and phases [14]. This was demonstrated in an experiment involving the  $(4, 4, 2)$  in Si, a forbidden reflection whose structure factor could be made positive and negative by simply changing temperature [15]. As noted above the phase of the resonant scattering structure factor is rotated by  $180^\circ$  between the two mechanisms for resonant scattering. To understand the mechanism of the resonant scattering in  $\text{LaMnO}_3$  by phase determination we perform the multiple Bragg scattering experiment on this material at the Mn  $K$  edge.

A small crystal ( $140 \mu\text{m} \times 70 \mu\text{m} \times 10 \mu\text{m}$ ) was chipped away from a large ingot. It was found that a large crystal (millimeter size) could not be used because of

twinning. Using a small crystal, the twinning problem does not disappear, but it becomes tractable. We found that a small fragment is likely to be untwinned, or (as was our case) composed by two fragments, widely different in size, related by twinning. We were able to beat the twinning problem by using as diffractometer angles the values associated with the big grain, thus minimizing the contribution from the small fragment (or fragments). It was found that the  $(3, 0, 0)$  was not a suitable reflection for our experiment. The symmetry of the lattice is such that all multiple beam cases involve two extra reflections, not one. It so happens that the phase shift produced by one extra reflection is perfectly compensated by the phase shift of the other extra reflection. The net effect is zero phase shift, and the asymmetry effect disappears. For this reason we picked another forbidden reflection, the  $(1, 0, \bar{4})$ , away from a high symmetry crystallographic axis such as the  $(1, 0, 0)$ . In this case there was no problem in finding situations in which only one extra reflection was excited. The mosaic spread on the  $(1, 0, \bar{4})$  was about  $0.05^\circ$ . The x-ray energy was adjusted to maximize the  $(1, 0, \bar{4})$  intensity at resonance, 6.554 keV.

In Fig. 2(a) we show the result of our 3-beam diffraction experiment where the asymmetry effect is quite evident. The simultaneous reflection (let us call it  $\mathbf{H}$ ) is the  $(\bar{1}, \bar{2}, 0)$ .

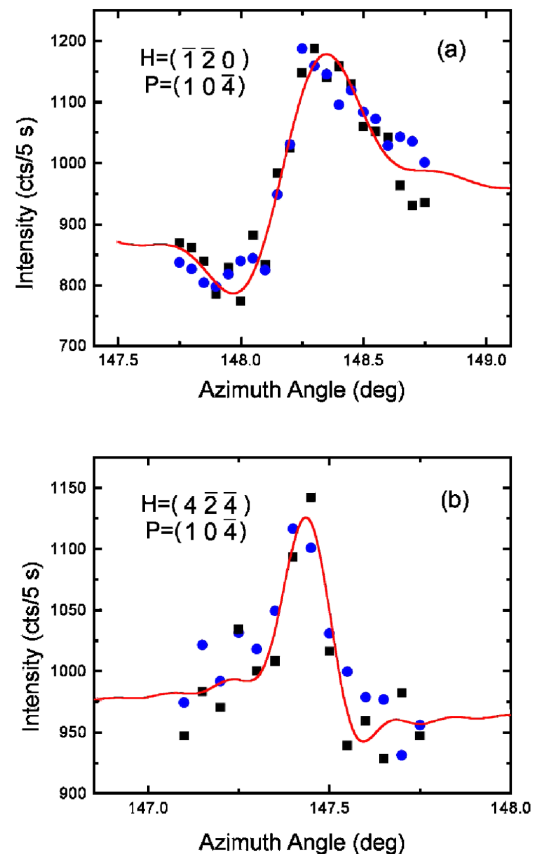


FIG. 2 (color online). The  $(1, 0, \bar{4})$  interference profiles for (a) the  $(\bar{1}, \bar{2}, 0)$  and (b) the  $(4, \bar{2}, \bar{4})$  simultaneous reflections.

It is not clear why we do not see a strong peak, as is customary in this kind of multiple beam experiments. The only possible reason is the effect of the mosaic spread, which is considerable. The effect of the mosaic spread is to broaden all peaks and to decrease the peak intensity. Figure 2(b) shows another peak, observed at a different azimuthal angle, the  $(4, \bar{2}, \bar{4})$ . The quality of the data is inferior to that of Fig. 2(a), but the asymmetry effect is still clearly visible, and it is opposite to that of Fig. 2(a). The solid lines in Figs. 2(a) and 2(b) are fits to data using Shen's theory [16].

In the theory of multiple Bragg scattering the diffracted wave field in a direction  $\hat{n}$  is given by [16]

$$\vec{D}(\vec{x}) = Nr_e \frac{\exp(-ik_0 r)}{r} \hat{n} \times \left\{ \hat{n} \times \left[ F_P \vec{D}_0 - \gamma \sum_H F_{P-H} F_H \frac{\vec{k}_H \times (\vec{k}_H \times \vec{D}_0)}{k_0^2 - k_H^2} \right] \right\}, \quad (1)$$

where  $\gamma = r_e \lambda^2 / \pi V_c$ ;  $r_e$  is the classical radius of an electron;  $\lambda =$  wavelength of the radiation;  $V_c =$  the unit cell volume;  $\vec{D}_0(\vec{x}) = \vec{D}_0 \exp(-i\vec{k}_0 \cdot \vec{r})$ ;  $\vec{k}_0 =$  incident wave vector;  $\vec{k}_H = \vec{k}_0 + \vec{H}$ ;  $\vec{H} =$  reciprocal vector. The intensity of the diffracted beam is then  $I = \vec{D} \cdot \vec{D}^* / D_0^2$ . As is clearly evident from Eq. (1), the interference profile is altered when the sign of structure factor  $F_P$  is changed. Note that both the  $(\bar{1}, \bar{2}, 0)$  and the  $(4, \bar{2}, \bar{4})$  as well as their  $\vec{P}\text{-}\vec{H}$  counterparts are allowed reflections and their structure factors can be easily calculated for a given crystal structure and experimental geometry using known atomic form factors. The  $(1, 0, \bar{4})$ , on the other hand, is space group forbidden and it is always zero in Thomson scattering. This is in contrast to point group forbidden reflections such as the  $(2, 2, 2)$  reflection in Si. In that case the nonzero structure factor can be modeled by placing small point charges in the middle of the covalent bonds, to simulate the fact that the charge density of the valence electrons is concentrated in the bonds rather than only in spherical symmetric shells around the nuclei. However, at energies close to an absorption edge, the scattering process becomes extremely sensitive to even small details in the local electronic structure provided that the anomalous part of the atomic form factor tensor  $\Delta f^{\alpha\beta}(\omega, \vec{k}, \vec{k}') = f^{\alpha\beta}(\omega, \vec{k}, \vec{k}') + i f'^{\alpha\beta}(\omega, \vec{k}, \vec{k}')$  is anisotropic and site dependent. In the case of the electric dipole allowed  $1s$  to  $4p$  transition, the elements of this tensor are given by

$$\Delta f^{\alpha\beta}(\omega) \approx \sum_{4p} \frac{\langle 1s | r^\alpha | 4p \rangle \langle 4p | r^\beta | 1s \rangle}{E_{1s} - E_{4p} + \hbar\omega - \frac{i\Gamma}{2}}, \quad (2)$$

where  $\alpha$  and  $\beta$  are Cartesian indices  $x, y,$  and  $z$  [17]. The resonance structure factor is then a sum over all atoms in the unit cell of the products between  $\Delta f$  and polarization vectors of incoming ( $\vec{\epsilon}_{in,\sigma}$ ) and outgoing ( $\vec{\epsilon}_{out,\sigma'}$ ) radiation,

$$F_P^{\text{res}}(\omega) = \sum_j e^{i\vec{P}\cdot\vec{R}_j} (\epsilon_{in,\sigma}^\alpha \epsilon_{out,\sigma'}^\beta \Delta f_j^{\alpha\beta}(\omega)). \quad (3)$$

From Eq. (3) it is easy to see that by changing the asymmetry of the  $\Delta f$  tensor one can alter the sign of the  $(1, 0, \bar{4})$  structure factor. Note that the Mn positions in the orthorhombic unit cell of  $\text{LaMnO}_3$  are  $(0, 0, 0)$ ,  $(0, 0, 1/2)$ ,  $(1/2, 1/2, 0)$ , and  $(1/2, 1/2, 1/2)$ , which sets the exponential factor to  $+1$  for the  $A$  sites and to  $-1$  for the  $B$  sites (see Fig. 1). If, for example, the energy of the  $1s\text{-}4p_x$  transition on  $B$  sites is close to the energy of incoming  $x$ -polarized photon and on the  $A$  sites it is much higher, then the only planes that can contribute to the resonant amplitude are of  $B$  type, which defines the sign of  $F_{(1,0,\bar{4})}$ . However, the sign is reversed when these energies are alternated.

We now turn to band theory in order to make a connection between line shapes observed in the experiment and the electronic structure of  $\text{LaMnO}_3$ . The resonance Mn form factor computed using Eq. (3) within the TB-LMTO computer code [18] for the crystal structure refined by Norby *et al.* [19] is shown in Fig. 3. The calculated imaginary part of  $\Delta f_{\text{Mn}}$  is in agreement with results of the fluorescence measurements by Murakami *et al.* [2] and XANES experiments by Qian *et al.* [5]. The band structure effects are clearly evident from the energy dependence of the  $x$  and  $y$  diagonal components of the tensor plotted in Fig. 3 for the  $B$  sites of Mn in the cubic coordinate system with the  $x$  and  $y$  axes pointed along the long and short Mn-O bonds, respectively (see Fig. 1). As it was reported earlier [6], the Mn  $K$  edge is governed by the partial density of states of the  $4p_x$  orbital which lies at about a 3 eV lower energy than the other two. On the neighboring Mn atom, however, the lowest  $4p$  orbital is  $4p_y$  since this is the longest Mn-O bond for  $A$  sites. Note that the core-hole potential is neglected in the calculation and  $\Gamma = 3$  eV is used to account for the  $1s$  core-hole lifetime. The neglect of the core-hole potential is justified because the  $1s$  core hole— $4p(U_{1s,4p})$  screened Coulomb interaction is much smaller than the  $4p$  band width. In the other extreme limit,

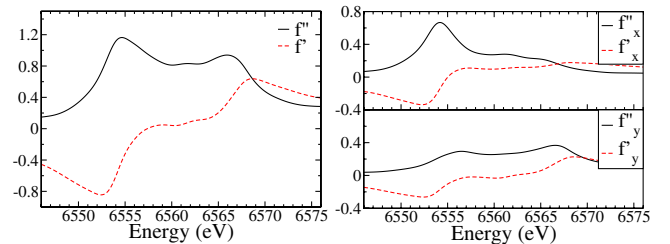


FIG. 3 (color online). Real and imaginary part of the trace of the Mn form factor calculated in local-density approximation with 3 eV core-hole lifetime (left panel). The  $x$  and  $y$  diagonal components of  $\Delta f_{\text{Mn}}$  are plotted for  $B$  sites in a cubic coordinate system with the  $x$  and  $y$  axes pointing along the long and short Mn-O bonds in the  $ab$  plane, respectively (right panel).

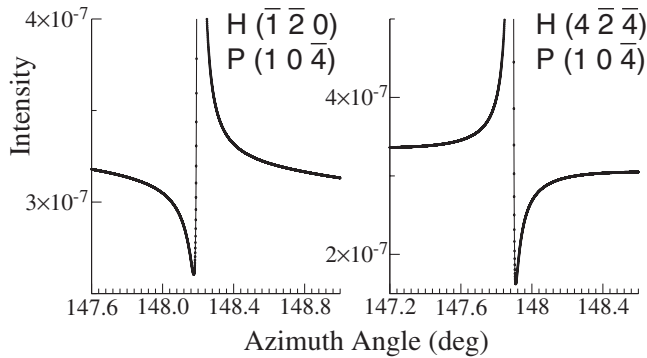


FIG. 4. Three-beam interference profile calculated for the  $(\bar{1}, \bar{2}, 0)$  (left panel) and the  $(\bar{4}, \bar{2}, \bar{4})$  (right panel) simultaneous reflections with the energy of the incident photons = 6.554 keV.

all the intensity would be in a sharp core-hole valence electron exciton peak.

To further understand which scattering mechanism leads to the observed asymmetry effect, we performed a calculation of the resonance intensity [Eq. (1)] with the structure factor of the forbidden  $(1, 0, \bar{4})$  reflection calculated according to Eq. (2) and (3) within density functional theory for 6.554 keV photon energy, which corresponds to the maximum resonance intensity. Note that resonant scattering in  $\text{LaMnO}_3$  is primarily determined by the electric dipole-dipole terms since the dipole-quadrupole cross term appears only in materials without inversion symmetry [20] and the pure quadrupole transitions are much too weak. Comparing Fig. 2 and 4, one can see that both the  $(\bar{1}, \bar{2}, 0)$  and  $(\bar{4}, \bar{2}, \bar{4})$  profiles agree with the experimental intensities. Of course, if we invert the  $4p$  orbitals on each site, the sign of the resonant structure factor changes and the interference profiles are opposite to what we find in the experiment.

In summary, we have performed a three-beam experiment on  $\text{LaMnO}_3$  with the energy of incident photons near the Mn  $K$  edge. The analysis of the recorded interference profiles involving *ab initio* band structure calculations and the theory of anomalous x-ray scattering shows that the mechanism of resonant scattering is indeed the cooperative JT distortion rather than  $4p$ - $3d$  Coulomb repulsion. In addition, we demonstrate that the resonant technique supplemented by multibeam diffraction is a very useful tool capable to provide unique information concerning the phase of the resonant scattering.

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