Electronic Structures of Perovskite-Type Oxides and Linear Dichroism in X-Ray Absorption

Takeo Jo and Hong Bin Huang
Department of Quantum Matter, ADSM, Hiroshima University

The purpose of this talk is to discuss the capability of x-ray absorption linear dichroism (XLD) in studying orbital orderings observed in perovskite-type oxides by choosing several examples. [1)] In systems with cubic symmetry, orbital degrees of freedom are represented by the basis set of one of more-than-one dimensional irreducible representations. In ferro-orbital orderings, needless to say, XLD signal is observed, since the net polarization of occupation among the basis set exists. In antiferro-orbital orderings, on the other hand, there are two cases: 1) one where each sublattice has the polarization of occupation (quadrupole moment), but, if averaged over two sublattices, the net polarization does not exist, i.e., the basis set being occupied with an equal weight; XLD signal is not observed. 2) one where each sublattice has the quadrupole moment and, furthermore, the net polarization of occupation among the basis set exists; XLD signal is observed. An example of 1) is the $4f$ antiferro-orbital ordering in CeB_6, where Ce atoms form a simple cubic lattice and the antiferro-modulation is described by (1/2, 1/2, 1/2). Ce^{3+} with $4f^1$ configuration gives the lowest 6-hold degenerate J = 5/2 multiplet and, in the cubic field, it splits into the doubly degenerate Γ_7 and the quadruply degenerate Γ_8 states. An atomic $4f$ quadrupole moment is represented by the polarization of occupation among the basis set of the lowest Γ_8. If averaged over the two sublattices, the basis set of Γ_8 is occupied with an equal weight in this case, i.e., no XLD signal.

There are several examples of 2) in perovskite-type transition metal oxides. The first example is e_g systems. $LaMnO_3$, where Mn atoms form a simple cubic lattice and the antiferro-orbital ordering is described by the modulation vector (1/2, 1/2, 0).[2)] In the cubic crystal field and the strong Hund coupling, Mn^{3+} with the $3d^4$ configuration gives the fully occupied triply degenerate t_{2g} states and one electron in the doubly degenerate e_g states for the majority spin state; minority spin state is empty. The orbital ordering accompanied by the Jahn-Teller distortion is that where $3x^2 - r^2$ and $3y^2 - r^2$ orbits are alternately arranged on the two sublattices. The basis set of e_g is either $(3x^2 - r^2, y^2 - z^2)$, $(3y^2 - r^2, z^2 - x^2)$, $(3z^2 - r^2, x^2 - y^2)$, or their superpositions. *The* $3x^2 - r^2$ *orbit is not orthogonal to the* $3y^2 - r^2$ *orbit*. In this case, even if averaged over two sublattices, there remains a polarization of occupation among the basis set; XLD signal *is* observed. We assume that the $3x^2 - r^2$ ($3y^2 - r^2$) orbit is occupied at the sublattice A (B). If we take the difference in Mn $L_{2,3}$ x-ray absorption between the light polarizations parallel to the z and x axes, the B sublattice is, by symmetry, found not to contribute to XLD; only the A sublattice contributes to it. If we choose the light polarizations parallel to z and y axes, on the other hand, the A sublattice does not contribute to XLD; only the B sublattice contributes to it.

In $KCuF_3$ and K_2CuF_4, where Cu^{2+} ion has one t_{2g} hole, the symmetry of $3d$ hole in the initial state is sensitively reflected in XLD compared with $LaMnO_3$ with many $3d$ holes. The sublattice selectivity in XLD also applies to this case. We denote by I_α the integrated intensity of Cu $L_{2,3}$ absorption for the light polarization parallel to the α

axis ($\alpha = x, y, z$). Then $(I_z - I_x)/(I_x + I_y + I_z) = 0.5$ for the $y^2 - z^2$ $3d$ hole site and $(I_z - I_y)/(I_x + I_y + I_z) = 0.5$ for the $z^2 - x^2$ hole site.

The second example of 2) is the perovskite-type vanadates.[3] For example, YVO_3 for the temperature lower than 78K shows the Jahn-Teller distortion, where VO_6 octahedra elongated in the x and y directions are alternately arranged and its modulation vector is (1/2, 1/2, 0); the x (y) direction denotes [110] ([$\bar{1}$10]). Two $3d$ electrons of V^{3+} ion occupy two of the triply degenerate t_{2g} orbits. At V ion in the octahedron elongated in the x (y) direction, which we call the A (B) site, the xy and zx (xy and yz) orbits are reported to be occupied, i.e., antiferro-orbital ordering. In this case, even if averaged over the two sublattices, the net polarization of occupation among the basis set of t_{2g} remains; the weight of xy orbit is double of the other two. If we take the difference in V $L_{2,3}$ absorption between the light polarizations parallel to the z and x axes, the B site does not contribute to XLD and only the A site to it. For XLD by using the light polarizations parallel to the z and y axes, on the other hand, only the B site contributes to it.[4].

In $LaMnO_3$, $KCuF_3$, K_2CuF_4 and YVO_3, we can observe the sublattice quadrupole moment by using XLD. This is convenient for detailed measurements of an atomic quadrupole moment. In $LaMnO_3$, an admixture of $y^2 - z^2$ ($z^2 - x^2$) orbit into the $3x^2 - r^2$ ($3y^2 - r^2$) is expected. In $KCuF_3$ and K_2CuF_4, an admixture of $3x^2 - r^2$ ($3y^2 - r^2$) hole orbit into the $y^2 - z^2$ ($z^2 - x^2$) $3d$ hole is also reported. In order to measure the extent of admixture, i.e., the decrease of atomic quadrupole moment, XLD will be powerful, since the above-mentioned sublattice selectivity in XLD is, by symmetry, found to be not disturbed by the admixure . By the admixture, $(I_z - I_x)/(I_x + I_y + I_z)$ ($(I_z - I_y)/(I_x + I_y + I_z)$) is reduced from 0.5 in Cu perovskites. For vanadates, in addition to YVO_3 below 78K, another antiferro-orbital ordering is also reported in YVO_3 above 78K and in $LaVO_3$ in the t_{2g} state. In the t_{2g} state, the $3d$ spin-orbit interaction is usually relevant and the orbital moment is expected to be induced.[3] This causes an admixture of yz orbit into the (xy, zx) site and the zx orbit into the (xy, yz) site.[3] XLD can also be powerful method to check the admixture.

In conclusion, we stressed the capability of XLD in investigating antiferro-orbital orderings in perovskite-type transition metal oxides, which is in sharp contrast to the disappearance of XMCD in antiferromagnets.

References

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