

9.3 Resonant X-ray Scattering as a Probe of Orbital and Charge Ordering by *C. S. Nelson, J. P. Hill, and Doon Gibbs*

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Resonant x-ray scattering is a powerful experimental technique for probing orbital and charge ordering. It involves tuning the incident photon energy to an absorption edge of the relevant ion and observing scattering at previously 'forbidden' Bragg peaks, and it allows high-resolution, quantitative studies of orbital and charge order — even from small samples. Further, resonant x-ray scattering from orbitally ordered systems exhibits polarization- and azimuthal-dependent properties that provide additional information about the details of the orbital order that is difficult, or impossible, to obtain with any other technique. To date, resonant x-ray scattering has been applied to studies of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_4$ [220, 221], LaMnO_3 [222], $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [223, 224], V_2O_3 [225], $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [226], DyB_2C_2 [227, 228], $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ [229, 230], Fe_3O_4 [231], $\text{LaSr}_2\text{Mn}_2\text{O}_7$ [232], YVO_3 [233], LaTiO_3 [234], NaV_2O_5 [235], YTiO_3 [236], CeB_6 [237], and UPd_3 [238] — and this long list of materials continues to grow.

In the manganites, the sensitivity to charge and orbital ordering is enhanced when the incident photon energy is tuned near the Mn K absorption edge (6.539 keV), which is the lowest energy at which a $1s$ electron can be excited into an unoccupied state. In this process, the core electron is promoted to an intermediate excited state, which decays with the emission of a photon. The sensitivity to charge ordering is believed to be due to the small difference in K absorption edges of the Mn^{3+} and Mn^{4+} sites. For orbital ordering, the sensitivity arises from a splitting— or difference in the weight of the density of states [239]— of the orbitals occupied by the excited electron in the intermediate state. In the absence of such a splitting, there is no resonant enhancement of the scattering intensity.

In principle, other absorption edges in which the intermediate state is anisotropic could be utilized, but the strong dipole transition to the Mn $4p$ levels — and their convenient energies for x-ray diffraction — make the K edge well-suited to studies of manganites. The Mn $4p$ levels are affected by the symmetry of the orbital ordering, which makes the technique sensitive to the orbital degree of freedom. Therefore resonant x-ray scattering can be used to obtain important quantitative information concerning the details of this electronic order.

Two mechanisms for splitting of the $4p$ states have been proposed: a Coulomb coupling of the Mn $3d$ and $4p$ states — either directly, or indirectly through the hybridization with O $2p$ states [240]— and the motion of oxygen ions due to the Jahn-Teller interaction. These two mechanisms have opposite signs in terms of the direction of the splitting, but both are consistent with experimental results to date. Which mechanism is dominant therefore remains an open question; however, in either case, the resonant scattering reflects the symmetry of the orbital ordering through the perturbation of the local electronic states at the Mn^{3+} sites, and the peak positions and widths determined in the x-ray experiments measure the orbital periodicity and correlation lengths, respectively. In addition, as is described below, detailed analysis of the resonant scattering provides information about the occupation of the ordered orbitals — a determination that cannot be made through the use of nonresonant scattering.

An example of resonant scattering from orbital order, in $\text{Pr}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$, is shown in Fig. 9.9. This material is believed to exhibit $(3x^2 - r^2/3y^2 - r^2)$ -type ordering of the e_g -orbitals, as sketched in the inset. The data show the energy dependence of the (100) orbital order peak, which is forbidden by the crystallographic space group, measured at room temperature. A large resonant signal is visible just above the Mn K absorption edge, at $\hbar\omega = 6.555$

keV. In addition, a pre-edge feature and two smaller peaks at higher energies reflecting the $4p$ density of states, can be seen. At energies more than ~ 50 eV away from the Mn K absorption edge, the scattering intensity is zero.

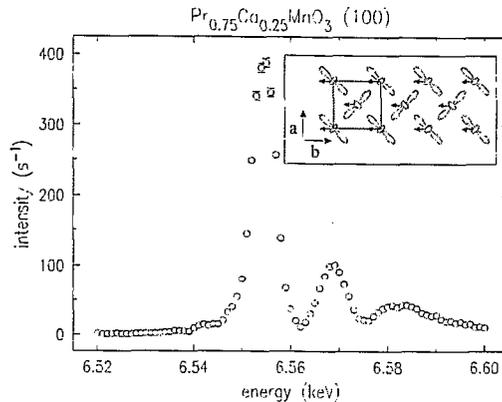


Fig. 9.9. Peak intensity versus incident photon energy of the orbital (100) reflection of the $\text{Pr}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ sample. Inset displays a schematic of the orbital and magnetic ordering believed to occur in this material. The shaded figure-8's represent the occupied e_g orbitals of the Mn^{3+} ions, and the arrows indicate the in-plane components of the magnetic ordering. In the absence of orbital order – e.g., if the materials were in an orbitally disordered, ferromagnetic, metallic state – no peak would be observed. For short-range orbital order, a very weak, very broad (in q -space) peak would be observed.

The data in Fig. 9.9 indicate the key requirement for resonant x-ray scattering measurements— tunability of the incident photon energy. Synchrotron radiation sources meet this requirement, and additionally provide high intensities and well-defined polarization states. This last property can be utilized in order to probe the polarization-dependence exhibited by resonant x-ray scattering from orbital order. Working in the linear polarization basis, which is appropriate for the polarization of x-rays produced at conventional bending magnet and undulator beamlines, it can be shown that for a σ -polarized (perpendicular to the scattering plane) beam, the resonant cross-section for a (100) reflection of the orbital structure shown in the inset to Fig. 9.9 results in a rotation of the polarization to a π' -polarized (parallel to the scattering plane) state. Since ordinary charge scattering results in a σ' -polarized beam, polarization analysis of the scattered beam is a useful technique for selecting the scattering contribution arising from orbital ordering.

In addition to this polarization dependence, resonant x-ray scattering from orbital and charge ordering also exhibits an azimuthal dependence. While nonresonant scattering is independent of the azimuthal angle (this angle characterizes the rotation of the sample about the scattering wavevec-

tor), resonant scattering from orbital and charge order exhibits characteristic azimuthal oscillations with intensity and periodicity that depend upon the type of ordering. These two properties of the scattering—the azimuthal and polarization dependences—are intimately connected in the cross-section, and measurements of both can allow additional information such as which orbital is occupied, as well as its periodicity (see, for example, Ref.[236]), to be obtained.

Examples of the polarization dependence of the scattering from orbital and charge ordering are shown in Fig. 9.10. These data were collected from measurements of $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, which is believed to exhibit CE-type charge and orbital ordering below a temperature of ~ 240 K. In this structure, charge and orbital order peaks occur at $(0\ 2k\pm 1\ 0)$ and $(0\ 2k\pm \frac{1}{2}\ 0)$, respectively, for integer k and using orthorhombic notation.

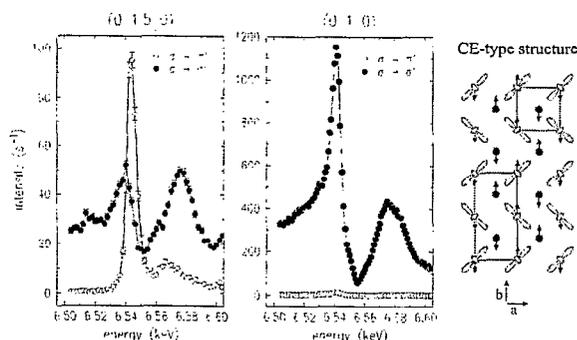


Fig. 9.10. Polarization-resolved scans of intensity versus incident photon energy of the orbital $(0\ 1.5\ 0)$ and charge $(0\ 1\ 0)$ reflections of the $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample [230]. A schematic of the orbital, charge, and magnetic ordering of the CE-type structure is shown on the right. The shaded figure-8's represent the occupied e_g orbitals of the Mn^{3+} ions, the filled circles represent Mn^{4+} ions, and the arrows indicate the in-plane components of the magnetic ordering. The rectangle in the lower left shows the orbital order unit cell; the square in the upper right shows the charge order unit cell.

At the $(0\ 1.5\ 0)$ orbital order peak, the energy dependences of the two scattered polarization states are clearly different: the π' component has a peak near the Mn K absorption edge, while the σ' component decreases as the incident photon energy is tuned through the edge. This latter behavior is consistent with ordinary charge scattering, suggesting that orbital ordering is accompanied by a longitudinal lattice distortion. At the (010) charge order peak, the scattering occurs entirely in the $\sigma \rightarrow \sigma'$ channel, to within the experiment detection limits, as expected for such charge order scattering (see Ref.[230] for a discussion of the lineshapes displayed in Fig. 9.10).

In summary, resonant x-ray scattering brings new strengths, such as enhanced scattering intensity and the additional information contained in the polarization- and azimuthal-dependences, to studies of orbital and charge ordering. Measurements are currently being carried out at many of the synchrotron radiation facilities throughout the world— e.g., the Photon Factory in Japan, the National Synchrotron Light Source at Brookhaven National Laboratory in New York, the European Synchrotron Radiation Facility in France, and the Advanced Photon Source at Argonne National Laboratory in Illinois— in order to investigate, for example, ordering wavevectors and correlation lengths as a function of temperature and applied field. Resonant x-ray scattering complements conventional x-ray and neutron crystallographic studies, and promises to be a widely used probe of the fascinating ordering phenomena exhibited by the manganites and other materials.

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