

Charge-Orbital Ordering and the Verwey Transition of Magnetite

Beamline

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Elucidating the nature of phase transitions is an subject in condensed-matter physics. Many phase transitions of correlated-electron materials are closely related to charge and orbital orderings, which manifest themselves in the spatial localization of the charge carriers on certain sites and in the periodic arrangement of occupancy of specific electron orbitals, respectively. One important example of phase transition which has fascinated generations of physicists is the metal-to-insulator transition in magnetite (Fe_3O_4), known as the Verwey transition. Such a transition was first interpreted as a transition of charge ordering in which the valence electrons order themselves over the octahedral sites to form a Fe^{2+} - Fe^{3+} superstructure in the insulating phase. Despite intensive investigations over half a century, the existence of charge ordering in magnetite remains controversial. The mechanism of the Verwey transition is a fundamental yet unresolved problem. Using resonant soft X-ray scattering measurements, we discovered a distinct charge-orbital order-disorder transition in magnetite across the Verwey temperature. Here we proffer experimental evidence for the charge-orbital-ordering mechanism of the Verwey transition, resolving the long-lasting debate.

The issue on charge ordering related to the Verwey transition in Fe_3O_4 has been one of the biggest mysteries in condensed-matter physics for many decades. Above the transition temperature T_V , Fe_3O_4 crystallizes in an inverse spinel structure with a cubic lattice. Upon cooling below T_V , Fe_3O_4 undergoes the Verwey transition in which the electrical conductivity decreases by two orders of magnitude and the lattice distorts from cubic to monoclinic structure. Manifestations of the Verwey transition also include abrupt changes in magnetic susceptibility and specific heat across the critical temperature. The low-temperature phase of magnetite has been regarded as a classic example of the charge ordering in transition-metal oxides. In contrast, electron-phonon interactions have been attributed to be the driving force of the Verwey transition, as the freezing of phonon modes relieves an instability of the Fermi surface nesting via a mechanism involving charge-density waves below T_V , and therefore increases the resistivity.

The mechanism of the Verwey transition is intricate, because neither charge-orbital ordering of valence electrons nor the soft phonon mode has been observed. Inelastic neutron scattering failed to observe the soft phonon mode. Experiments on neutron diffuse scattering, nuclear magnetic resonance, and resonant X-ray scattering cast strong doubt on the existence of charge ordering in magnetite. Recent measurements of Fe K -edge resonant X-ray scattering concluded the absence of charge ordering in magnetite with a modulation vector $q = (001)_c$ and $(00\frac{1}{2})_c$ in units of $2\pi/a$ with a denoting the lattice parameter of the undistorted

cubic phase (script “c” denotes the high-temperature cubic structure throughout). In contrast, the existence of a small charge disproportionation with modulations of $(001)_c$ and $(00\frac{1}{2})_c$ was suggested by refinements of X-ray and neutron diffraction. Band-structure calculations in the local density approximation explicitly including the on-site Coulomb interactions (LDA+U) also predict that Fe_3O_4 has a charge-orbital ordered ground state. 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 for detecting of the charge ordering in Fe_3O_4 .

The detection of temperature-dependent charge-orbital ordering in magnetite is thus a decisive measurement for revealing the mechanism of the Verwey transition. Resonant soft X-ray scatterings around the O K -edge ($1s \rightarrow 2p$) and the Fe L -edge ($2p \rightarrow 3d$) are dipole-allowed and are, respectively, suitable for probing the O $2p$ and the Fe $3d$ charge-orbital orderings directly and with high sensitivity. In particular, the structure factor of diffraction arising from oxygen atoms in cubic or distorted Fe_3O_4 vanishes. Resonant scattering around the O K -edge can separate charge and orbital orderings from the effect of pure lattice distortion, and is thus an effectively experimental method for unambiguously examining the existence

charge-orbital ordering in Fe_3O_4 . We performed resonant soft X-ray scattering on single crystals of Fe_3O_4 which were polished with fine Al_2O_3 powder to achieve a mirror-like surface and fully characterized with X-ray diffraction.

Resonant elastic X-ray scattering is a second order process in which a core electron is virtually excited to some intermediate states above the Fermi level, and subsequently decays to the same core level. The intensity of resonant elastic X-ray scattering is determined by the structure form factor and the resonant atomic scattering tensor. Figure 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 E vector of the incident soft X-ray in the scattering plane. 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 the ordering of O $2p$ electronic states with a periodicity of $2a$, instead of the doubling of the unit cell, because of the symmetry-forbidden structure factor arising from the oxygen lattice in Fe_3O_4 .

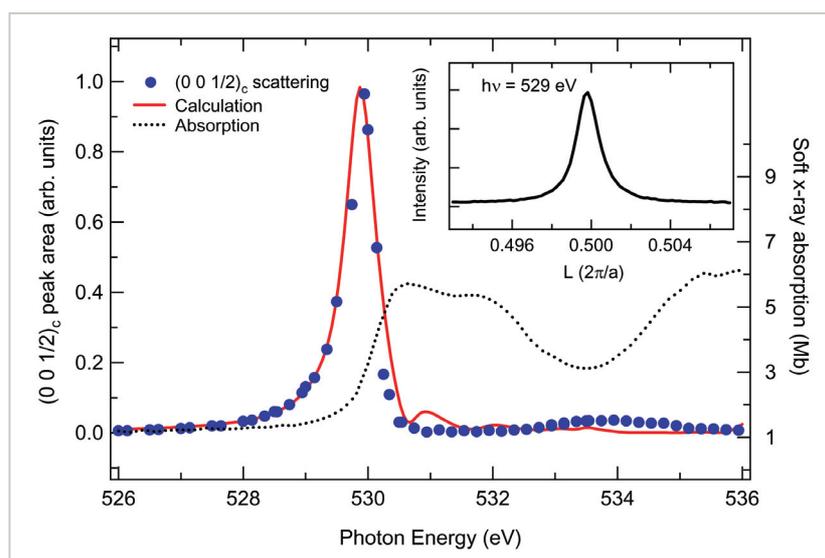


Fig. 1: Photon-energy dependence of the $(00\frac{1}{2})_c$ scattering intensity (blue circles) and soft X-ray absorption cross section (dotted line) of Fe_3O_4 around the O K -edge. The inset displays the q_z scan at photon energy of 529 eV. The scattering measurements are compared with calculated resonant spectrum (red line) obtained by employing the results of LDA+U calculations as discussed in the text.

To ensure that the measurements of resonant scattering are not obscured by the self-absorption effect of soft X-ray in the sample, we compared the correlation length ξ of the O $2p$ ordering and the penetration depth of soft X-ray. Here we define the correlation length as $\xi = \frac{a}{2\pi} \frac{1}{\Delta q}$ with Δq denoting the full width at half maximum of the q_z scan in reciprocal lattice units of $2\pi/a$. The inset of Fig. 1 depicts the width of the diffraction peak in the q_z scan at the onset energy of the resonant scattering, giving rise to a correlation length $\xi \sim 900 \text{ \AA}$. Deduced from the measured absorption cross section, the penetration depths of photons with the energy between 528 and 531 eV are greater than 1300 \AA , which is larger than the measured correlation length. In the following discussions on the polarization and temperature dependence of O $2p$ ordering, we present data measured with photon energy of 529 eV, at which the penetration depth is 5500 \AA , to avoid the experimental complication caused by the sample self-absorption effect.

The observed resonance can be an effect of pure charge modulation or charge-orbital ordering. The latter would lead to a resonant scattering depending on the polarization of the incident soft X-ray. To disentangle this uncertainty, we calculated spatial distribution of O $2p$ orbitals using LDA+U calculations on Fe_3O_4 . Our calculations show that distorted Fe_3O_4 exhibits localized O $2p$ orbitals in the vicinity of the

Fermi level with a modulation vector $(00\frac{1}{2})_c$, i.e., O $2p$ charge-orbital ordering, in addition to the charge-orbital ordering of the Fe $3d$ predicted previously. With the O $2p$ orbitals from LDA+U calculations, we also calculated the resonant X-ray scattering spectrum at the O K -edge of Fe_3O_4 , as plotted in the solid curve of Fig. 1. The calculations qualitatively explain the resonance feature of the measured spectrum, further corroborating that the observed resonance arises from the O $2p$ charge-orbital ordering.

In addition, we found the $(00\frac{1}{2})_c$ resonant scattering at the O K -edge exhibits a polarization dependence. Figure 2 shows that the $(00\frac{1}{2})_c$ scattering spectra taken with the \mathbf{E} vector of the incident soft X-ray in the scattering plane (\mathbf{E}_π) and perpendicular to the scattering plane (\mathbf{E}_σ). As the polarization of the soft X-ray is rotated from \mathbf{E}_π to \mathbf{E}_σ , the scattering intensity is reduced. Such a polarization dependence can be explained by LDA+U calculations. O $2p$ orbitals at elevations of $z = 0$ and $z = a$ ($z = \frac{a}{4}$ and $z = \frac{5a}{4}$) are nearly orthogonal; the projection of the O $2p$ orbitals along the direction of \mathbf{E}_s has a stronger contrast between these elevations than that of the O $2p$ orbitals along the direction of \mathbf{E}_σ . The results of LDA+U calculations are thus consistent with our polarization-dependent measurement, lending further support for the existence of orbital ordering in magnetite.

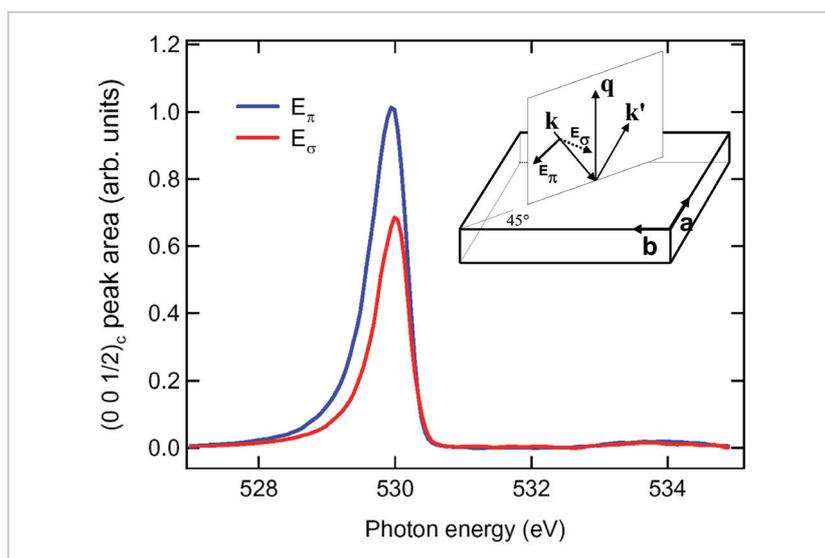


Fig. 2: Polarization dependence of the $(00\frac{1}{2})_c$ O K -edge scattering intensity. The data were measured at sample temperature of 100 K with photons of polarization in the scattering plane (\mathbf{E}_s) and perpendicular to the scattering plane (\mathbf{E}_p) defined by the incoming wave vector \bar{k} and the scattered wave vector \bar{k}' , as illustrated in the inset.

After experimentally establishing the existence of charge-orbital ordering in Fe_3O_4 , we scrutinized the nature of the Verwey transition by carrying out temperature-dependent measurements. The $(00\frac{1}{2})_c$ superstructure peak also exhibits a temperature hysteresis that is the characteristic of a first-order transition, similar to the hysteresis of resistivity. Figure 3 displays resistivity and the intensities of the $(00\frac{1}{2})_c$ O K -edge resonant scattering of Fe_3O_4 measured simultaneously for temperatures across the Verwey temperature 116.5 K. Upon increasing the temperature and concurrently with the decrease of resistivity, the 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 O $2p$ states at the Fermi level contribute to the electric conduction above T_V and undergo a dramatic change upon cooling below the Verwey temperature at which these states form an orbital ordering, opening up an energy gap and thus leading to the insulating phase. Such charge-orbital ordering is further stabilized by the lattice distortion. With the results of soft X-ray resonant scattering and LDA+U calculations, we found that the ground state of Fe_3O_4 at $T = 0$ K is a charge-orbital ordered state and this ordering is melted by the thermal fluctuation of lattice when the temperature increases above T_V . Our results unravel that the $(00\frac{1}{2})_c$ scattering has the same temperature-dependence as that of resistivity, indicating that the Verwey transition is a transition of charge-orbital ordering. In addition, LDA+U calculations show that orbital ordering already exists in Fe_3O_4 with atomic positions as those in the cubic phase but of monoclinic symmetry, whereas LDA calculations without Coulomb interaction explicitly included indicate that charge-orbital ordering is absent in the distorted lattice. The Coulomb interaction is hence the driving force for the existence of charge-orbital ordering.

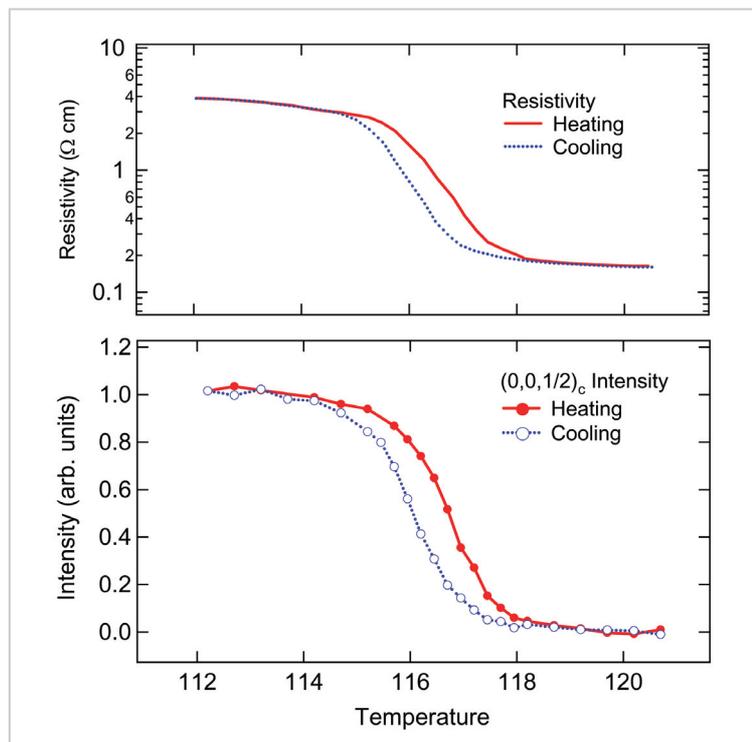


Fig. 3: Temperature-dependent resistivity (upper panel) and the $(00\frac{1}{2})_c$ O K -edge scattering intensity (lower panel) of Fe_3O_4 across the Verwey transition. The $(00\frac{1}{2})_c$ measurements in heating and the cooling are with connecting solid and dotted lines for visual guidance, respectively. The scattering data were measured with photon energy of 529 eV and with the \mathbf{E} vector in the scattering plane and along the a -axis.

Experimental Station

Soft X-ray scattering chamber

Publications

- D. J. Huang, H.-J. Lin, J. Okamoto, K. S. Chao, H.-T. Jeng, G. Y. Guo, C.-H. Hsu, C.-M. Huang, D. C. Ling, W. B. Wu, C. S. Yang, and C. T. Chen, *Phys. Rev. Lett.* **96**, 096401 (2006).

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