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Single-particle gap above the Verwey transition in Fe_3O_4

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The Verwey transition in magnetite, Fe_3O_4 , has been studied using temperature-dependent high-resolution photoemission spectroscopy. On heating through the transition temperature T_V the band gap is not collapsed, but is merely reduced by ~ 50 meV, showing that a metal-insulator transition does not occur. The change in the gap is perfectly consistent with the two orders of magnitude conductivity jump at T_V . Thus even above T_V short-range charge ordering rather than site equivalency dominates the single-particle excitations and the electrical properties. We also point out important implications for efforts to model the electrical transport above T_V . [S0163-1829(97)03419-X]

Magnetite, Fe_3O_4 , is the archetype mixed valent $3d$ transition metal compound. Fe_3O_4 crystallizes in an inverted cubic spinel structure in which tetrahedral A sites contain one-third of the Fe ions as Fe^{3+} , while octahedral B sites contain the remaining Fe ions, with equal numbers of Fe^{3+} and Fe^{2+} in $B3$ and $B2$ sites, respectively. Below 860 K, magnetite is ferrimagnetic with the A -site magnetic moments aligned antiparallel to the B -site moments. Immediately apparent is the fundamental tension between the mixed valence of the B sites and their crystallographic equivalence in this crystal structure. This tension is manifested in a first order phase transition, the so-called Verwey transition¹ at $T_V \approx 120$ K, in which the dc conductivity abruptly increases by

two orders of magnitude on heating through T_V .² Although a large number of papers^{3,4} have been published since its discovery in 1941, the Verwey transition was the subject of an entire international workshop³ as recently as 1979 and continues as a paradigm of the classic condensed matter problem—how to describe electron motion if the kinetic energy, electron-electron interactions, and electron-lattice interaction are all comparably important.

Verwey and Haayman¹ interpreted the transition as an order-disorder transformation of Fe ions on the B sites. Indeed, studies by electron and neutron diffraction and nuclear magnetic resonance⁵⁻⁷ show that below T_V the $B2$ and $B3$ sites are structurally distinguishable in a distorted crystal

structure. In the simplest view, the ordering below T_V results in an insulator, and the abrupt conductivity increase at T_V implies a metal with electron motion on equivalent B sites. In agreement, band-structure calculations^{8,9} using the local spin density approximation find that the high-temperature phase is metallic due to the half filling of the Fe $3d$ bands associated with the B sites. Further, it was reported that photoemission measurements¹⁰ show the width of the valence-band spectrum, and also its shape near E_F , to be consistent with the calculation of Ref. 8. However, Anderson¹¹ pointed out the essential role of short-range order (SRO) in the thermodynamics of the transition. The observed entropy change in the transition [$(\sim 0.3$ to $0.35)R/B$ -site mole] is decisively smaller than the $R \ln 2 = 0.69R$ expected in a complete order-disorder transition. A B -site ion and its three nearest B -site neighbors form a tetrahedral unit, and he showed that the intersite Coulomb energy is lowered greatly when each unit has two $B2$ and $B3$ sites, a circumstance now known as Anderson's condition. According to him, long-range order (LRO) is lost above T_V , while SRO satisfying his proposed condition is maintained. In fact, SRO above T_V has been observed in diffuse neutron scattering.¹² Mott¹³ then asked why, if SRO is maintained through the transition, does the conductivity nonetheless increase?

Conventional transport studies have not provided a clear answer to Mott's question. Both below and above T_V the dc conductivity σ_{dc} is exponentially activated with increasing temperature, suggesting^{14,15} that the material is a semiconductor in both phases. However, σ_{dc} passes through a maximum around 300 K and then decreases with increasing temperature like a metal. Metal models feature various explanations^{8,16,17} for the "anomalous" variation of σ_{dc} above T_V . Unfortunately, a direct and model-free separation of the charge carrier number and mobility entering σ_{dc} above T_V has not been achieved. Analysis of temperature-dependent thermopower data assumed a zero gap¹⁷ and then inferred an activated mobility. Different Hall effect studies^{14,18–20} reach differing conclusions about the number and sign of the carriers, e.g., at 300 K, ranging from $\frac{1}{4}$ electron/ Fe_3O_4 molecule¹⁴ to one hole/ Fe_3O_4 molecule.¹⁸ The reason for this is that the small ordinary component can only be separated from the larger extraordinary component by making various assumptions, all of which have been shown to be questionable for this material.²⁰

Various spectroscopic studies have contributed new information but not a unified picture. The broadening of the B -site Mössbauer spectrum^{21,22} has been analyzed²² to imply a B -site electron hopping time τ ranging from 7×10^{-9} s at 120 K to 1.1×10^{-9} s at 300 K. Since $1/\tau$ was found to change by roughly the same factor as σ_{dc} over this temperature range, a model of incoherent metallic transport with temperature-dependent mobility was advanced in Ref. 22. However, assuming roughly one electron/ Fe_3O_4 molecule, as suggested by the Hall effect, and using the experimental value of $1/\tau$ to evaluate the incoherent hopping mobility, a value of σ_{dc} which is too small by a factor of 350 was found.²² Using instead the smaller value of $\tau = 0.5 \times 10^{-12}$ s inferred from spectra of diffuse neutron scattering from SRO yields¹² a value for σ_{dc} which is too large by a factor of 6. Drude fits to the infrared optical conductivity $\sigma(\omega)$ at 300 K yielded²³ a carrier number in the range

0.01/ Fe_3O_4 to 0.05/ Fe_3O_4 , very much smaller than the value suggested by the Hall effect. Deviations of the observed ω dependence from simple Drude behavior have been attributed to polarons, i.e., very strong electron-phonon correlation, and analyzed²⁴ in the metal model of Ref. 16. In this model the loss of LRO at T_V decreases SRO enough to induce at E_F a small density of states which then increases exponentially with temperature as SRO decreases further. However, polaron effects could just as well be present for the Drude conductivity of carriers thermally excited across a gap, and a gap picture could equally well explain the small carrier number and the activated σ_{dc} .

Photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) offer a direct attack on the question of a single particle gap. These spectroscopies measure the spectra to create single holes and electrons, respectively, and thus, within the experimental resolution, can show whether an excitation energy is required to create the unbound holes and electrons entering the conductivity, or whether there is a Fermi edge and no energy barrier as in a metal. Because it has much better resolution PES is favored over IPES. In fact, a very recent PES study²⁵ using laboratory He lamp excitation has reported that as the temperature increases through T_V , a gap present in the low-temperature phase disappears and the PES spectrum yields the metallic Fermi edge in the high-temperature phase. This study would seem to settle the matter and to answer Mott's question in favor of the view^{16,17} that the SRO is not sufficient to maintain a gap and the dc conductivity jump at T_V is induced by the insulator to metal transition. However, we report here a PES study using synchrotron radiation which reaches quite the opposite conclusion. The gap does not collapse and the spectrum at μ remains zero just above T_V . The answer to Mott's question is instead that the loss of LRO reduces the gap by ~ 50 meV on heating through T_V and this reduction of the gap is nicely consistent with both the conductivity jump in a semiconductor picture and the small carrier density inferred from the optical conductivity. As explained below, the differing PES results can be attributed to the differing monochromaticities of the photon sources used.

X-ray absorption and photoemission measurements were performed at the AT&T Bell Laboratories Dragon beamline at the National Synchrotron Light Source (NSLS).²⁶ The PES spectra were normalized to the incident photon flux, and the binding energies are referred to the chemical potential of a clean Cu sample in electrical and thermal contact with the sample. The IPES, the so-called bremsstrahlung isochromatic spectroscopy (BIS), was performed with a Vacuum Generators ESCALAB spectrometer using photon energy $h\nu = 1486.6$ eV, with affinity energies referred to the chemical potential of a clean silver sample. Samples were cut from a well annealed stoichiometric Fe_3O_4 single crystal and cleaved *in situ* in a vacuum better than 2×10^{-10} Torr to expose a (100) plane. During the measurements, the temperature was controlled to within 1 K.

As background information, this paragraph and the next provide an overview of the single particle electron structure of Fe_3O_4 . Figure 1 shows the large energy scale spectra. Below μ is the 130-K valence-band spectrum taken with $h\nu = 110$ -eV and 80-meV resolution. The PES spectrum consists of broad overlapping emissions from strongly hy-

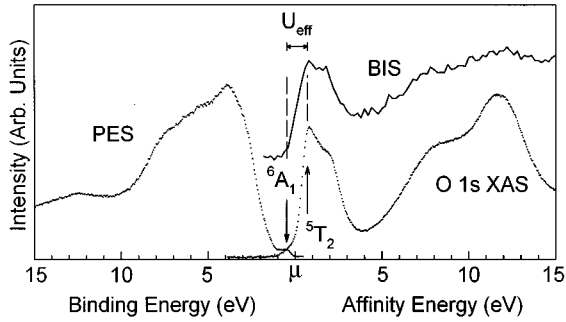


FIG. 1. Valence-band PES and BIS and O 1s XAS spectra. The XAS spectrum is aligned with the BIS spectrum by a 529.1-eV shift.

bridized Fe 3d and O 2p states. The Fe 3d emission has been discerned and studied by exploiting resonances in the Fe 3d PES cross section for $h\nu$ near the Fe 3p (Ref. 27) and 2p (Ref. 28) absorption edges, and by comparing to the resonantly enhanced spectra of reference compounds FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}). These studies have found^{27,28} that the Fe 3d spectrum extends throughout the entire range of the PES spectrum of Fig. 1, and consists of overlapping components associated with the three sites. The lowest ionization states of the A, B3, and B2 sites occur near 2.4, 2.6, and 0.5 eV, respectively. Our 2p resonance studies, which we plan to report elsewhere,²⁸ are generally consistent with previous 3p resonance work. However, the 2p resonance is much stronger than that at the 3p edge, and thus permits conclusions to be drawn with more confidence than previously. For example, the A and B3 Fe^{3+} ionization energies have not been distinguished before. Above μ are spectra from BIS and x-ray absorption spectroscopy (XAS), the former taken at 300 K with 600-meV resolution, and the latter taken at the O 1s edge at 130 K with 200-meV resolution. The XAS spectrum is generally consistent with previous data.²⁹ It has been shifted by 529.1 eV to align it with the BIS spectrum, which is new. The two spectra closely resemble one another, reflecting the hybridized character of O 2p and Fe 3d and 4s states. The broad Fe 4s antibonding states can be seen above 4 eV. The structure below 3 eV contains the Fe 3d BIS transitions for all three sites, with the peak shape probably reflecting the cubic crystal field splitting of the Fe 3d states rather than individual site contributions.

The gross features of the PES and BIS spectra on a large energy scale can be fairly well described²⁸ by using the Anderson impurity model, while the low-energy scale behavior requires a model which also includes the lattice. The impurity model serves to treat the effect of hybridization of oxygen electrons to the strongly interacting 3d electrons bound into ionic states on each site. The usefulness of this approach has been demonstrated for various transition metal oxides.^{30–34} Most relevant for the Verwey transition are the lowest-energy PES and BIS transitions. As identified previously³⁵ the former is the $d^6 \rightarrow d^5$ [6S] transition on the B2 site. The latter is the $d^5 \rightarrow d^6$ [5D] transition on the B3 site. Including the octahedral crystal field, the PES and BIS final states are denoted as 6A_1 and 5T_2 in Fig. 1. Their peak energy separation, which corresponds to the charge fluctuation barrier for the electron hopping process [B2]

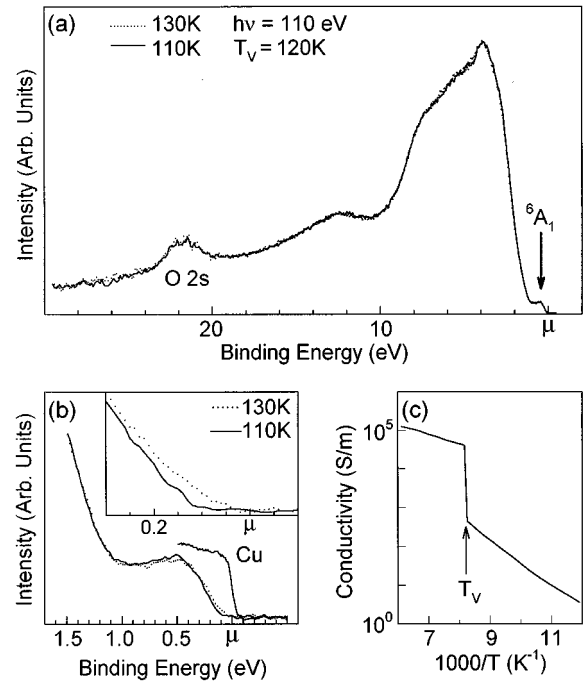


FIG. 2. (a) High-resolution valence-band PES spectra of Fe_3O_4 at $T=110\text{ K} < T_V$ (dashed) and at $T=130\text{ K} > T_V$ (dotted). (b) Spectra in the region near the chemical potential. The data of the inset and the main figure were taken in separate cyclings of the temperature. (c) The dc conductivity was taken from Ref. 2.

+ $[B3] \rightarrow [B3] + [B2]$, is found to be $U_{\text{eff}}=1$ to 1.5 eV, as shown in Fig. 1. As discussed in Ref. 11, U_{eff} is the result of intersite Coulomb repulsion, reduced by various solid-state screening mechanisms. There is then a competition between this effective Coulomb repulsion, which self-consistently stabilizes B-site ordering, and the effective single particle bandwidth for electron motion on the B-site sublattice. This bandwidth, the existence of which is signaled¹⁶ by the high ferrimagnetic transition temperature, is due to Fe/O hybridization and perhaps direct Fe/Fe overlap. It broadens the lowest-energy peaks and enables the gap below T_V to be reduced from U_{eff} to its much smaller observed value. Whether the B-site electron hopping can close the gap above T_V in the presence of SRO is a difficult theoretical issue. We address the question experimentally in the spectra discussed next.

Figure 2(a) compares the PES spectrum of Fig. 1 with an equivalent spectrum taken at 110 K, ~ 10 K below T_V . Except in the region very near μ , both spectra are exactly identical to each other, showing that the large energy scale electronic structure is preserved through the transition. The near- μ spectra above and below T_V , taken with 60-meV resolution, are compared in Fig. 2(b), including a reference spectrum showing the sharp Fermi edge of Cu metal. The spectra of both phases merge smoothly with the background well below μ and do not show a Fermi step. On heating through T_V there is no detectable change in the emission at μ . Rather, the near- μ peak and its threshold energy are shifted by ~ 50 meV to lower binding energy while the leading edge of the high-energy structure is maintained. This small change is perfectly reproducible with temperature cy-

cling. For example, in the data of Fig. 2(b) the temperature was first cycled to obtain the two narrow energy scans of the inset and then fully cycled again to obtain the two wide energy scans. Thus both phases show a single particle gap, which is reduced ~ 50 meV above T_V .

We have been unable to observe the gap just above T_V in spectra taken using the $h\nu=21.22$ -eV line of a laboratory helium lamp. Data for our samples always show weak emission at μ consistent with the He lamp results reported in Ref. 25. However, we understand this emission to be spurious and to result from the weak He lamp satellite lines 2 to 3 eV away. Interfering emissions due to these lines are normally negligible. But for Fe_3O_4 the intrinsic emission at μ is essentially zero, while there is intense emission around 2-eV binding energy. For the satellite lines this emission coincidentally has the same kinetic energy as that near μ in the $h\nu=21.22$ -eV emission. Similarly the strong O $2s$ emission between 19- and 25-eV binding energy in the $h\nu=40.82$ -eV spectrum coincidentally appears at μ in the $h\nu=21.22$ -eV spectrum. Thus a truly monochromatic source, as was available in our synchrotron measurements, is essential for studying Fe_3O_4 very near μ .

The activation energies Δ (half the total gap if μ lies in the center of the gap) inferred from the data of Fig. 2(b) imply carrier densities in generally good accord with dc transport and infrared optical data. We estimate Δ values of 150 ± 30 and 100 ± 30 meV (Ref. 36) below and above T_V , respectively. In a gap model the density of carriers is $n_0\exp(-\Delta/k_B T)$. The decrease in activation energy then implies a jump of the conductivity at T_V by a factor of $\exp(50\text{ meV}/k_B T_V)=\exp(50/10.35)=125$, very consistent with the observed two orders of magnitude conductivity jump in Fig. 2(c). If we take n_0 to be the number of Fe_3O_4 molecules/cm³ and use the 300-K value of 1.35×10^{22} /cm³, we estimate the carrier density to jump from 6.9×10^{15} /cm³ to 8.6×10^{17} /cm³ across the transition and then to increase to

2.9×10^{20} /cm³ at 300 K. The 300-K value is consistent with the range of values of $(2\text{ to }7)\times 10^{20}$ /cm³ inferred²³ from the infrared optical spectrum. Carrier densities of this size can be observed in PES and the increased emission near μ as the temperature approaches 300 K reported in Ref. 25 can perhaps be interpreted in this way. From the transport data of Fig. 2(c), we deduced activation energies of 100–150 and 40–60 meV below and above T_V , respectively. The spectroscopic and transport values of the activation energies are very similar and small differences can plausibly be ascribed to the neglect in the above discussion of a temperature dependence of the carrier mobility.

To conclude, our main result is that the single particle gap is not eliminated, but only reduced by ~ 50 meV in the Verwey transition. This finding is consistent with the conductivity jump at the transition and with other evidence for a small carrier density $\sim 3\times 10^{20}$ /cm³ at 300 K. For this small carrier density even the larger mobility estimated from neutron scattering in the incoherent hopping picture is 7.5 times too small to account for σ_{dc} . Although SRO continues to maintain a gap against free carrier generation above T_V , it appears that carriers so generated are much more mobile than in the incoherent hopping model. We must then conclude that it remains to establish a clear connection between the mobility and the time scales inferred from Mössbauer spectroscopy and neutron scattering.

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- ³⁶The end of the gap is obscured by the experimental broadening and the phonon broadening. Taking the end of the gap about 10% intensity of the ~ 0.5 -eV binding energy peak, we obtained Δ to be 150 and 100 meV above and below T_V , respectively.