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Oxygen *K*-edge shift at the Verwey transition of magnetite

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The temperature dependence of the O *K*-edge threshold has been investigated in a temperature range encompassing the Verwey transition. Both above and below T_V the O *K*-edge threshold changes linear with temperature whereas there is discontinuous energy shift of 13 meV at T_V. A comparison of our results to published low and high energy photoemission experiments suggests the presence of an asymmetric gap with respect to the Fermi level. This explains present fundamental differences between photoemission and infrared derived gap energies, and supports the polaronic image of the electrical conductivity of Fe_3O_4 above the Verwey transition temperature.

Magnetite (Fe_3O_4), which has been investigated since the last 2000 years, has recently attracted enormous interest. This is clearly related to its proposed half metallic behavior and a corresponding spin polarization at the Fermi level of about 100%,[1,2] which transforms Fe_3O_4 into a promising candidate for spintronic applications.[3,4]

In addition, magnetite exhibits a first order phase transition, the so called "Verwey transition"[5–7] at $T_V \approx 123$ K, which is under intensive discussion for many decades. This phase transition is accompanied with a jump in the electrical conductivity of about two orders of magnitude (see Refs. 8 and 9 and references therein).

Fe_3O_4 crystallizes at room temperature in the antiferromagnetic cubic inverse spinel structure ($Fd\bar{3}m$), formally written as $Fe(A) Fe(B)_2O_4$.[10] The *A*-type ions are tetrahedrally coordinated and nominally in a Fe^{3+} configuration. The *B*-site ions are located on octahedral sites and mixed valent with equally distributed Fe^{3+} and Fe^{2+} ions. The magnetic moments of the *A* and *B* sites are aligned antiparallel to each other with a resulting magnetization per formula unit of $4.07\mu_B$.[11] Verwey has explained the phase transition at T_V in terms of a charge localization–delocalization of the conducting *B*-site electrons, and Anderson has proposed criteria for the charge order to minimize the Coulomb energy.[10]

Nevertheless, the total observed entropy change is too small for the charge ordering into a pure ionic configuration. This discussion is recently revived by new structure refinements, performed at the low and high temperature phase of Fe_3O_4.[12,13] In contradiction to the Verwey model an average charge of $2.5e$ has been observed at the *B*-site below T_V, with a slightly corrugated charge order between $2.4-2.6e$. The interpretation of resonant x-ray scattering experiments discount the model of strong charge separation into Fe^{3+} and Fe^{2+}, and corresponding fast hopping processes.[8] Very recent theoretical band structure calculations, based on the local density approximation, have taken into account the refined low temperature structural results.[14,15] In both references the authors found simultaneously an insulating low temperature phase, where orbital ordering occurs, and a half metallic high temperature phase.

Photoemission experiments (PES) have been performed above and below the Verwey transition to monitor temperature dependent variations near the chemical potential. Chainani *et al.*[16] and Park *et al.*[17] observed a shift in energy but nearly no spectral weight has been found at the chemical potential (near T_V). Only at higher temperatures a small spectral weight appears.[16] This has resulted into two different interpretations of the Verwey transition as an "insulator to metal" or "insulator to insulator" transition. Recent high energy PES ($h\nu = 705 eV$) of a cleaved single crystal exhibits a discontinuous shift at T_V of about 50 meV,[18] roughly consistent to previous cleaved sample PES results of Park *et al.*[17] In contradiction, only a continuous shift has been observed for extensively *in situ* prepared single crystal surfaces, which indicates a long range surface modification reaching inside the sample.[19] However, no spectral weight has been found at the chemical potential (near T_V), which is in contradiction to early[1,2] and recent[14,15,20] band structure calculations of the high temperature phase. To explain this nonmetallic behavior alternative theoretical approaches have been proposed, based on small-polarons,[21] electron–electron correlations,[22] and bond dimerization.[23] The gap and shape of the PES results have been modeled by a small-polaron picture.[18] A similar explanation, also based on polarons, has been used for the heavy electron behavior ($m^* \approx 100m_e$) observed in recent infrared and Raman experiments.[24]

Nevertheless, from the recent high energy photoemission data full energy gaps up to 2×150 meV (at $T=50$ K$<T_V$ from Ref. 18) and down to 0 meV (at $T=180$ K$>T_V$ from Ref. 18) could be estimated, assuming a gap center position of the chemical potential.[16,17,24] This is in contrast to the infrared derived optical gap information, which suggest only a full gap between 140 meV [at 10 K (Ref. 25)] and 200 meV [at 50 K (Ref. 24)].

In this contribution, we report high quality x-ray absorption results at the O *K*-edge of magnetite, monitoring the energy position of the unoccupied density of states. Compared to the abovementioned PES results we found a much smaller gap variation as the temperature is cycled through
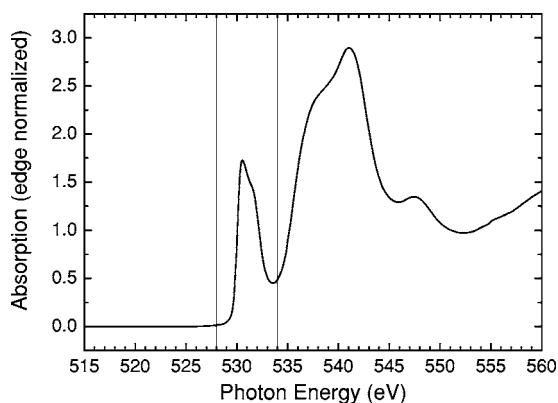
FIG. 1. X-ray absorption spectrum at the O K edge of Fe_3O_4 ($T=300$ K).

FIG. 2. (Color online) Temperature dependence of the O K-edge preedge in the vicinity of the Verwey transition temperature region.

the Verwey transition. This suggests an asymmetric gap, which is able to resolve the abovementioned discrepancies between IR and PES results concerning the total excitation gap.

High quality synthetic single crystalline sample have been prepared in an arc-image furnace using the floating zone technique.[26] The single crystals have been annealed and cooled under equilibrium conditions to obtain highly stochiometric single crystals.[27] The vacancy concentration of the used $Fe_{3-x}O_4$ single crystal is smaller than $x < 10^{-6}$, proven by measuring magnetic after spectra.[9,28] O K-edge spectra were recorded in total electron yield mode (TEY) at the new high resolution bending-magnet-beamline PM III at BESSY II with an energy resolution of about $E/\Delta E = 6000$, utilizing circular polarized light. Corresponding x-ray magnetic circular dichroism results will be discussed in detail elsewhere. No smoothing or further not mentioned data manipulation has been performed. The single crystal sample has been *in situ* cleaved at room temperature under UHV conditions. The ambient pressure during the measurement was lower than 8×10^{-10} mbar. The resulting surface has been oriented in normal incidence geometry. The temperature has been continuously warmed up at rate of 1 K/min in the range of 85–134 K. Each O K "preedge"[29] spectrum (range from 528 to 534 K; see Fig. 1) has been measured in less than 3 min (energy step width of 0.1 eV). To prevent small possible energy variations related to the synchrotron beam position shifts, all spectra have been taken at low synchrotron ring currents and increased current lifetime The energy step width and temperature slope have been chosen to obtain the best compromise between thermalization, necessary measurement time, and synchrotron related beam intensity variations. During the warming up procedure a diode thermometer has monitored the sample cryostat temperature, which has been verified with an extra thermometer located at the sample position. The sample magnetization has been measured using a commercial SQUID magnetometer (Quantum Design MPMS).

Figure 1 shows the room temperature (RT) O K-edge spectrum of the freshly cleaved Fe_3O_4 single crystal. The shape of the spectrum is in excellent agreement to previously published x-ray absorption data,[17,29–31] where the "preedge" region between 528 and 534 eV has been identified to O $2p$
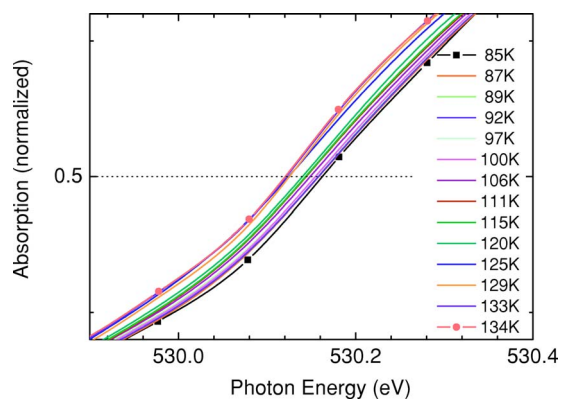
states, which are strongly hybridized with unoccupied Fe $3d$ t_{2g^-} and e_{g^-} orbitals. The observable splitting at 531 eV is originated by a mixture of crystal field effects and the chemical environment of A and B site Fe ions.[29] The features at higher energies are related to transitions into O $2p$ states hybridized with O $4s$ and $4p$ states (534–550 eV).[29]

Figure 2 shows background subtracted and peak-height-normalized spectra of the O K-edge onset region, as a function of the sample temperature. A continuous shift of the near threshold region from 85 K up to the 120 K is observable, followed by a step-like jump to lower excitation energies. We would like to emphasize that the energy shifts in Fig. 2 are just about the linewidth used in Fig. 1 (only visible in this expanded view). To quantify this variation the half height position of the shown spline-extrapolated curves have been extracted and plotted in Fig. 3 as a function of temperature. A continuous linear shift of about 20 meV is observed at the low temperature phase (85–120 K). Between 120 and 125 K a clear step of 13 meV width is observable, followed again by a linear variation. In the whole temperature range from 85 to 134 K the half height position is shifted by 40 meV. These relative energy position shifts at different temperatures have been reproduced (not shown) at different synchrotron runs. The maximum energy variation between different in-
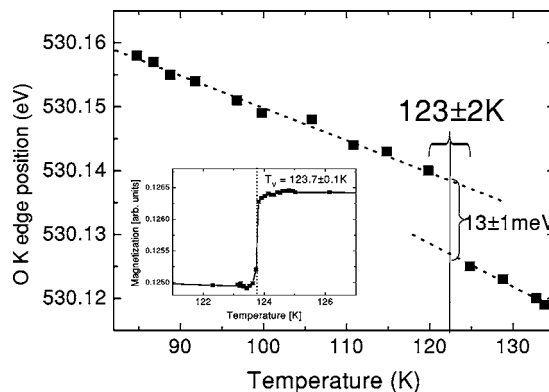

FIG. 3. Temperature dependency of the half height position of the O K edge threshold, extracted from Fig. 1(b). Inset: Sample magnetization of the Fe_3O_4 single crystal. The Verwey transition is directly visible at 123.7 K.
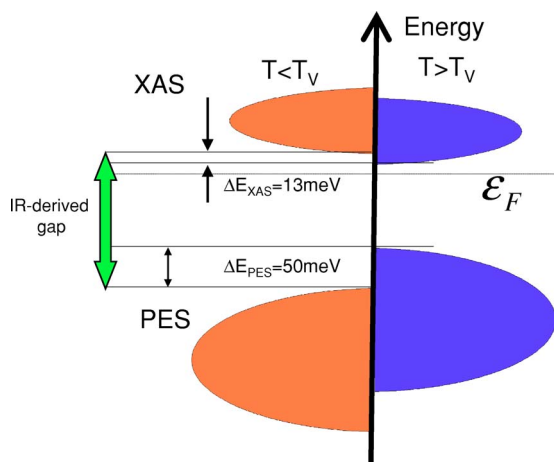
FIG. 4. (Color online) Schematic of the nonspin resolved band positions and shifts as the temperature evolves through the Verwey transition. The left site is related to the more insulating behavior below T_V, and the right site to the situation above T_V. The total gap shift is 63 meV. The green arrow at the left indicates the IR-derived gap of about 200 meV at 50 K.

jection cycles, related to synchrotron orbit variations, was below 50 meV and no significant shift in energy has been realized in the second half of an injection.

The inset in Fig. 3 shows the field cooled temperature dependence of the sample magnetization, measured at 5000 Oe. The Verwey transition is clearly observable at 123.7 ± 0.3 K, and at the same temperature of the O K-edge energy position jump in Fig. 3. This demonstrates that the observed position shift is indeed related to the Verwey transition.

A comparison of these results to PES data shows that the energy difference of the conduction band is about 4 times smaller than the valence band difference. For illustration, the whole gap scenario is sketched in Fig. 4. While PES gives an absolute energy position of the valence band, XAS is not absolute to the chemical potential. In Fig. 4 the conduction band has been positioned respectively to the valence band

regarding to infrared spectroscopy. If we add the energy position shift of XAS (13 meV) and PES (50 meV), a total gap change of 65 ± 10 meV could be estimated. This is now consistent with the transport activation energy of ≈50 meV at T_V,[17] and explains the inconsistencies in the gap magnitudes inferred from PES and infra red spectroscopy, as mentioned by Gasparov et al.[24] In addition, the observed continuous and abrupt gap differences near T_V are consistent to the simple two band Stoner like model of the Verwey transition supporting the polaronic band picture.[32]

This asymmetry suggests a pinning of the chemical potential more close to the conduction band, related to a small number of defect states. This results in a nonsymmetric gap variation at the Verwey transition. We would like to mention, that this behavior could also be explained (in principle) by strong modifications of the O K-edge core hole screening of the conduction electrons. Due to the fact that only small[12] or even no[8] charge redistributions are present, one would not expect such a behavior. Comparable systems exhibiting even stronger metal to insulator transitions, for example VO_2, have shown comparable shifts of the occupied (PES[33]) and unoccupied states (O K-edge[34]). Therefore, we believe that the observed asymmetric behavior is truly originated by an anisotropic gap shift.

In conclusion, we have investigated a clear, sharp, but also very small energy shift at the O K-edge of Fe_3O_4 of only 13 meV, present at the Verwey transition. This shift is much smaller, compared to photoemission results and clearly suggests the presence of an asymmetric gap opening in magnetite. Like in PES a clear gap variation is observable below T_V. Our results remove inconsistencies between photoemission and infrared spectroscopy, which have both explained the activated conductivity in terms of small polarons, even above the Verwey temperature,

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