X-Ray Resonant Scattering as a Direct Probe of Orbital Ordering in Transition-Metal Oxides

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X-ray resonant scattering at the K-edge of transition-metal oxides is shown to measure the orbital order parameter, supposed to accompany magnetic ordering in some cases. Virtual transitions to the $3d$ orbitals are quadrupolar in general. In cases with no inversion symmetry, such as V_2O_3, treated in detail here, a dipole component enhances the resonance. Hence, we argue that the detailed structure of orbital order in V_2O_3 is experimentally accessible. [S0031-9007(98)05756-1]

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The orbital ordering in compounds containing ions with unfilled shells is a long standing problem [1], and has recently attracted new attention given the interest in the physics of transition metal oxides stimulated by high-T_c and colossal magnetoresistance materials. In fact, while many experiments give direct information on magnetic structures, which are also due to partially empty shells, only indirect evidence points to the existence and structure of orbital order, unless it is accompanied by a cooperative Jahn-Teller effect with a lattice distortion. An important example is the Mott-Hubbard insulator V_2O_3 [2]. At ambient pressure, this compound undergoes a metal-insulator transition at $T_c \simeq 150$ K [3]. The insulating phase below T_c is antiferromagnetically ordered with a peculiar structure having both ferro- and antiferromagnetic bonds [4]. Castellani *et al.* [5] argued that such a magnetic ordering implies an orbital ordering. Quite recently, neutron diffraction data [6] showed that spin correlations in the metallic phase behave quite differently from the insulating one, giving further evidence of the importance of the orbital degrees of freedom.

Actually, Castellani *et al.* [5] showed that (at least) two orbital structures, with different order parameters and wave vectors, are compatible with the observed magnetic one. Later, based on the exchange constants fitted to neutron scattering data, one of the two orbital structures came to be favored [2,6,7]. However, there is still no direct observation of the orbital ordering, nor a firm experimental determination of its wave vector, and of the temperature at which it appears, which may not coincide with the Néel temperature. In addition to V_2O_3, there are many other examples where the orbital degrees of freedom are believed to play an important role, as the colossal magnetoresistance material $La_{1-x}(Cr,Sr)_xMnO_3$.

In this Letter, we argue that it is indeed possible to have direct experimental access to the orbital ordering by x-ray resonant scattering, and that this process should be sufficiently intense to be readily observable with modern synchrotron radiation sources.

First of all we notice that the *nonresonant* x-ray diffraction has extremely little sensitivity to orbital order. We have estimated the cross section for orbital order scattering in this case by using hydrogenic $3d$-wave functions, and we find the corresponding scattering power at the orbital order wave vector to be less then 0.1 electrons per unit cell.

Let us now show how an x-ray resonant elastic scattering experiment can detect orbital ordering in transition metal compounds. The energy $\hbar\omega$ of the incoming beam is supposed to resonate with the K edge of the transition element. Virtual transitions to the conduction band d-like components are quadrupolar, and the corresponding transition operator at a given atom in the lattice takes the form

$$-C_2\sqrt{n_{\epsilon,k}}\,\frac{c}{\omega}\sum_{\sigma}[\sqrt{3}\,\epsilon_z k_z\, d^{\dagger}_{3z^2-r^2,\sigma} + (\epsilon_x k_x - \epsilon_y k_y)\, d^{\dagger}_{x^2-y^2,\sigma} + (\epsilon_x k_y + \epsilon_y k_x)\, d^{\dagger}_{xy,\sigma} + (\epsilon_x k_z + \epsilon_z k_x)\, d^{\dagger}_{xz,\sigma} + (\epsilon_y k_z + \epsilon_z k_y)\, d^{\dagger}_{yz,\sigma}]s_{\sigma} \equiv -C_2\sqrt{n_{\epsilon,k}}\sum_{\sigma}\hat{D}^{\dagger}_{\sigma}(\epsilon,k)s_{\sigma}\,, \tag{1}$$

which also defines the dimensionless absorption operator $F \equiv \sum_\sigma \hat{D}^{\dagger}_{\sigma}s_{\sigma}$. The operator $d^{\dagger}_{i,\sigma}$ creates an electron of spin σ in the i d-orbital, while s_σ creates a hole in the $1s$ shell. The constant $C_2 = (e\omega^2 r_{2,ds}/c)\sqrt{2\pi\hbar/15\omega}$, and $n_{\epsilon,k}$ is the density of incoming photons with polarization $\vec{\epsilon}$ and wave vector $\vec{k}$. The radial matrix element is defined by $r_{2,ds} = \int r^2\,dr\,\chi^*_d(r)r^2\chi_s(r)$, in terms of the radial wave functions χ_s and χ_d.

If the atom is at position $\vec{R}$, a phase factor $e^{i\vec{k}\cdot\vec{R}}$ weights the contribution of this single process. In obvious notation, the absorption operator at this site is denoted by $\hat{F}_R$. The transition probability amplitude of an elastic scattering in which the above absorption process is followed by the emission of a photon with the same energy but polarization $\vec{\epsilon}'$ and wave vector $\vec{k}'$ is given by

$$C_2^2\sqrt{\frac{n_{\epsilon,k}}{V}}\sum_{n,\vec{R},\vec{R}'} e^{i(\vec{k}\cdot\vec{R}-\vec{k}'\cdot\vec{R}')} \times \frac{\langle g|\hat{F}^\dagger_{R'}(\epsilon',k')|n\rangle\langle n|\hat{F}_R(\epsilon,k)\,|g\rangle}{\hbar\omega - \hbar\omega_{ng} + i\Gamma}, \quad (2)$$

where $|g\rangle$ is the ground state, $|n\rangle$ an intermediate state, and $\Gamma/\hbar$ the inverse lifetime of the core hole.

At resonance (2) becomes through (1)

$$-i\,\frac{C_2^2}{\Gamma}\sqrt{\frac{n_{\epsilon,k}}{V}}\sum_{\sigma,\vec{R}} e^{i\vec{Q}\cdot\vec{R}}\langle g|D_{\sigma,R}(\epsilon',k')\hat{D}^\dagger_{\sigma,R}(\epsilon,k)\,|g\rangle. \quad (3)$$

In going from Eqs. (2) to (3) we have assumed that all the intermediate states involved into the orbital ordering and not too far from resonance have energies distributed on an interval not larger than Γ. This assumption is certainly correct in the case of V_2O_3, where the K-photoabsorption spectrum [8] shows that the only splittings which are observed in the pre-edge peaks are those due to the crystal field. Therefore, the splittings due to multiplet effects of the partially occupied t_{2g} orbitals, which are relevant for orbital ordering, are smaller than the natural linewidth of the resonance. Within the above assumption, the resonant scattering via a K-edge quadrupole transition is a measure of the Fourier component at momentum $\vec{Q} = \vec{k} - \vec{k}'$ of an operator

$$O\sum_\sigma \hat{D}_\sigma(\epsilon',k')\hat{D}^\dagger_\sigma(\epsilon,k), \quad (4)$$

which is a combination of products of d-orbitals annihilation and creation operators, uniquely defined by the scattering geometry. The form of the scattering operator (4) is similar to that of the orbital order parameter, generally written as $\hat{\Delta} = \sum_{i,j} a_{ij} d_i^\dagger d_j$, where a_{ij} depend on the system under consideration (see below the specific case of V_2O_3). For a suitable choice of the scattering geometry, the scattering operator (4) includes a component equal to the orbital order parameter. This component will result in the only nonvanishing amplitude for momentum transferred $\vec{Q}$ equal to the orbital order wave vector. The treatment sketched here can be applied without modification to cases like $LaMnO_3$, in which the quadrupolar scattering channel is the only available one [9]. In the case of V_2O_3, the absence of inversion symmetry at V sites in the insulating phase allows dipole transitions as well. We will consider this more complicated but interesting case in detail.

According to the general wisdom, the V ions in this compound have an oxidation state V^{3+}, thus containing two d-electrons [2]. The five d-orbitals are split into a lower t_{2g} triplet and a higher e_g doublet. It is common to use a reference frame in which the z axis coincides with the c axis of the nonprimitive hexagonal cell, while the x axis is parallel to one of the bonds connecting the V atoms in the honeycomb lattice of the ab plane. In this reference frame, the three t_{2g} orbitals become: $d_1 = d_{3z^2-r^2}$ and

$$d_2 = \sqrt{\frac{2}{3}}\,d_{xy} + \sqrt{\frac{1}{3}}\,d_{xz}\,, \qquad d_3 = -\sqrt{\frac{2}{3}}\,d_{x^2-y^2} - \sqrt{\frac{1}{3}}\,d_{yz}\,. \quad (5)$$

The d_1 orbital points towards the only nearest neighbor V along the c axis, thus forming a strong covalent bond which is filled. Hence the d_1 orbital, being inert, does not participate in the orbital ordering, which involves only the d_2 and d_3 orbitals. We notice that these orbitals, because of the crystal field in the corundum structure, acquire also a component of p-like symmetry, which we need to identify. A V atom is surrounded by a distorted oxygen octahedron and by four vanadium second neighbors, providing a nonsymmetric environment, as described in Ref. [10]. The crystal field potential felt by the central vanadium may be parametrized by $V_{\mathrm{cf}} = V_1(Y_{3,-3} - Y_{3,3}) + V_2 Y_{3,0}$. As a result, the modified d-orbitals involved in the orbital ordering are, apart from the normalization,

$$d_2 \rightarrow d_2 + \eta(up_y + vp_x); \qquad d_3 \rightarrow d_3 + \eta(up_x - vp_y)\,, \quad (6)$$

where ηu and ηv ($u^2 + v^2 = 1$) are proportional to V_1 and V_2, respectively, and inversely proportional to the energy difference between the vanadium $3d$ orbitals and the p orbitals involved. In order to estimate this hybridization, an Xα calculation in the $Z + 1$ approximation for a VO_6 cluster was performed, and provided $\eta \simeq 0.2$ and $u \simeq -0.37$. A test of the adequacy of this approximation for a quantitative estimate is given by comparing the energy difference between the lowest absorption peak related to the $d - p$ hybridized levels and the main absorption edge, which is 20.7 eV in the cluster calculation, and 20.1 eV experimentally [11]. Also, the relative intensities are in satisfactory agreement with experiment.

According to Ref. [5], two orbital orderings are compatible with the observed magnetic structure. For the first one, the staggered orbital parameter is proportional to the operator

$$\text{case (A): } \hat{\Delta}_A = d_2^\dagger d_3 + d_3^\dagger d_2\,. \quad (7)$$

In the hexagonal reciprocal lattice, the $\vec{Q}$ vector of this orbital ordering is predicted to be different from that of the magnetic ordering. In fact, while the latter has maximum diffraction at $\vec{Q} = (0.5, 0.5, 0)$ and zero at $\vec{Q} = (0.5, 0.5, 1)$, for the former the situation is reversed. This makes the search for the orbital ordering easier. In Cartesian coordinates, the wave vector of the orbital order (A) is

$$\vec{Q}_A = 2\pi\left(0, \frac{1}{a\sqrt{3}}, \frac{1}{3c}\right), \tag{8}$$

where a is the bond length in the basal plane honeycomb lattice, and c is the shortest distance between two V atoms in the z direction. The hexagonal cell that we use contains three layers, which is compatible with the notations used by Moon [4] and McWhan and Remeika [3].

The other orbital order compatible with the magnetic structure has an order parameter

$$\text{case (B)}: \hat{\Delta}_B = d_2^\dagger d_2 - d_3^\dagger d_3 . \tag{9}$$

In this case the ordering is no more staggered in the basal plane, while it remains staggered along the c direction. However, since the two V atoms on the basal plane belonging to the same hexagonal cell have opposite values of the order parameter, the smallest $\vec{Q}$ at which we expect a diffraction peak is

$$\vec{Q}_B = 2\pi\left(\frac{1}{3a}, \frac{1}{a\sqrt{3}}, \frac{1}{3c}\right). \tag{10}$$

Let us now apply the general treatment described above to this specific example. Since the conduction band has both d and p character, we have to extend the general formalism to include, besides the quadrupole, also a dipole component in the transition amplitude.

We first consider the quadrupole channel already discussed. Since only the d_2 and d_3 combinations of Eq. (5) are involved in the orbital ordering, it is more useful to pick up from (1) only the part involving these orbitals. All the other allowed transitions are not expected to give a contribution to the elastic scattering at that particular $\vec{Q}$. Hence, the relevant quadrupole absorption operator simplifies to

$$\hat{F}_2 = \frac{1}{\sqrt{1+\eta^2}} \frac{c}{\omega} \times \sum_\sigma [(\vec{\epsilon} \cdot \hat{M}_2 \vec{k})\, d_{2\sigma}^\dagger - (\vec{\epsilon} \cdot \hat{M}_3 \vec{k})\, d_{3\sigma}^\dagger] s_\sigma , \tag{11}$$

where $1/\sqrt{1+\eta^2}$ weighs the d component in the conduction band [see Eq. (6)], and

$$\hat{M}_2 = \begin{pmatrix} 0 & \sqrt{2} & 1 \\ \sqrt{2} & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \qquad \hat{M}_3 = \begin{pmatrix} \sqrt{2} & 0 & 0 \\ 0 & -\sqrt{2} & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

In the dipole channel, using the same notations as above, the dimensionless dipole absorption operator at resonance $\hat{F}_1 = \sum_\sigma \hat{P}_\sigma^\dagger s_\sigma$ is defined through the dimensional one by

$$iC_1 \sqrt{n_{\epsilon,k}} \sum_{j=x,y,z} \sum_\sigma \epsilon_j p_{j,\sigma}^\dagger s_\sigma \equiv iC_1 \sqrt{n_{\epsilon,k}} \sum_\sigma \hat{P}_\sigma^\dagger s_\sigma , \tag{12}$$

where $p_{j,\sigma}^\dagger$ creates a spin-σ electron in the j p orbital, and $C_1 = e\omega r_{1,ps}\sqrt{2\pi\hbar/(3\omega)}$, where $r_{1,ps} = \int r^2\, dr\, \chi_p^*(r) r \chi_s(r)$, in analogy with the definition of $r_{2,ds}$.

The component of the dipole absorption operator $\hat{F}_1$ which is sensible to the orbital ordering can be easily found through Eq. (6), namely

$$\hat{F}_1 = \frac{\eta}{\sqrt{1+\eta^2}} \sum_\sigma [(\vec{v}_2 \cdot \vec{\epsilon})\, d_{2,\sigma}^\dagger + (\vec{v}_3 \cdot \vec{\epsilon})\, d_{3,\sigma}^\dagger] s_\sigma , \tag{13}$$

where the factor in front of the sum is the weight of the p component in the conduction band wave functions, and we have introduced the two vectors $\vec{v}_2 = (v, u, 0)$ and $\vec{v}_3 = (u, -v, 0)$.

The whole transition operator is the sum of the quadrupole and dipole components. However, Eqs. (2), (3), and (4) are still correct, provided we take

$$\hat{F} = \frac{1}{\sqrt{1+\eta^2}} \left[\hat{F}_2 + i\eta \frac{C_1}{C_2} \hat{F}_1 \right]. \tag{14}$$

As a result, the scattering cross section will include, besides pure quadrupole and dipole contributions, an interference term. To further proceed, we need to extract from (4) the term proportional to the orbital order parameter, which can be in general written as $(T_{11}^\alpha + T_{22}^\alpha - iT_{12}^\alpha)\hat{\Delta}_\alpha$. Here $\alpha = A, B$ refers to the two possible order parameters, Eqs. (7) and (9), and T_{11}^α, T_{22}^α, T_{12}^α indicate the contributions of the pure dipole, the pure quadrupole, and the interference channels, respectively. For these polarization and wave vector dependent quantities, we find

$$T_{22}^A = \frac{c^2}{\omega^2(1+\eta^2)} [(\vec{\epsilon}'^* \hat{M}_2 \vec{k}')(\vec{\epsilon} \hat{M}_3 \vec{k}) + (2 \leftrightarrow 3)], \tag{15}$$

$$T_{11}^A = \frac{\eta^2}{1+\eta^2} \frac{C_1^2}{C_2^2} [(\vec{\epsilon}'^* \cdot \vec{v}_2)(\vec{\epsilon} \cdot \vec{v}_3) + (2 \leftrightarrow 3)], \tag{16}$$

$$T_{12}^A = \frac{\eta}{1+\eta^2} \frac{cC_1}{2\omega C_2} [(\vec{\epsilon}'^* \hat{M}_2 \vec{k}')(\vec{\epsilon} \cdot \vec{v}_3) + (\vec{\epsilon}'^* \cdot \vec{v}_2)(\vec{\epsilon} \hat{M}_3 \vec{k}) - (2 \leftrightarrow 3)], \tag{17}$$

$$T_{22}^B = \frac{c^2}{\omega^2(1+\eta^2)} [(\vec{\epsilon}'^* \hat{M}_2 \vec{k}')(\vec{\epsilon} \hat{M}_2 \vec{k}) - (2 \leftrightarrow 3)], \tag{18}$$

$$T_{11}^B = \frac{\eta^2}{1+\eta^2} \frac{C_1^2}{C_2^2} [(\vec{\epsilon}'^* \cdot \vec{v}_2)(\vec{\epsilon} \cdot \vec{v}_2) - (2 \leftrightarrow 3)], \tag{19}$$

$$T_{12}^B = \frac{\eta}{1+\eta^2} \frac{cC_1}{2\omega C_2} [(\vec{\epsilon}'^* \hat{M}_2 \vec{k}')(\vec{\epsilon} \cdot \vec{v}_2) + (\vec{\epsilon}'^* \cdot \vec{v}_2)(\vec{\epsilon} \hat{M}_2 \vec{k}) + (2 \leftrightarrow 3)]. \tag{20}$$

From the cluster calculation, we obtain the radial matrix elements for dipole and quadrupole transitions, which allow us to establish that the relative weight of the two terms in Eq. (14) is given by $\eta C_1/C_2 \simeq 7.4$. Therefore we expect the pure dipole term alone to reproduce the total cross section within $\simeq$13% accuracy. Hence, for the purpose of the present paper, it will be sufficient to calculate just this term.

We are now in a position to describe the cross section as a function of experimental configuration. The scattering angle 2γ is determined by $\sin\gamma = Qc/2\omega$, ω being the

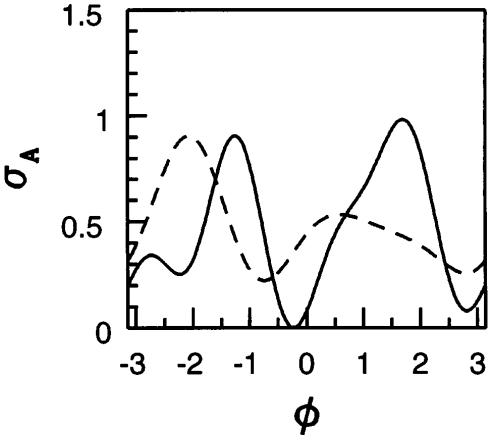

FIG. 1. Orbital order (A) scattering cross section in arbitrary units for the σ polarization (solid line) and π polarization (dashed line).

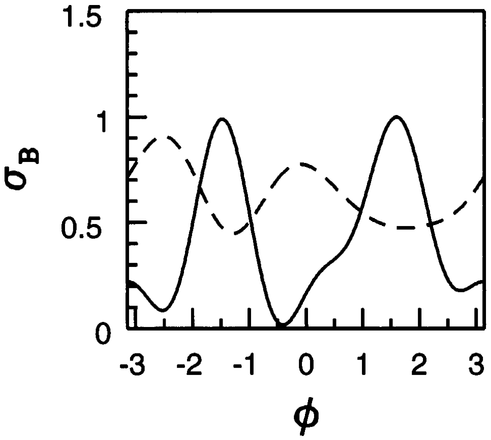

FIG. 2. Orbital order (B) scattering cross section in arbitrary units for the σ polarization (solid line) and π polarization (dashed line).

photon frequency, and Q the modulus of the wave vector for the orbital ordering, which will be either (8) or (10). Taking the K edge of the vanadium $\hbar\omega = 5465$ eV, and the lattice parameters in the insulating phase $a = 2.88$ Å and $c = 2.70$ Å, we find the two scattering angles $\gamma_A = 15.490°$ and $\gamma_B = 17.313°$. If we assume not to detect the polarization of the emitted light, only three degrees of freedom for the scattering geometry remain. The first is the angle ϕ of rotation of the scattering plane around the transferred momentum $\vec{Q}$, with $\phi = 0$ corresponding to the component of the incoming wave vector $\vec{k}$ normal to $\vec{Q}$ lying in the ab plane. The other two free scattering parameters are related to the polarization of the incoming beam, and reduce to one for a linearly polarized light.

Let us now estimate the scattering cross section. The radial dipole matrix element as obtained from the cluster calculation is $r_{1,ps} = 780 r_0$, where r_0 is the classical electron radius. We also take $\Gamma = 0.8$ eV [12]. The resulting cross section is very large, of the order of $10^3 r_0^2$, which is not surprising in view of our assumption of a single resonating level (similarly large cross sections for magnetic x-ray scatterings were estimated by Hannon *et al.* [13], for the $3d$ to $4f$ resonance of a rare earth with one f hole per atom). The dependence of the cross section on the angle ϕ is shown in Fig. 1 for the orbital order (A) of Eq. (7) and in Fig. 2 for the case (B) of Eq. (9).

In conclusion, it was shown that elastic resonant x-ray scattering in an appropriate experimental configuration provides a direct probe of the orbital order parameter. Numerical estimates show that, in general, the effect should be observable in transition metal oxides at the metal K edge. This is even more so in the particularly interesting case of V_2O_3, where the absence of inversion symmetry in the insulating phase allows dipole transitions to relevant intermediate states. Interestingly, the same dipole matrix elements are expected to enhance the resonant magnetic scattering from the antiferromagnetic structure, allowing one to monitor the interplay of the orbital and magnetic order in the same experiment.

Our results imply that resonant x-ray experiments can determine the temperature dependence of the orbital order parameter, as well as its wave vector. These quantities have so far eluded any direct measurement.

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[1] For a review, see K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk. **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].

[2] For a recent short review article, see T. M. Rice, in *Spectroscopy of Mott Insulators and Correlated Metals*, edited by A. Fujimori and Y. Tokura (Springer, New York, 1995).

[3] D. B. McWhan and J. P. Remeika, Phys. Rev. B **2**, 3734 (1970).

[4] R. M. Moon, Phys. Rev. Lett. **25**, 527 (1970).

[5] C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B **18**, 4945 (1978); **18**, 4967 (1978); **18**, 5001 (1978).

[6] W. Bao, C. Broholm, G. Aeppli, P. Dai, J. M. Honig, and P. Metcalf, Phys. Rev. Lett. **78**, 507 (1997).

[7] R. E. Word, S. A. Werner, W. B. Yelon, J. M. Honig, and S. Shivashankar, Phys. Rev. B **23**, 3533 (1981).

[8] A. Bianconi and C. R. Natoli, Solid State Commun. **27**, 1177 (1978) (see also Ref. [11]).

[9] In a recent preprint (Report No. cond-mat/9712163), Ishihara and Maekawa argue that a dipolar resonance is detectable due to the $4p$-level energy splitting caused by the d-orbital ordering. This is an interesting alternative mechanism. However, our numerical results on $LaMnO_3$ indicate that this splitting mostly reflects the static Jahn-Teller distortion of this compound.

[10] P. D. Dernier and M. Marezio, Phys. Rev. B **2**, 3771 (1970).

[11] J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Maylotte, Phys. Rev. B **30**, 5596 (1984).

[12] A. Kotani and Y. Toyozawa, in *Synchrotron Radiation, Techniques and Applications,* edited by C. Kunz, (Springer, Berlin, 1979).

[13] J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988).