High-energy photoemission on Fe₃O₄: Small polaron physics and the Verwey transition

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We have studied the electronic structure and charge ordering (Verwey) transition of magnetite (Fe₃O₄) by soft x-ray photoemission. Due to the enhanced probing depth and the use of different surface preparations we are able to distinguish surface and volume effects in the spectra. The pseudogap behavior of the intrinsic spectra and its temperature dependence give evidence for the existence of strongly bound small polarons consistent with both dc and optical conductivity. Together with other recent structural and theoretical results our findings support a picture in which the Verwey transition contains elements of a cooperative Jahn-Teller effect, stabilized by local Coulomb interaction.

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Magnetite (Fe₃O₄) is not only the oldest magnetic material known to mankind, with high potential for applications in spin-electronics, but also displays a rather unique electronic phase transition whose explanation has remained a challenge to modern condensed matter physics [1, 2]. At low temperatures magnetite is an insulator. Upon heating its resistivity drops abruptly in a first-order phase transition at \( T_V \approx 123 \) K by about two orders of magnitude to that of a bad metal, although its temperature dependence up to 300 K remains non-metallic. Verwey [3] was the first to suggest that the transition is related to charge ordering (CO) in this mixed-valent oxide. In this picture the Fe³⁺ and Fe²⁺ ions, which occupy the octahedral \( B \)-sites of the inverse spinel structure in equal numbers, form below \( T_V \) an ordered pattern, whereas above the transition they become statistically distributed over the \( B \)-sublattice (with the possible preservation of short-range order). The driving force for the Verwey transition has been suggested to be the \emph{intra}atomic Coulomb interaction [4]. However, as first pointed out by Ihle and Lorenz [5], strong coupling to the lattice may also be of importance.

While the Verwey transition has thus been studied for decades, very recent experiments have raised fundamental questions. Based on new high-resolution powder diffraction data it has been estimated that the actual charge disproportionation is only very small, of order \( \pm 0.1e \) [6]. From resonant x-ray diffraction other authors even concluded on the complete absence of any CO in the insulating phase of magnetite [7, 8]. These results suggest that the electrostatic energy minimization implied by the proposed CO cannot be the dominant force behind the Verwey transition contrary to previous ideas.

Another controversial question concerns the electronic nature of the high-temperature phase. In a high-resolution photoemission study Chainani \emph{et al.} [9] found above \( T_V \) finite spectral weight at the chemical potential and concluded on a metallic state. In contrast, Park \emph{et al.} [10] reported photoemission spectra measured just below and above \( T_V \) which display a notable change in the gap but leave it finite above \( T_V \). The Verwey transition was thus identified as insulator-to-insulator transition. We note however that all previous photoemission experiments have been performed at low photon energies, where the probing depth [11] is small (\( \sim 15 \) Å) and the spectra are very surface-sensitive.

In this letter we demonstrate that low-energy photoemission spectra of magnetite are indeed strongly affected by surface orientation and preparation, thus limiting their reliability for a study of the bulk electronic structure. We show how this problem can be overcome by use of soft x-ray photoemission which due to its enhanced probing depth (\( \sim 45 \) Å) allows much better access to the volume. It is
observed that the intrinsic spectra both above and below $T_V$ show an exponential suppression of spectral weight towards the chemical potential and bear no resemblance to the prominent doublet of quasiparticle peak and lower Hubbard band as observed in other oxides with Mott-like metal-insulator transitions. In fact, from the temperature dependence of the spectra we conclude on a semiconductor-semiconductor character of the Verwey transition. We analyze the pseudogap-like line shape and demonstrate that it can consistently be attributed to strong electron-phonon coupling. The results yield evidence that small polaron physics plays an essential role for the electronic properties and the Verwey transition of magnetite.

The experiments were performed on high-quality synthetic magnetite crystals. From these we cut oriented (111) and (100) surfaces which after polishing were exposed to an in situ treatment involving Ar ion sputtering and annealing (up to 800$^\circ$C). Loss of surface oxygen was compensated by a subsequent oxidation step (further details are described in [12]). Long-range order and stoichiometry of the surfaces were checked by LEED and XPS, respectively. Alternatively, clean surfaces were also obtained by fracturing single crystals in situ at 100 K. Because magnetite has no natural cleavage plane, the resulting surfaces are rather rough and faceted. Low-energy photoemission was performed at our home lab using He I radiation ($h\nu = 21.2$ eV). The soft x-ray experiments were performed at BL25SU of SPring-8 using Fe 2p-3d resonance photoemission ($h\nu = 707.6$ eV). In both cases the energy resolution was 100 meV or lower. The position of the chemical potential was calibrated by the Fermi edge of an evaporated Au film in electrical contact with the magnetite crystals.

Figure 1(a) and (b) show the valence band spectra of the different magnetite surfaces measured with vacuum ultraviolet (VUV) and soft x-ray (SX) radiation, respectively. The VUV spectra display dramatic differences depending on surface preparation and orientation, reflecting strong electronic structure rearrangements in the outermost atomic layers. In contrast, the SX spectra show only very small (though reproducible) differences, indicating that due to the larger probing depth they are dominated by signal from the bulk. This is particularly evident in the spectral weight distribution near the chemical potential $\mu$ (see insets in Fig. 1) which originates from the $d^6 \rightarrow d^5$ transition at the $B$-site Fe$^{2+}$ ions [14, 15] and is directly related to the low-energy physics of magnetite. For all three surfaces the SX data yield the same spectral line shape with a broad maximum at $\approx -0.6$ eV and a strong suppression of intensity towards the chemical potential. We hence conclude that this is the intrinsic low-energy spectrum of magnetite.

For a further analysis of the $d^6 \rightarrow d^5$ signal we now turn to its temperature dependence. Figure 2(a) shows SX spectra of the fractured surface measured for temperatures within a few Kelvin around
Below the Verwey transition the spectrum is consistent with a small energy gap, as expected for an insulator. Going through the Verwey transition the spectral onset becomes abruptly shifted towards the chemical potential. However, no indication of a metallic Fermi edge or quasiparticle feature is observed in the high-temperature phase, in notable contrast to the spectra of oxide materials with a Mott transition such as, e.g., V$_2$O$_3$ [16]. For a more quantitative examination we define the spectral onset phenomenologically as the intersection of the leading edge with the zero intensity base line (see inset of Fig. 2(a)). A plot of this phenomenological parameter versus temperature is shown in the inset of Fig. 2(a). The onset energy jumps exactly at $T_V$ and is consistent with the hysteretic behavior of the conductivity, confirming that these spectra reflect intrinsic bulk behavior. This conclusion is further corroborated by the observation that the onset energy agrees well with the activation energy of the conductivity on both sides of the transition [2]. If the onset energy is indeed identified with the insulator half-gap (with $\mu$ assumed to be in mid-gap position), its discontinuous change $\Delta E_{on} \approx 50$ meV will cause the concentration of thermally activated charge carriers to increase by a factor of $\exp(\Delta E_{on}/k_B T_V)$. This accounts quantitatively for the observed two-order of magnitude jump in the conductivity, as was already argued by Park et al. [10]. A decrease rather than a complete closing of the gap at $T_V$ also identifies the Verwey transition as an insulator-to-insulator transition [10].

We also note that temperature effects are not restricted to the immediate vicinity of $T_V$. The discontinuity observed at the Verwey transition is actually superimposed on top of a continuous energy shift of the spectral onset over a wide temperature range, as shown in Fig. 2(b). The identification of a first-order Verwey transition thus requires a very fine temperature grid around $T_V$. Previous photoemission studies, besides being strongly surface-sensitive, used rather wide temperature steps, so that the reported effects resulted (at least partly) from the gradual temperature evolution and not from the Verwey transition.

Interestingly, the discontinuous first-order transition of the onset is only observed for fractured surfaces, but not for the (111) and (100) surfaces (also shown in Fig. 2(b)). For the (111) sample the onset shifts continuously towards the chemical potential and reaches it at $\sim T_V$ without any evidence for a discontinuous phase transition or a metallic Fermi edge. The onset of the (100) spectra shows also a continuous but much smaller temperature shift. Moreover, the onset remains clearly below the chemical potential even up to 190 K, well above $T_V$. It is tempting to relate this finding to reports of room-temperature charge order at the (100) surface [14,15]. These surface effects in the temperature evolution can be traced back to the fact that any termination of a bulk magnetite crystal will result in a polar surface, which in order to minimize its energy has to undergo a geometric (or electronic) relaxation. The resulting atomic reconfiguration may then lead to a suppression of the Verwey transition, similar to the adverse
effects of other lattice deformations in the volume induced by defects or hydrostatic pressure. For the (111) and (100) samples the thickness of the relaxed surface layer is obviously comparable to the relatively large photoemission probing depth and therefore extends over at least one unit cell (lattice constant \(a = 8.4 \, \text{Å}\)). As their preparation involves high temperature annealing, the resulting surface configurations are in thermal equilibrium. In contrast, crystal fracture at cryogenic temperatures will result in a non-equilibrium surface in which the topmost atomic layer may be disturbed but a full surface relaxation is hindered by the lack of sufficient thermal energy. The subsequent layers (accessible by SX photoemission) will remain frozen in a bulk-like configuration and thus display the Verwey transition.

In any case, the above results establish that the broad spectral distribution and the absence of a well-defined quasiparticle peak near the chemical potential are intrinsic properties of the electron removal spectrum and not a surface artefact. The non-observation of a sharp Fermi edge, particularly above \(T_V\), is in clear disagreement with LDA band calculations which predict a metallic state (see Fig. 3(a)). Furthermore, even if one allows for an insulating state as suggested by the activated conductivity on both sides of the transition, the inflexion point of the leading edge of the spectrum (which in a band insulator would mark the gap edge) lies at much higher binding energy than expected from the transport (half)gap. Rather, the gap coincides with the energy of the spectral onset (as defined above), very reminiscent of observations recently made in photoemission spectra of quasi-one-dimensional Peierls systems and attributed there to polaronic effects. In this picture strong electron-lattice coupling leads to the formation of polaronic quasiparticles, i.e., electron (or hole) excitations heavily dressed by virtual phonons. Removing an electron from the coupled system (as in photoemission) results in a spectrum consisting of a coherent quasiparticle peak, greatly reduced in spectral weight and renormalized in energy, and an incoherent background of phonon side bands shifting weight away from the chemical potential. If the coupling is sufficiently strong, a pseudogap-like behavior of the spectrum will result. Indeed, for magnetite strong coupling to the lattice and the formation of small polarons have already been inferred from other properties, e.g., the small carrier mobility, the unusual temperature behavior of the conductivity above \(T_V\), and the observation of a mid-infrared polaron peak in the optical conductivity, from which a polaronic binding energy of \(\varepsilon_p \sim 300 \, \text{meV}\) has been derived.

In order to further substantiate the above qualitative picture we have analyzed the data using the theoretical model of Alexandrov and Ranninger, in which the electron removal spectrum of a system with strong electron-phonon coupling can be written as

\[
I(\varepsilon) \propto e^{-g^2 \tilde{N}_p(\varepsilon)} + \sum_{n=1}^{\infty} e^{-g^2 \frac{\varepsilon}{\omega_0}} \tilde{N}_p(\varepsilon + n\omega_0).
\]

The first term represents the polaronic quasiparticle band (\(\tilde{N}_p(\varepsilon)\)) renormalized in spectral weight and width (i.e., its inverse mass) by a factor \(e^{-g^2}\), where \(g^2 = \varepsilon_p/\omega_0\) is a dimensionless electron-phonon coupling constant and \(\omega_0\) a characteristic phonon energy. The remaining intensity is transferred to multiple phonon side bands shifted by \(n\omega_0\) away from \(\varepsilon\). For strong coupling \((g^2 >> 1)\) the polaron quasiparticle weight is thus exponentially suppressed in the photoemission spectrum, but its binding energy still defines the lower edge of the transport gap. According to band theory the (non-coupling) density of states (DOS) near the chemical potential consists of two peaks, one right at \(\mu\) and a second one at \(-0.6 \, \text{eV}\) (Fig. 3(a)). The polaronic effects in the electron removal spectrum have now been modeled for the first DOS peak by eq. (1) and for the second by a Gaussian of similar width. Figure 3(b) shows the result for the 180 K spectrum of the fractured sample, with the phonon energy scale \(\omega_0\) fixed to the highest optical mode (70 meV) and the theoretical spectrum broadened by \(\sim 100 \, \text{meV}\) to account for instrumental resolution and a possible residual polaron bandwidth. The best agreement with experiment is obtained for a coupling strength of \(g^2 \sim 5\), which accurately reproduces the observed pseudogap behavior near the chemical potential and the shift of spectral weight to higher binding energy with respect to the band theory DOS. The value for \(g^2\) is consistent with both the polaronic binding energy and the effective polaron mass \((\sim 100 \ldots 200m_0)\) derived from infrared spectroscopy. This analysis corroborates the qualitative arguments from above for a pronounced electron-phonon coupling and formation of small polarons in magnetite.

The strong coupling to the lattice can be traced back to the fact that \(\text{Fe}^{2+}\) in a high-spin \(d^6\) configuration is a Jahn-Teller (JT) ion. In fact, the low-temperature distortions of the oxygen octahedra surrounding the formally divalent B-site ions can be understood as JT-active modes. Very recent LSDA+U calculations based on the refined structure of Ref. confirm this view. They find that the local occupation of
FIG. 3: (a): Near-\(\mu\) spectrum of a fractured Fe\(_3\)O\(_4\) crystal at 180 K (i.e. above \(T_V\)) superimposed on the band theory DOS for the high-temperature phase \[15\], cut-off by a Fermi function for the same temperature. (b): Model fit (red curve) of the background-subtracted spectrum (black dots) and its decomposition into the polaronic single-particle spectrum of Ref. \[26\] and an additional Gaussian (see text for details). “QP” denotes the location of the exponentially suppressed polaronic quasiparticle band.

\(t_{2g}\)-orbitals on the \(B\)-sublattice follows octahedral distortions as expected from the JT effect, except that the actual charge disproportionation is less than ±0.1e, leading to non-integer Fe valencies (2.4+/2.6+). As a consequence, the low-temperature phase is characterized by orbital order (OO) and much less so (if at all) by CO, consistent with the recent diffraction experiments \[6, 7, 8\]. It is thus tempting to conclude that the physics of the Verwey transition contains elements of a cooperative JT effect, which requires additional stabilization by local \(dd\) Coulomb interaction \[28, 29\].

We thus arrive at a picture in which the charge carriers in magnetite are small polarons, presumably of the JT type, forming a narrow band of high effective mass. At high temperatures they contribute to the charge transport by both coherent tunneling and activated hopping, as originally proposed by Ihle and Lorenz \[5\]. Below \(T_V\) the polarons condense into an orbitally-ordered phase (possibly with an additional small CO amplitude), whose microscopic origin remains to be revealed. This opens a gap in the polaronic quasiparticle band and causes the sudden drop in the conductivity. The polarons are much more stable than the OO/CO as inferred from our spectra of the annealed surfaces, for which the Verwey transition is suppressed but not the polaronic line shape. Our results demonstrate that the Verwey transition in magnetite is not a purely electronic effect and that any microscopic model has to account for the important role of electron-phonon coupling in the simultaneous presence of interatomic Coulomb interaction.

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