Orbital ordering, Jahn-Teller distortion, and anomalous X-Ray scattering in Manganates

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We demonstrate with LSDA+U calculations that x-ray scattering at the K edge of Mn is sensitive to orbital ordering in one energy range and Jahn-Teller distortion in another. Contrary to what is suggested by atomic or cluster models used to date we show that band structure effects rather than local Coulomb interactions dominate the polarization dependence of the K edge scattering and therefore it is sensitive to nearest neighbour bond length distortions and next nearest neighbour orbital occupation. Based on this we propose a new mechanism for K edge x-ray scattering in the manganates which we suggest is also applicable to transition metal compounds in general.

A very popular topic in strongly correlated 3d transition metal systems has to do with the influence of orbital degeneracy and orbital ordering on the magnetic and magneto-electronic properties. It is well established in the early works of Khomskii and Kugel that the superexchange interactions between neighboring transition metal ions is strongly dependent on the spatial orientation of occupied d orbitals leading to even sign changes in this interaction for different orbital occupations. Very much studied recent examples are the so called colossal magnetoresistance materials containing trivalent Mn ions with four 3d electrons which in a cubic crystal field and the usual strong atomic Hund’s rule coupling results in an electronic configuration with three electrons with parallel spins in the threefold degenerate t₂g level and the fourth electron in a twofold orbitally degenerate e₉ level. The remaining twofold orbital degeneracy is in accordance with the Jahn-Teller theorem lifted either by local lattice distortions and or by ordering the e₉ level occupation on neighboring ions and thereby strongly affecting the magnetic structure which in its turn stabilizes a particular orbital ordering. Also the electrical transport properties are strongly affected because of the so called double exchange like mechanisms in which the electron band widths are strongly influenced by the spin structure and also of course by the relative orientation of occupied orbitals on neighboring ions. Similar situations can and do occur in Fe and Co oxides which also are recently a subject of intense investigation. A somewhat different influence of orbital ordering has been invoked to explain the very strange magnetic behavior of various V compounds like LiVO₂ with its transition from a paramagnetic state to a non magnetic state at 500K and YVO₃ with its magnetization reversal transitions at 90K and 77K. So the problem of orbital ordering is quickly becoming a central issue in a broad range of materials. A problem is to find an accurate and direct experimental method to determine the nature of the orbital ordering and also study the changes which occur at magnetic and crystallographic transitions.

Orbital ordering manifests itself in the site dependent orientation of the quadrupole moment resulting from the spatial distribution of the outermost valence 3d electrons. Unfortunately x-ray scattering under normal conditions is primarily controlled by the core electrons of atoms and the sensitivity to the valence electron distribution is usually very low. However as has been demonstrated recently for the manganates the use of x-ray energies corresponding to K absorption edges can greatly enhance the sensitivity of x-ray scattering cross sections to the valence electron distribution making a direct observation of orbital ordering possible. Since we really want to study the 3d electron distribution the use of an absorption edge corresponding to a transition directly into the empty 3d states would have the most sensitivity but for the 3d transition metals these involve 2p or 3p like core levels which are relatively shallow and therefore involve long wavelengths restricting the information obtainable to systems with large lattice parameters. In the above mentioned K edge experiments the direct transitions to the 3d states are not dipole allowed and therefore involve weak quadrupole transitions. So where does the sensitivity come from? Several models have been proposed one indeed involving the quadrupole transitions and the other involving transition to the empty 4p band states which will be influenced by the 3d electron occupation because of the d-p Coulomb interactions. Ishihara et al recently used a nearest-neighbors MeO₆ octahedron to demonstrate the sensitivity of the Mn 4p states to the d electron orbital occupation establishing a basis for this effect. However in this model the 4p states are atomic like levels whereas in the real solid the 4p states form very broad bands which would tend to wash out the influence of the local d-p Coulomb interactions at first glance. For the analysis of the data it is important to have a good understanding of the origin of the effect in detail.

In this paper we present the results of a band structure study of the effect of orbital ordering on the 4p density of

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In this paper we present the results of a band structure study of the effect of orbital ordering on the 4p density of
states and especially the local symmetry projected density of states. We find indeed that the 4p bands are much broader than the d-p Coulomb interactions so that this is unlikely to be the dominant effect. However because the extended 4p states so strongly hybridize either directly or via the O states, with the 3d states of the neighboring atoms the local \( p_x, p_y, \) and \( p_z \) projected density of states is extremely sensitive to the local distortion of the oxygen octahedron and the \( d \) orbital occupation of the neighboring Mn atoms. So by using the polarization and energy dependence of the scattering, as was done in the experiment one can probe the orbital orientation of the occupied \( d \) states on the neighboring Mn atoms at energies corresponding to the empty \( d \) bands and the Jahn-Teller distortion of the oxygen octahedron at energies corresponding to the 4p bands. This mechanism is quite different from that previously reported since it is not the core hole parent atoms own orbital orientation which we claim is measured but rather that of the neighboring atoms. In addition we present calculation both with and without the local Jahn-Teller distortions so that the effects of a lattice distortion and a pure orbital ordering effect can be separated.

In order to address those problems we performed LSDA+U calculations on the prototypical orbital ordered compound LaMnO\(_3\) and especially studied the Mn-4p-DOS corresponding to \( p_x \) and \( p_y \) states. It is necessary to realize that in standard LSDA orbital polarization can be obtained only if MnO\(_6\) octahedrons are distorted due to the Jahn-Teller effect. However if one takes into account on site \( d-d \) Coulomb interaction, the resulting ground state is an orbitally polarized insulator even for the crystal structure without Jahn-Teller distortion \([10]\).

LaMnO\(_3\) has an orthorhombic \( Pbnm \) crystal structure which can be considered as a cubic perovskite with two types of distortions: the first one is a tilting of the MnO\(_6\) octahedra, so that Mn-O-Mn angles become less than 180\(^\circ\), and the second one is a Jahn-Teller distortion (shortening of the two Mn-O bond and elongation of a third one). The later is usually considered responsible for the insulator ground state in LaMnO\(_3\). The configuration of a Mn\(^{+3}\) ion in this compound is a high-spin \( d^4 \) state which is represented by \( 3t_{2g}^2 e_g \) and \( 1e_{g1} \) electrons. Because of weak hybridization of \( t_{2g} \) orbitals with O2p states these states can be regarded as forming the localized spin \( 3/2 \). In contrast to that, \( 3e_g \) orbitals, which hybridize much more strongly with O2p produce in the end rather broad bands. The strong exchange interaction with \( t_{2g} \) subshell leads to the splitting of the \( e_g \) band into unoccupied \( e_{g1} \) and half-occupied \( e_{g1} \) subbands.

The electronic structure of undoped LaMnO\(_3\) was calculated by the LSDA+U method in LMTO calculation scheme \([11]\) (based on Stuttgart TBLMTO-47 computer code) with the values of U and J equal 8 and 0.88 eV for Mn 3d electrons, respectively. For the Mn atoms, the

![FIG. 1. LSDA+U partial DOS of the Mn 3d orbitals in LaMnO\(_3\). Upper half denotes majority spins and lower half the minority spin states in each case. The zero of energy is at the Fermi energy.](image)

...basics from 4s, 4p, and 3d orbitals were used, while for La and O atoms it was 6s, 6p, 5d, 4f and 2s, 2p, 3d states, respectively.

As a first step we used the real crystal structure of the LaMnO\(_3\) (with Jahn-Teller distortions). The result of the self-consistent calculation was an orbital ordered antiferromagnetic insulator with a band gap of 1.41 eV and the magnetic moment 3.84\( \mu_B \) per Mn atom. The \( e_{g1} \)-band is split by this gap into two subbands: the occupied one with the predominantly \( \phi_1 \) character, and the empty one with the \( \phi_2 \) character Fig.\([2]\). Here, \( \phi_1 \) is a 3\( x^2-r^2 \) character orbital Fig.\([2]\) (the coordinate system is the same as in Fig.\([1]\)). For the second Mn type the 4p DOS has the same character but the \( p_x \) and \( p_y \) states are interchanged.

Before we discuss these results in more detail we note that there are, two interesting regions in the 4p partial density of states and therefore in the K edge x-ray absorption spectra: the first about 1.7 eV above the Fermi energy corresponding to the Mn 3d \( e_g \) empty states with some 4p character mixed in and the second between 12 and 32 eV corresponding to states of mainly 4p character. We note here the very strong difference in the \( p_x \) and \( p_y \) density of states which is the reason for the strong
anomalous polarization dependent scattering at the K edge. In order to understand the reason for why these two regions are interesting we performed the calculation of the LaMnO$_3$ electronic structure in the crystal structure of the P$\bar{1}$/$2$Sr$_1$/2MnO$_3$ which does not have the Jahn-Teller distortion. This allows to separate the contribution of Jahn-Teller distortion in the polarization of 4p states from the influence of Mn 3d shell. This calculation was made in the same way as the previous one and the result was also an antiferromagnetic insulator with the orbital ordering of Mn $e_g$ electrons but with a smaller band gap (0.39 eV) and the magnetic moment 3.81$\mu_B$ per Mn atom.

The calculated $d$-orbital polarization for real and P$\bar{1}$/$2$Sr$_1}$/2MnO$_3$ crystal structures has the same character as Fig.1, so, it is not shown here. The comparison of these two calculations (Fig.2 and Fig.3) allows us to conclude that the Mn 4p orbital polarization in the second energy region is caused mainly by the Jahn-Teller distortion of oxygen octahedra and in the first one by pure orbital ordering of Mn 3d electrons. In order to confirm the later supposition we performed the LSDA calculation of the LaMnO$_3$ in the crystal structure without Jahn-Teller distortions and without the local Coulomb correction resulting in a metal without any orbital ordering and also almost without polarization of Mn 4p states Fig.4. The magnetic moment is 3.17$\mu_B$ per Mn atom.

Recently, Muracami et al. have applied anomalous x-ray scattering techniques to the LaMnO$_3$. They observed a resonant-like and polarization dependent character of the scattering intensity near the K edge of the Mn ion in this compound. The comparison of calculated 4p densities of states Fig.2 and the measured fluorescence Fig.2 in [8] shows that they are very similar: the broad total 4p DOS has also two peaks (in the region 12-32 eV) and the distance between them is about 13 eV. Next, according to this experiment, the LaMnO$_3$ has the same type of the orbital ordering as was given by Goodenough and which we found in our calculations too. Based on the splitting of the Mn 4p states Muracami et al. proposed a theoretical description of the scattering mechanism but they did not specify the origin of this splitting. From the MeO$_6$ cluster calculations it was shown that the main reason of the Mn 4p polarization consists in the Coulomb interaction between Mn 3d and 4p electrons. So, this should lead to the raising in the energy of the $p_z$ orbital which is oriented along the direction of the occupied 3$s^2$-$r^2$ orbital (in the cubic coordinate system) but according to our calculation the picture is completely different. First of all, we should note again that the polarization of the Mn 4p orbitals in the region of 12-32 eV above Fermi energy originates mainly from the Jahn-Teller distortion of the oxygen octahedra which is indirectly connected with the orbital ordering. Second, in contrast to the cluster calculation, the $p_y$ Mn orbital which is perpendicular to the occupied 3$s^2$-$r^2$ orbital (in cubic coordinate system
and for one particular Mn atom) is almost absent in the region about 1.7 eV above Fermi energy. It means that the hybridization of this orbital with the neighboring Mn 3d orbitals has a much stronger influence on the band structure of 4p states then the d-p Coulomb interaction on the same site.

Summarizing, the LSDA+U calculation for the undoped LaMnO$_3$ demonstrates that there are two main contributions to the polarization dependence of the K edge scattering both of which involve the 4p orbitals and band structure effects. The first is caused by the hybridization of the Mn 4p orbitals with the ordered Mn 3d orbitals on neighboring Mn ions either directly or via the intervening O orbitals. This effect is therefore sensitive to the d orbital occupation not on the central Mn ion with the core hole but rather that of the neighboring Mn ions and occurs at energies corresponding to the empty Mn 3d bands. We should note here that if the Mn atoms are not in lattice sites with inversion symmetry the 4p states can mix directly with the 3d states of the same atom. In this case orbital ordering of the core hole parent atom will directly be measured. This would be the case for example in the corundum structure like V$_2$O$_3$. The second effect originates from the hybridization of the central Mn 4p states with states centered on the neighboring O ions and is therefore very sensitive to the local Jahn-Teller distortion but at most weakly affected by the d orbital occupation of the Mn 3d states. This effect is visible at about 10 eV higher in energy corresponding to the threshold of the predominantly 4p band. We note that although we have here demonstrated this for Mn the physics described is very general and will be applicable to transition metal compounds in general although the details like energy scales will depend on the system.

This investigation was supported by the Russian Foundation for Fundamental Investigations (RFFI grants 96-15-96598 98-02-17275), and by the Netherlands Organization for Fundamental Research on Matter (FOM) with financial support by the Netherlands Organization for the Advance of Pure Science (NWO). The Groningen group also acknowledges the financial support of the EU via the TMR OXSEN network.

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