Resonant scattering and multiple Bragg X-ray diffraction in LaMnO$_3$; a classical view

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The mechanism for resonant scattering in LaMnO$_3$ has been the subject of some controversy between two models. Model (A) is based on orbital ordering, whereas model (B) invokes the Jahn–Teller distortion. From the structural point of view, the two models lead to different d-electron densities. The forbidden reflection 300 is turned on by resonance, leading to a well defined scheme for the lobes of the Mn d electrons [model (A)]. It turns out that the same experimental results could have been interpreted according to model (B). The only difference is that this alternative interpretation would have required a structure factor F_{300} of *opposite* sign. This is a typical example of a phase problem. An experimental technique has been applied for phase determination based on multiple Bragg scattering. This shows that the multiple-beam results are in agreement with model (B), not with model (A), laying to rest a long overdue controversy.

This paper complements and expands results already discussed in a short paper by Shen *et al.* (2006), which has to do with resonant scattering and charge density of d electrons in manganese. Resonant scattering was discussed in that paper using the language of quantum theory. It is felt that a qualitative description based on a classical view of resonant scattering is useful in order to fully understand the issues presented in the paper by Shen *et al.* (2006). The classical description of resonant scattering cannot be used for quantitative estimates but it clarifies the scattering mechanisms at play.

The whole subject of resonant scattering of X-rays is presented in a thorough and exhaustive review article by Dmitrienko *et al.* (2005). A study somewhat similar to the present one is described in a paper by Kokubun *et al.* (2004).

Manganites have been thoroughly investigated over the last few years because of their unusual magnetic properties such as their colossal magneto-resistance, which makes them ideal candidates for spintronics materials. Their magnetic properties are strongly related to the charge density of the d electrons of Mn, which are responsible for directional bonds (lobes) surrounding the Mn atoms. In a free atom, the d electrons are anisotropically distributed around their nuclei and there is no preferred direction, therefore they are randomly oriented. The crystal field provides preferred directions, therefore, *in a crystal*, these lobes of electron density may be stabilized by the crystal potential, giving rise to what is normally called 'orbital ordering'. An early classical example of orbital ordering is provided by the p electrons in Si, which give rise to lobes along the [111] directions, the covalent bonds. These lobes are responsible for the weak 222 reflection, which is forbidden for spherical atoms. Orbital ordering has also been observed in LaMnO$_3$ (Murakami *et al.*, 1998) using again a forbidden reflection, 300. There is, however, an important difference between 222 in Si and 300 in LaMnO$_3$. The 300 reflection is *space-group*-forbidden, which the 222 is not. The structure of LaMnO$_3$ has been determined by Norby *et al.* (1995), who made use of space group *Pnma* (No. 62). The notation used in the literature, however, is consistent with the setting *Pbnm*, which we will follow, to be consistent with the current literature.[1] The space group *Pbnm* (or *Pnma*) has eight equivalent positions. This means that, if we assume that an electron is present in (x, y, z), we must put one electron in seven other positions.[2] We find that the structure factor of a space-group-forbidden reflection is *always zero*, no matter what the electron density within the unit cell looks like. For an *accidentally* forbidden reflection, such as 222 in Si, the structure factor can be different from zero if, for example, small point charges are placed in strategic positions such as the covalent bonds, which amounts to a description of the charge density in terms of non-spherical atoms.

The fact that a space-group-forbidden reflection such as 300 in LaMnO$_3$ or 600 in Ge (Lee *et al.*, 2001) can be excited at a particular X-ray energy (the resonant energy) indicates that

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[1] The only difference between the two space-group symbols is the way in which the lattice constants a, b, c are chosen. The values (a, b, c) in *Pnma* become (c, a, b) in *Pbnm*.
[2] See *International Tables for X-ray Crystallography* (1969, p. 151).

resonant scattering owes its origin to an imperfect cancellation effect between the charges present at the eight equivalent positions of the lattice.

For the case of LaMnO$_3$, we concentrate our attention on those lobes of the *d* electrons associated with the Mn atoms (see Fig. 1). Those lobes form directional bonds and are the source of scattering for the forbidden reflections. In principle, a space-group-forbidden reflection such as 300 is always zero, even considering scattering from the bonding charges. The 300 reflection is alive because the incident X-ray beam is polarized, and different directional bonds form different angles with the polarization vector of the incident radiation. For this reason, the cancellation effect due to negative interference between different directional bonds is incomplete and some intensity can be measured for the 300 and other space-group-forbidden reflections.[3] The scheme of directional bonds described in Fig. 1 is consistent with the experimental results obtained by measuring 300. However, it has been pointed out that a different interpretation of the same experimental results could lead to a different configuration of directional bonds, one in which all the lobes of Fig. 1 would be rotated by 90° (Sawatzky, 2000).

Using a model in which every lobe is replaced by a bonding point charge, and considering the different responses of lobes pointing to different directions, it can be verified that the two configurations correspond to structure factors of equal magnitudes but opposite signs.

This is a typical example of a 'phase problem', which cannot be resolved by conventional X-ray diffraction techniques. One technique that has been successfully used to beat the phase problem, at least in some situations, is based on the principle of multiple Bragg scattering (Chapman *et al.*, 1981; Shen & Colella, 1987; Weckert & Hümmer, 1990), a situation in which two or more Bragg reflections are excited at the same time. When a crystal is rotated around the scattering vector of a particular reflection (let us call it **P**, 10$\bar{4}$ in our case), the intensity plot *versus* ψ (azimuthal angle) will in general exhibit sharp peaks due to other simultaneous Bragg reflections. The slow modulation with ψ typical of resonant scattering can be ignored in this kind of experiment. It has been found, a number of years ago, that those sharp peaks due to multiple Bragg scattering will 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 phase information (Chapman *et al.*, 1981; Shen & Colella, 1987). For the case of a centrosymmetric crystal (like LaMnO$_3$), for which the only phase information is the sign of the structure factors, the method works particularly well. This was shown in an experiment involving 442 in Si, a forbidden reflection whose structure factor could be made positive and negative by simply changing temperature (Tischler *et al.*, 1985). The asymmetry effect was reversed, as expected from theory.

A similar experiment has been done on LaMnO$_3$, in order to decide between the configuration of directional bonds as given in Fig. 1 and an alternative configuration in which all the bonds are rotated by 90°.

A small crystal (140 × 70 × 10 µm) was chipped away from a large ingot. It was found that a large crystal (millimetre size) could not be used because of twinning. Using a small crystal, the problem due to twinning does not disappear but it becomes tractable. We found that a small fragment is likely to be untwinned or (as it was in our case) composed of 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 of the small fragment. It was found that 300 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, 10$\bar{4}$, away from a high-symmetry
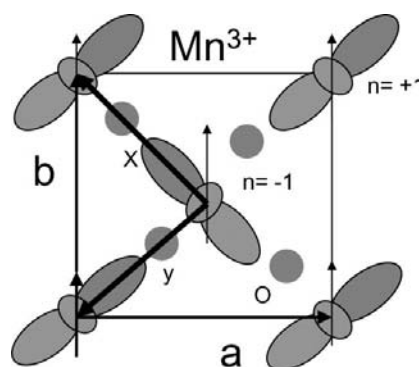
Figure 1
Schematic view of the orbital ordering in the *ab* plane of the perovskite manganite LaMnO$_3$. The orbital ordering along the *c* axis is expected to repeat the same pattern. Reprinted figure with permission from Murakami *et al.* (1998). *Phys. Rev. Lett.* **81**, 582–585. Copyright (1998) by the American Physical Society.
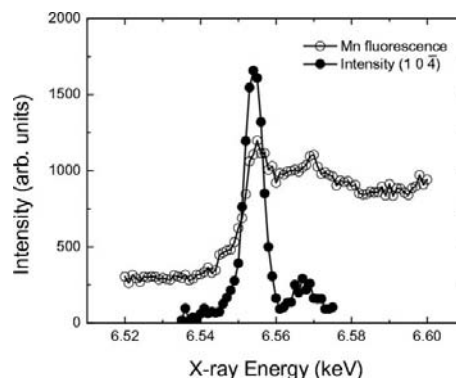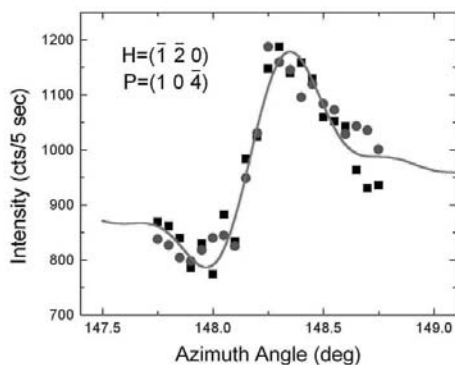

Figure 2
Plot of the 10$\bar{4}$ intensity *versus* X-ray energy. A careful analysis of this plot gives a resonant energy of 6554 eV.

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[3] There are forbidden reflections in LaMnO$_3$, such as 201 or 403, which are strictly zero even when reflections like 300 or 10$\bar{4}$ are turned on.

crystallographic axis such as [100]. In this case, there was no problem in finding situations in which only one extra reflection was excited. The mosaic spread on $10\bar{4}$ was about 0.05°. The X-ray energy was adjusted to maximize the $10\bar{4}$ intensity at resonance. It was found that $E = 6.554$ keV, as obtained from Fig. 2.
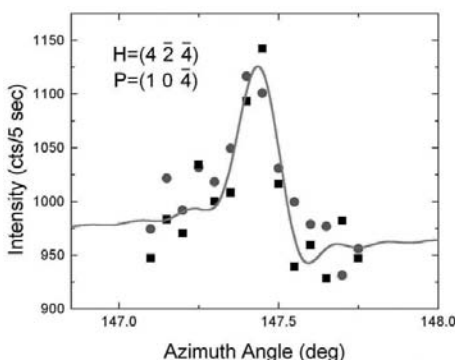
A typical result of three-beam diffraction is shown in Fig. 3. The simultaneous reflection (let us call it **H**) is $\bar{1}\bar{2}0$. The asymmetry effect is quite evident. It is not clear why we do not see a strong peak, as customary in this kind of multiple-beam experiment. The only possible reason 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. Fig. 4 shows another peak, observed at a different azimuthal angle, $4\bar{2}\bar{4}$. The quality of the data is inferior to that of Fig. 3 but the asymmetry effect is still visible, and it is *opposite* to that of Fig. 3. The solid lines in Figs. 2 and 3 are fits to data using Shen's theory (Shen, 1986; Shen & Huang, 2001), to be used as guides to the eye.

We must now correlate the observation of the asymmetry effects visible in Figs. 3 and 4 with the lobes of *d*-electron density as described in Fig. 1 of Murakami *et al.* (1998). The theory of multiple-beam diffraction (Chapman *et al.*, 1981; Tischler *et al.*, 1985; Shen, 1986; Shen & Colella, 1987; Shen &
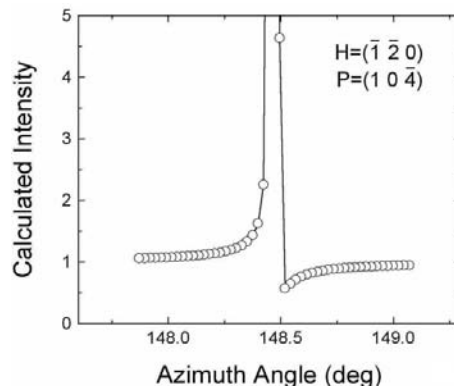
Huang, 2001) can tell us for sure the *sign* of the structure factor $F_{10\bar{4}}$. The sign of a structure factor, however, depends on the choice of origin within the unit cell. We follow the conventions used by Norby *et al.* (1995) in their paper describing the crystal structure of LaMnO₃. The problem is that we do not really know, at this stage, whether a given $F_{10\bar{4}}$ (say positive) corresponds to a set of directional bonds like those in Fig. 1 or to a set of directional bonds rotated by 90°. We introduced earlier a model in which each lobe is replaced by a point charge. There are eight equivalent positions in the unit cell of LaMnO₃, so we must introduce eight identical point charges. This is not enough to simulate resonant scattering for space-forbidden reflections, which are always zero by symmetry. We now recall that the incident X-ray beam is polarized and that the response of the bonding charges will presumably be different for different bonds, depending on the angle between the **E** vector of the incident beam and the directional bonds. We see in Fig. 1 that there are two types of directional bonds. There are bonds parallel to the *y* axis (we call them 'type 1 bonds') and bonds parallel to the *x* axis (we call them 'type 2 bonds'). There are also bonds along directions perpendicular to the *ab* plane of Fig. 1, along the *c* axis. They do not play any role in our analysis. The incident X-ray beam is plane-polarized and the angle formed by the incident
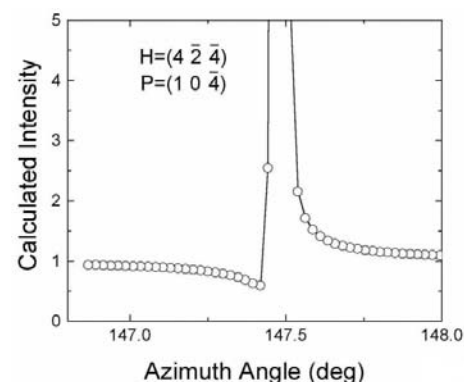

Figure 3
Intensity *versus* azimuthal angle for the $10\bar{4}$ reflection in proximity of full excitation of the $\bar{1}\bar{2}0$ reflection. The azimuthal angle ψ is zero when the [010] axis is on the scattering plane, mostly antiparallel to the incident beam. Clockwise rotations are positive for an observer looking against the scattering vector.

Figure 5
Calculated azimuthal profile for the $10\bar{4}$ reflection in proximity of full excitation of the $\bar{1}\bar{2}0$ reflection. Full-blown *n*-beam theory without approximations has been used (Colella, 1974).

Figure 4
The same as Fig. 3 except that the simultaneous reflection is now $4\bar{2}\bar{4}$.

Figure 6
The same as Fig. 5 except that the simultaneous reflection is now $4\bar{2}\bar{4}$.

E vector will in general be different for type 1 and type 2 bonds. In fact, these two angles can be calculated from the diffractometer angles χ, ϕ, θ, 2θ, which completely specify the orientation of the crystal with respect to the diffractometer. In our case, these two angles turn out to be 20.5° for type 1 bonds and 79.5° for type 2 bonds. In our band-theory calculations (Sawatzky, 2005; see also Elfimov *et al.*, 2002), it can be shown that the highest scattering at threshold would be for light polarized in the y direction, which is perpendicular to type 2 bonds. If we calculate the $F_{10\bar{4}}$ structure factor using the bond-charge model, following Murakami *et al.*'s charge density for d electrons in accordance with Fig. 1, for plausible values of the interstitial charge (say 1 electron) and the distance of the interstitial charge from the center of the nearest Mn atom (say 1 Å), we find that $F_{10\bar{4}}$ is *negative*. Therefore, a higher scattering for type 2 bonds is consistent with a *negative* structure factor. Our computer simulations (Colella, 1974) of the three-beam experiments (Figs. 5 and 6) were done using a negative $F_{10\bar{4}}$, so the plots of Figs. 5 and 6 should show the same kind of asymmetry effects as those observed experimentally. But we see that the opposite is true in both cases. So the only possible explanation is that the directional bonds must be rotated by 90°. In this case, the $F_{10\bar{4}}$ structure factor *is positive*, so Shen's theory agrees with the computer simulations of Figs. 5 and 6, which are based on Colella's (1974) theory. The phase problem for the d electrons of Mn in LaMnO$_3$ can therefore be solved using three-beam diffraction. The method is completely general and other applications will be considered.

In conclusion, we have shown in this paper that three-beam diffraction can be used to resolve ambiguities in determining valence-electron densities obtained by means of resonant scattering. The choice between a negative and a positive structure factor is a particular aspect of the phase problem for which the technique of three-beam diffraction is particularly suited.

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