

Charge-orbital ordering of magnetite studied by soft resonant X-ray scattering

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Abstract

We report direct experimental evidence for the existence of charge and orbital ordering in magnetite. In particular, measurements of oxygen K-edge resonant X-ray scattering on magnetite reveal that the oxygen 2p states in the vicinity of the Fermi level exhibit a charge-orbital ordering with a spatial periodicity of the doubled lattice parameter of the undistorted cubic phase.

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Magnetite (Fe_3O_4) exhibits a classic metal-to-insulator phenomenon known as the Verwey transition [1]. Such a transition was first interpreted as an order–disorder transition in which the valence electrons of Fe^{2+} and Fe^{3+} ions order themselves over the octahedral sites [2]. Abrupt changes in the crystallographic structure, magnetic susceptibility, specific heat and electric resistivity of magnetite at the critical temperature T_v are manifestations of the Verwey transition. Despite intensive investigation over 60 years, the mechanism of the Verwey transition remains unresolved; even the existence of charge ordering in magnetite is controversial [3–9].

Experiments with neutron diffuse scattering [3], nuclear magnetic resonance [4] and resonant X-ray scattering [5,6], however, cast strong doubt on the existence of charge ordering in magnetite. Refinements of X-ray and neutron diffraction [7,8] suggested the existence of charge ordering in magnetite with modulation vectors $q = (001)_c$ and $(00\frac{1}{2})_c$ in units of $2\pi/a$ (script “c” denotes the high-temperature cubic structure throughout); such ordering occurs with a

small charge disproportionation—octahedral $\text{Fe}^{2.4+}$ and $\text{Fe}^{2.6+}$. On the contrary, measurements of Fe K-edge resonant X-ray scattering concluded the absence of charge ordering with $q = (001)_c$ or $(00\frac{1}{2})_c$ in magnetite [9].

One main reason for the aforementioned controversy is that experimental techniques used in the measurements discussed above are not sensitive enough to provide direct and orbital-sensitive data on the charge ordering in Fe_3O_4 . Among them, resonant X-ray scattering around the Fe K-edge is the most sensitive technique to detect charge ordering. However, this technique is unable to probe the Fe 3d charge ordering directly, because the Fe 1s \rightarrow 3d transition is not dipole-allowed and hence the detection of charge ordering relies on the Fe 1s \rightarrow 3d transition and the hybridization between the Fe 4p and Fe 3d states. In contrast to Fe K-edge resonant scattering [5,6,9], resonant soft X-ray scattering around the O K-edge (O 1s \rightarrow 2p) and the Fe L-edge (Fe 2p \rightarrow 3d) are dipole-allowed and can probe the Fe 3d charge-orbital ordering directly and with high sensitivity. Because the structure form factor with $q = (00\frac{1}{2})_c$ arising from oxygen atoms in Fe_3O_4 vanishes, resonant scattering around the O K-edge can be used to separate charge-orbital ordering from the effect of pure lattice distortion, and is thus an effective experimental

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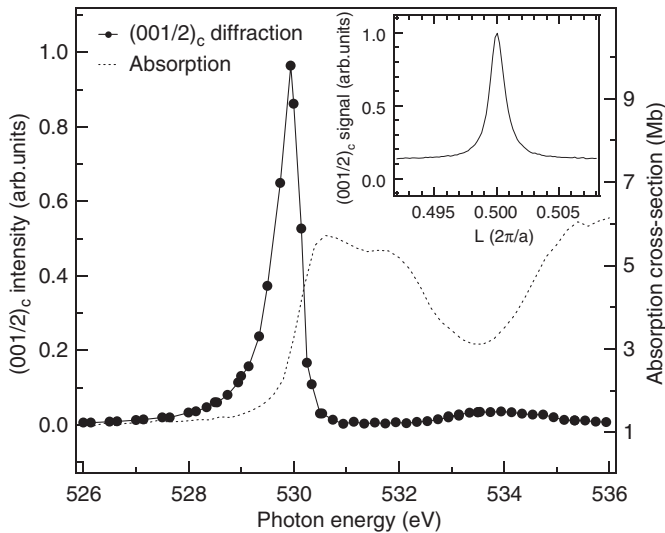


Fig. 1. Photon-energy dependence of the $(00\frac{1}{2})_c$ scattering intensity (circles) and soft X-ray absorption cross section (dotted line) of Fe_3O_4 around the O K-edge. The inset displays the q_z scan at photon energy of 529 eV.

method for unambiguously examining the existence of charge-orbital ordering in Fe_3O_4 .

We carried out resonant soft X-ray scattering at O K-edge on polished single crystals of Fe_3O_4 to detect its charge-orbital ordering, using a UHV X-ray diffractometer and the EPU beamline of National Synchrotron Radiation Research Center, Taiwan. The crystals were fully characterized by X-ray diffraction; resistivity measurements show a sharp Verwey transition at 116 K.

Fig. 1 displays the photon-energy-dependent resonant scattering intensities of Fe_3O_4 around the O K-edge with constant momentum transfer. The data were measured at sample temperature of 80 K with the \mathbf{E} vector in the scattering plane and its surface projection along the a -axis. Remarkably, the $(00\frac{1}{2})_c$ scattering at energy below the absorption edge (in a narrow energy window from 528.5 to 530.5 eV) enhances dramatically, whereas the scattering intensity is insignificant throughout the absorption white lines (from 530.5 to 536 eV). The observed $(00\frac{1}{2})_c$ resonance scattering is a manifestation of O 2p ordering instead of the doubling of the unit cell. If the resonant diffraction were a pure structural effect, the half-order scattering intensity would mimic the absorption cross section. In contrast, the ordering of the O 2p orbitals with a periodicity of $2a$ will lead to the enhancements of scattering intensity $I(\mathbf{q}, \hbar\omega)$ only at photon energy $\hbar\omega$ corresponding to the excitations of these ordered orbitals

and at $q = (00\frac{1}{2})_c$, rather than throughout the O K-edge absorption white line. Our measurements therefore provide direct evidence for the existence of the ordered unoccupied O 2p states. Similar to the O 2p ordering in Fe_3O_4 , the Zener polarons [12,13] and oxygen stripes [14] in manganites have been discussed previously.

The $(00\frac{1}{2})_c$ superstructure peak also exhibits a temperature hysteresis (not shown here because of limited space) that is the characteristic of a first-order transition, similar to the hysteresis of resistivity. Upon increasing the temperature, the $(0, 0, \frac{1}{2})_c$ peak scattering intensity decreases abruptly at T_V and diminishes completely at temperature beyond 119 K, manifesting the disappearance of charge-orbital ordering at temperature slightly higher than T_V . The temperature-dependent data indicate that the Verwey transition is a transition of charge-orbital ordering, providing a new insight for understanding the classic yet long debated issue on the Verwey transition.

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Further Reading

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