

Scanning tunneling spectroscopy study of the electronic structure of Fe₃O₄ surfaces

K. Jordan,* A. Cazacu, G. Manai, S. F. Ceballos, S. Murphy, and I. V. Shvets

Center for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College, Dublin 2, Ireland

(Received 11 May 2006; revised manuscript received 17 July 2006; published 24 August 2006)

Scanning tunneling spectroscopy (STS) experiments were performed on the (001) and (111) surfaces of single crystalline magnetite. Room temperature spectra exhibit a ~ 0.2 eV gap around E_f . The importance of perfect surface order to the existence of this gap is illustrated. STS is also carried out on the (111) surface, at 140 and 95 K, just above and below the Verwey transition temperature ($T_V \sim 120$ K), respectively. It is confirmed that above T_V a ~ 0.2 eV gap exists in the surface density of states (DOS) around E_f . Furthermore, broad bands are resolved on both sides of E_f , with peaks centered on $\sim +0.5$ eV and ~ -0.45 eV. Below T_V it is shown that the value of the gap in the surface DOS remains similar, however, the peaks resolved in the conduction and valence bands shift markedly away from E_f . The similarity of the gap value before and after the transition points away from an ionic charge ordering occurring at the magnetite surface below T_V . However, the shifting of the bands points to a certain degree of electronic ordering or charge disproportionation playing an integral part in the Verwey transition, at the magnetite surface.

DOI: [10.1103/PhysRevB.74.085416](https://doi.org/10.1103/PhysRevB.74.085416)

PACS number(s): 68.37.Ef, 68.47.Gh, 71.30.+h, 73.20.At.

I. INTRODUCTION

Magnetite Fe₃O₄ has attracted much interest in recent times due mainly to two factors. First, it is expected to be a room temperature half-metallic ferromagnet, possessing 100% spin polarized charge carriers at the Fermi level (E_f).^{1,2} Second, it exhibits a metal-to-insulator type transition, known as the Verwey transition.^{3,4} This is a spontaneous intercorrelated change of both the lattice symmetry and electrical conductivity at a critical temperature, which for stoichiometric magnetite is ~ 120 K.

Magnetite crystallizes in the inverse spinel structure. The unit cell has a lattice constant of 8.3963 Å, and contains 32 O²⁻ anions arranged in a face centered cubic lattice. This O²⁻ lattice results in the formation of 64 tetrahedral interstices and 32 octahedral interstices. Fe³⁺ cations occupy 8 of the 64 tetrahedral sites, whereas the octahedral sites are occupied by 8 Fe²⁺ ions and 8 Fe³⁺ ions. It is clear from both experiments^{5,6} and calculations^{2,7} that the Fe_{oct} ions dominate the electronic properties of magnetite. At room temperature electron hopping occurs between the Fe²⁺ and Fe³⁺ sites of the mixed valence octahedral plane, resulting in an average of Fe^{2.5+} per occupied site. It is electron hopping between the Fe²⁺ and Fe³⁺ sites of the octahedral plane that mediate the relatively high room temperature conductivity of magnetite. The reduction in conductivity by two orders of magnitude, which occurs below T_V , is thought to be the result of the inhibition of electron hopping. The drop in conductivity is coupled to a structural change, from the inverse spinel structure above T_V , to a monoclinic structure below.^{8,9} It was initially postulated by Verwey that this is a metal-insulator transition, and that the reduction in conductivity is brought about by a complete freezing of electron hopping and a resultant ionic charge ordering of Fe_{oct}²⁺ and Fe_{oct}³⁺ ions. It is also worth noting here that Anderson later proposed that, contrary to a purely metallic behavior of the conduction electrons above T_V , a degree of short range order (SRO) must exist, as the change in entropy through the transition is not sufficient to allow for complete charge disorder.¹⁰ While the exact pattern of the charge ordering on the octahedral planes remained a matter of intense study and debate, over time the subject

appeared to be nearing an agreement that the transition was of a metal-insulator type and that fully ionic charge ordering was an integral part of the transition.¹¹ Now, however, the exact degree of electron localization on Fe_{oct} sites that occurs below the transition temperature is the subject of much debate. Recent experimental results have suggested that below T_V charge ordering (i.e., the formation of an equal number of discrete Fe_{oct}²⁺ and Fe_{oct}³⁺ ions) does not, in fact, occur, and instead a limited degree of charge segregation, or disproportionation, on the Fe_{oct} ions best explains the changes in electronic structure below the transition temperature.^{12,13} Based on nuclear magnetic resonance (NMR) (Ref. 14) and extended x-ray absorption fine structure studies,¹⁵ it has been suggested that while the transition may result in a small degree of charge disproportionation ($< 0.1e^-$), its origin is better explained in terms of structural changes, as opposed to a pure electronic ordering.

Given the clear lack of agreement and understanding of both the Verwey transition and the half-metallic nature of magnetite, the elucidation of the electronic structure of magnetite, and its changes across T_V , is clearly an essential area of research. As stated in the previous paragraph it is the Fe_{oct} ions of magnetite that dominate the density of states (DOS) around the E_f . The DOS of the B-site Fe ions, shown schematically in Fig. 1, can be thought of in terms of a spin-up (\uparrow) band and a spin-down (\downarrow) band which are split by an exchange energy.¹⁶ Due to crystal field splitting the fivefold d levels of the Fe_{oct} ions are split into three degenerate t_{2g} levels and two degenerate e_g levels. For both ion types, Fe_{oct}²⁺ and Fe_{oct}³⁺, the majority spin band is located below E_f and is occupied by five (\uparrow) electrons. The extra electron of the Fe_{oct}²⁺ ion, responsible for the previously discussed electron hopping at room temperature, occupies the t_{2g} level of the minority (\downarrow) spin band. Only this t_{2g} subband is located at the Fermi level, resulting in 100% spin polarized electrons at E_f . Despite years of intensive research, quite how the advent of the Verwey transition affects the electronic structure of magnetite is still unknown. Leaving aside the arguments over whether the origin of the Verwey transition is structural or electronic, one can say that, whatever the driving force, for the transition to be of a metal-insulator nature the t_{2g} sub-

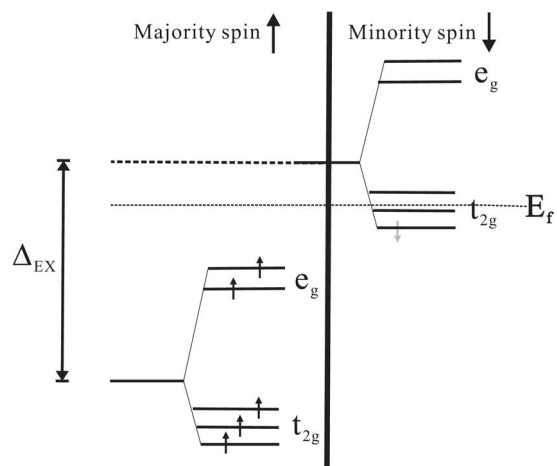


FIG. 1. Schematic representation of the energy levels of the Fe_{oct} ions of magnetite, which dominate the DOS around E_f . The majority (\uparrow) spin band and minority (\downarrow) spin band are split by an exchange energy Δ_{EX} . The five degenerate d -electron levels of the Fe_{oct} ions are further split by the crystal field into three degenerate t_{2g} and two degenerate e_g levels. For both Fe^{2+} and Fe^{3+} ions five electrons occupy the majority t_{2g} and e_g levels. The extra electron of the Fe^{2+} ion (in gray) occupies the minority t_{2g} band, which is the only band located at E_f , giving rise to half-metallic behavior. The high room temperature conductivity of magnetite is attributed to the hopping of this (\downarrow) electron between Fe_{oct} sites.

band must have a metallic nature at room temperature, and that a gap in the DOS at E_f should open up following the transition. Furthermore, if either complete charge ordering or some degree of electron disproportionation occurs below T_V , due to the increased Coulomb repulsions inherent in such an ordering, an increased splitting of the conduction and valence d -electron bands of the magnetite DOS should occur.

There have been many previous experiments aimed at understanding the highly complex electronic structure of magnetite,^{6,17} and the changes that occur following the Verwey transition.^{18–20} Photoelectron spectroscopy (PES) experiments by Chainani *et al.*¹⁸ show that below T_V a clear gap in the DOS exists at E_f . This gap was found to close above T_V . This was said to show that the Verwey transition is indeed a metal-semiconductor transition. The spectral weight at E_f was found to systematically increase as the temperature is increased to room temperature, suggesting that a degree of SRO persists just above T_V , but that this gives way to fully metallic behavior at room temperature. The spectra also reveal the existence of Fe 3d derived features, resolved at binding energies of 0.5 and 1.5 eV. These features are resolved below the transition temperature, but also just above it (140 K). The states were no longer resolved for room temperature spectra, again in agreement with a SRO sustaining just above T_V , but not persisting at room temperature. However, in contrast to these results, PES experiments by Park *et al.*¹⁹ show that, while a gap is present below T_V , rather than closing above T_V it merely shrinks by ~ 50 meV. The magnitude of this gap change can only account for the experimentally measured decrease in conductivity across the transition if a semiconducting behavior is assumed for $T > T_V$. This, therefore, leads to the conclusions that above the Ver-

wey transition SRO is present, and that the Verwey transition is, in fact, of a semiconductor-semiconductor nature, as opposed to the traditional metal-insulator concept. This work also included room temperature inverse-PES (IPES) spectra. A value for the effective energy barrier to electron hopping, $U_{\text{eff}} \sim 1-1.5$ eV, was obtained from the magnitude of the energy difference between the lowest energy occupied and unoccupied peaks. This U_{eff} is essentially a measure of the intersite Coulomb repulsion, which is reduced from its ideal value by solid state screening mechanisms.^{10,19} IPES was not, however, carried out at low temperature, and so the effect of the Verwey transition on this energy barrier could not be assessed. Most recently, PES experiments have been carried out by Schrupp *et al.*,²⁰ and these are in broad agreement with the results of Park *et al.* Both low energy PES and soft x-ray PES were performed. Soft x-ray PES allowed a larger penetration depth (~ 45 Å), as opposed to a penetration depth of ~ 15 Å for previous studies. Once again no evidence for a metallic Fermi edge is found above T_V and a decrease in the gap by ~ 50 meV was measured, casting still further doubt on the concept of the Verwey transition as a metal-insulator transition.

More practical issues also make studies of the magnetite surface a matter of interest. Despite the fact that magnetite is predicted to be a half-metallic ferromagnet, measurements of the spin polarization using spin resolved PES have not shown the expected full polarization.^{21,22} Furthermore, this problem of reduced spin polarization has affected the fabrication of magnetic tunnel junctions, as the junctions fabricated so far do not have properties consistent with 100% spin polarization of the charge carriers.^{23–25} These issues are most likely related to either the magnetite surface itself (such as the generation of surface states which could destroy the half-metallic nature of magnetite) or interface properties, and therefore further understanding of the properties of magnetite surfaces is essential.

Here we present a study that adds to the current understanding of the surface electronic structure of magnetite. The electronic structure of the magnetite (001) and (111) surfaces at room temperature is studied using scanning tunneling spectroscopy (STS) which, unlike PES, provides information on both the occupied and unoccupied states of the surface of magnetite. The existence of a gap in the DOS near E_f is shown. The importance of surface order to the existence of this gap is illustrated. STS is also performed on the (111) surface just above and below T_V . The results show that the magnitude of the gap near E_f remains similar following the transition; however marked changes occur in the features of the occupied and unoccupied bands, consistent with some degree of electron delocalization-localization occurring at the Verwey transition.

II. EXPERIMENT

Synthetic Fe_3O_4 single crystals were used for these experiments. For the study presented here, it is important to note that resistivity vs temperature measurements on these single crystals reveal a $T_V \sim 120$ K. The *in situ* sample preparation consisted of cycles of Ar^+ ion etching and postanneal-

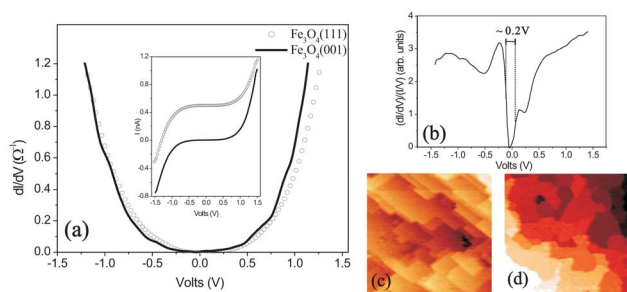


FIG. 2. (Color online) (a): Room temperature dI/dV tunneling spectra of the magnetite (001) and (111) surfaces. Inset shows the $I(V)$ curves, which are offset for clarity. Both surfaces show the same tunneling behavior. The presence of a semiconducting band gap at the magnetite surface is evident from the spectra. (b): Representative normalized room temperature spectrum. The spectra for both surfaces were found to be the same. A band gap of 0.2 ± 0.05 eV is reproducibly measured from the FWHM of the gap in normalized spectra. (c) and (d): (1000×1000) \AA^2 STM image of the magnetite (001) surface and (1500×1500) \AA^2 image of the (111) surface, described in detail elsewhere (Refs. 26, 27, and 29).

ing in oxygen, which is described in detail for the magnetite (001) surface in Ref. 26 and for the (111) surface in Ref. 27. The sample preparations described routinely result in a clean surface, as determined by Auger electron spectroscopy (AES), displaying sharp low energy electron diffraction patterns. The scanning tunneling microscopy (STM)/STS measurements presented here were carried out using a home built instrument in conjunction with a commercial Omicron Scala STM controller. Low temperature experiments were carried out on the (111) surface. This is mainly due to the fact that this surface was found to be more easily prepared, and that the formation of large terraces on the surface was found to be more reproducible than for the (001) surface, making it very suited to STS experiments. Electrochemically etched W tips, prepared as described in Ref. 28, were used. All STS curves presented here were obtained for tunneling set points of +1 V and 0.1 nA; however, the curves are reproducible over the range we studied (5–20 G Ω). STS $I(V)$ spectra were collected at predefined points on a grid and all presented curves are averaged over a minimum of 100 individual points from these grids.

III. RESULTS AND DISCUSSION

A. Room temperature STS of magnetite (001) and (111) surfaces

STS has been carried out on well-ordered (001) and (111) surfaces of magnetite, at room temperature. Our previous STM studies, including the surface preparation procedures and proposed surface terminations, are presented in detail in Refs. 26–29. We, therefore, concentrate here on the STS results obtained on these surfaces. Figure 2(a) presents the room temperature $I(V)$ and dI/dV spectra for these surfaces. It is immediately apparent that both surfaces exhibit very similar behavior, as previously noted for the conduction band side using PES.^{6,17} It is evident, from the spectra, that a semiconducting type gap exists. A band-gap value of

0.2 ± 0.05 eV is obtained from the full width at half maximum (FWHM) of the gap in normalized³⁰ $I(V)$ spectra. Such a representative normalized curve is shown in Fig. 2(b). The pronounced peaks at either edge of the band-gap region result from the normalization process.³¹ Apart from the gap, and a shoulder at $\sim +0.5$, the normalized room temperature spectra are found to be generally featureless. This gives rise to some distinctiveness between them as there are no major features away from the gap region. The presence of the semiconducting gap, at room temperature, shows that the magnetite surface does not exhibit metalliclike conductivity, even far above T_V . The existence of a degree of electronic ordering on the surface of magnetite can be inferred from the presence of this gap, which can essentially be thought of as a barrier to room temperature electron hopping. This gap could be indicative of a SRO at room temperature, of the type proposed by Anderson.¹⁰ However, we note that we have previously obtained STM images on the (001) surface, using MnNi tips, consistent with some degree of room temperature electronic ordering on surface Fe_{oct} ions.^{26,29} It is possible that this gap in the surface DOS around E_f at room temperature is a manifestation of the previously imaged charge frozen state.

B. Importance of surface order to electronic properties of the magnetite (001) surface

The importance of surface morphology, roughness, and stoichiometric inhomogeneities to the electronic properties of the magnetite surface has been observed using STS. The existence of step edges, which result in compositional inhomogeneity and deviations from ideal stoichiometry, are shown to alter the tunneling spectra of the surface. Alterations in tunneling behavior were first evident due to the existence of localized areas which exhibit step bunching on the (001) surface. A spectroscopy map of such a step-bunched region of the surface (in an otherwise well-ordered area), and the associated averaged dI/dV spectra, is shown in Figs. 3(a) and 3(b). STS in this region shows that step-bunching results in tunneling behavior that is strikingly different to that observed on the terraces of magnetite (001). As seen from Fig. 3(b), there is a marked enhancement of the magnitude of the tunnel current from stepped-bunched areas. The most likely reason for this effect is that at step edges the structure of the crystal is not truly that of magnetite. Such areas could, for example, be oxygen deficient, resulting in the observed changes in the $I(V)$ behavior. The notion that surface disorder and oxygen deficiency can lead to an alteration of the electronic properties of the surface is supported by the fact that, immediately following light Ar^+ ion bombardment of the magnetite (001) surface (0.5 kV ions for 5 min), the O/Fe ratio, as measured by AES, is reduced from ~ 1.6 to ~ 1.1 . STM reveals a highly disordered surface, and STS of this oxygen deficient surface reveals a complete closing of the semiconducting band gap observed on the well-ordered magnetite (001) surface.

A simple experiment was carried out to further illustrate this point. A ~ 0.5 ML ultrapure Fe film was deposited onto the (001) surface of magnetite. A STM image of the surface

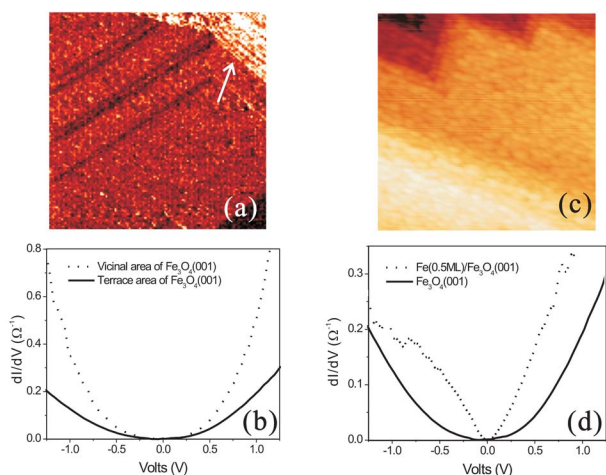


FIG. 3. (Color online) (a) $(1200 \times 1200) \text{ \AA}^2$ STS map (-0.9 V) of the (001) magnetite surface. The area at the top right, marked with a white arrow, exhibits localized step bunching. A resultant change in tunneling behavior is seen in the $I(V)$ map. (b) $I(V)$ tunneling spectra of this step-bunched area (dotted line) in comparison with the flat terrace area (whole line). The step-bunched area shows markedly different tunneling behavior to that of the flat terraced surface. (c) $(850 \times 850) \text{ \AA}^2$ STM image of magnetite (001) surface following deposition of $\sim 0.5 \text{ ML}$ of Fe. (d) STS of this surface (dotted line), in comparison with the clean magnetite (001) surface (whole line), reveals the generation of metallic states in the gap region resulting in the complete closing of the semiconducting gap that exists for the clean, well-ordered, magnetite surface.

following such a deposition is shown in Fig. 3(c). The surface is characterized by the formation of $\sim 1.1 \text{ \AA}$ high Fe islands, covering roughly half of the surface area. A room temperature dI/dV spectra for this surface is presented in Fig. 3(d). It is apparent that even this ultrathin Fe film results in the complete closing of the semiconducting band gap of the magnetite (001) surface. Therefore, in order to obtain the true electronic signature of magnetite one must ensure that measurements are obtained only from well-ordered surfaces, and specifically the presence of Fe rich areas of the surface, which can induce metallic states in the gap region, must be avoided. We note that large area averaging techniques, such as PES, would be affected by surface disorder such as step bunching, or localized stoichiometry deviations, possibly resulting in the presence of states in the gap region. This offers an explanation as to why some PES experiments of magnetite surfaces have observed metal states,¹⁸ while others have not.^{19,20} We also note that the observed changes in tunneling behavior caused by local disorder suggests that such disorder could contribute to the well-known difficulty in measuring 100% spin polarization of the magnetite surface,^{21,22} and fabricating tunnel junction devices with magnetoresistance values consistent with a half-metallic nature.^{23–25}

C. Tunneling spectra of magnetite (111) surface above and below T_V

STS was performed on the (111) surface of magnetite just above and below the Verwey transition temperature, at 140 and 95 K, respectively. First we compare the spectra ob-

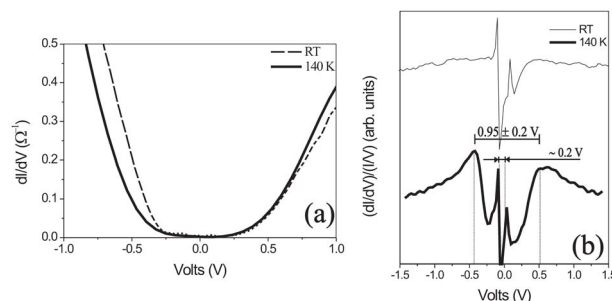


FIG. 4. (a) Comparison of dI/dV spectra at room temperature (dashed line) and at 140 K (whole line). The existence of a gap of similar magnitude is apparent. (b) Normalized spectra, showing enhanced structure away from the gap region for $T=140 \text{ K}$ (thick line), compared to room temperature spectra (thin line). At 140 K distinct peaks in the occupied and unoccupied d -electron bands are resolved at $-0.45 \pm 0.1 \text{ V}$ and $+0.5 \pm 0.1 \text{ V}$, respectively, giving a separation of $0.95 \pm 0.2 \text{ V}$.

tained at 140 K with those at room temperature. It can be seen from the dI/dV spectra, presented in Fig. 4(a) that the tunneling behavior at room temperature and 140 K is broadly similar. The normalized version of the spectra [Fig. 4(b)] shows the surface to exhibit the same band gap at 140 K as for RT, $0.2 \pm 0.05 \text{ V}$. However, whereas the RT normalized curves are generally featureless, other than the resolved band gap and a shoulder at $\sim +0.5 \text{ V}$, spectral features away from E_f are clearly resolved at 140 K. Broad bands are resolved at either side of E_f , with distinct peaks at $-0.45 \pm 0.1 \text{ V}$ for the occupied band, and $+0.5 \pm 0.1 \text{ V}$ for the unoccupied band. This improved resolution of the electronic structure points to an increasing degree of electronic order as temperature is reduced, even prior to reaching T_V . We note that STS spectra consistent with the resolution of the occupied and unoccupied d -electron bands have previously been observed for the half-metallic ferromagnetic oxide $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at 77 K.³² The value of the occupied peak in our spectra is similar to the previously discussed PES work on magnetite, which found a peak centered on $\sim +0.5 \text{ eV}$ (Refs. 17–19) or $\sim +0.6 \text{ eV}$.²⁰ The distance between the peaks resolved on both sides of E_f can be interpreted in terms of the charge fluctuation barrier for electron hopping, as in Ref. 19. From the STS spectra one obtains a value of $U_{eff} = 0.95 \pm 0.2 \text{ eV}$. This compares well with the value of 1–1.5 eV found from room temperature PES and IPES measurements.¹⁹ We also note that the resolution of these features with STS shows them to be present at the surface, rather than being purely bulk states, and shows that the characteristic electronic states of magnetite are maintained at the surface. This is an important point in terms of exploiting the proposed half-metallicity of magnetite for devices such as tunneling junctions, as successful device operation is dependent on the half-metallic nature remaining intact at surfaces and interfaces.

We now move to compare the spectra obtained at 140 and 95 K. Derivative spectra for both temperatures are presented in Fig. 5(a). Three representative normalized spectra at 95 K are shown in Fig. 5(b). From Fig. 5(a) it is apparent that, despite the advent of the Verwey transition, a large opening

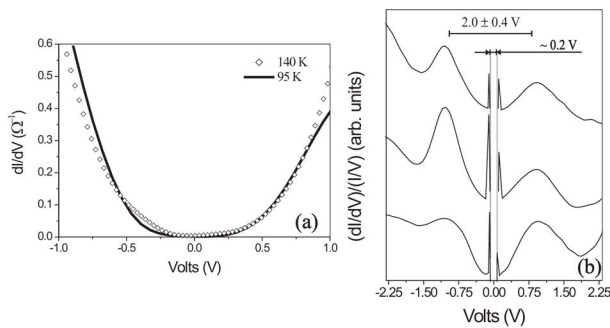


FIG. 5. (a) Comparison of dI/dV spectra above and below T_V ; 140 K (dotted line) and 95 K (whole line), respectively. It is clear that a large opening of the band-gap E_f does not occur below T_V . (b) Normalized spectra, obtained at 95 K. The three averaged spectra were obtained using the same parameters and are presented only to show the degree of reproducibility of the resolved features. It is confirmed that the magnitude of the band gap remains ~ 0.2 eV below T_V . Marked changes occur away from E_f , with the peaks resolved in the conduction and valence bands shifted dramatically compared with the spectra at 140 K. The peaks are now resolved at -1.1 ± 0.2 eV and $+0.9 \pm 0.2$ eV, giving a doubling of the peak separation energy to 2 ± 0.4 eV.

of the observed band gap, which one would expect for a metal-insulator transition, does not occur. Instead the gap value remains extremely similar, with any increase in magnitude limited to at most 20%. This suggests that the Verwey transition at the magnetite surface is not a metal-insulator transition, rather the surface is semiconducting both before and after the occurrence of the transition. This supports the PES work of Park *et al.*¹⁹ and Schrupp *et al.*²⁰ We note that the fact that the gap does not change markedly through the transition could point to the surface of magnetite behaving in an entirely different manner to bulk through the transition temperature. As STS is purely surface sensitive, the results presented here show only that the surface does not exhibit a metal-insulator transition, while the situation for bulk may be entirely different. Indeed, the very existence of the discontinuity in conductivity for bulk magnetite at T_V suggests that a marked difference does exist between the electronic behavior of the surface and the bulk through the transition. It must be mentioned here that recent PES work has had purposefully large penetration depths ~ 45 Å. One would, therefore, expect a degree of bulklike contribution to these spectra, and yet this study also does not show the opening of a gap in the DOS below T_V ,²⁰ illustrating that the separation of surface and bulk contributions to the electronic behavior of magnetite is clearly not a trivial matter.

While the magnitude of the surface band gap is unaffected by the transition, marked changes to the spectra do occur away from E_f . The normalized spectra of Fig. 5(b) confirm that the band-gap opening does not occur following the transition, however, the peaks resolved in the 140 K spectra (-0.45 ± 0.1 V and $+0.5 \pm 0.1$ V) are no longer present. Broadbands are still found at both sides of the band gap, however, the peaks of the bands are instead resolved at -1.1 ± 0.2 eV on the occupied side of the spectra, and $+0.9 \pm 0.2$ eV on the unoccupied side. This shift indicates that below T_V the occupied and unoccupied d -electron bands

of the magnetite surface both shift away from E_f . We again recall that the magnitude of the energy difference between these peaks on either side of E_f can be interpreted in terms of the charge fluctuation barrier to electron hopping.¹⁹ Above T_V this energy difference is 0.95 ± 0.2 eV, whereas below it is dramatically increased to 2 ± 0.4 eV. This is consistent with increased electron localization occurring on the Fe_{oct} sites below the transition temperature. The increased splitting can also be interpreted as direct evidence that the well-known decrease in the conductivity of magnetite below T_V can be explained in terms of an increase in any barrier to electron hopping. However, there is no way to separate the surface and bulk contributions to the overall conductivity changes of single crystalline magnetite through T_V . It is not, therefore, possible to state with certainty that the surface layers of magnetite also exhibit the step change in conductivity that occurs for the bulk. As no marked increase in the magnitude of the energy gap around E_f is observed following the transition, the spectra suggest that if surface conductivity is decreased below T_V , it is not due to the opening of a larger band gap, but is instead the result of a larger energy difference between the centers of the d -electron valence and conduction bands. Essentially, while there is no marked opening of a gap around E_f for $T < T_V$, carrier concentration near the gap is reduced because the center of the conduction band and the valence band are localized farther away from E_f than for $T > T_V$. This may also be viewed in terms of a much increased region around E_f with only a limited DOS to facilitate conductivity, as opposed to an increase in the energy range around E_f that is completely devoid of states.

While it is both desirable and useful to discuss the present results in terms of the recent arguments over whether charge ordering or charge disproportionation best describes the states of magnetite below T_V , it is important to again bear in mind during this discussion that STS is a purely surface sensitive technique and that the results obtained here are not necessarily indicative of what occurs in the bulk. In our view, a complete charge ordering, into discrete Fe_{oct}^{2+} and Fe_{oct}^{3+} ions, should result in the opening of a large gap in the DOS around E_f . This is due to the fact that such a charge ordering would completely inhibit the electron hopping conduction mechanism of magnetite. The results presented here show that such a gap does not open, and therefore points away from a complete charge ordering occurring below T_V , at the magnetite surface. The fact that the center of the occupied and unoccupied d -electron bands shift away from each other below T_V does, however, suggest that there is an enhanced barrier to electron hopping at the surface. This is consistent with the transition being responsible for some degree of charge disproportionation at the surface. This is in addition to any electronic order that may already exist at the surface, at room temperature. We also explicitly note that STS cannot provide results that aid in the recent arguments over whether the driving force behind the Verwey transition is electronic or structural. However, this elucidation of the surface electronic structure above and below T_V provides direct evidence that, at the surface at least, the transition alters the electronic signature of magnetite. These alterations could be due to the structural changes known to occur at T_V . For example, a change in crystal symmetry from cubic to monoclinic may

well result in the observed shifting of the centers of the occupied and unoccupied d -electron levels. From our results it is clear that while models of the transition must provide for the known structural changes, the observed alterations to the surface electronic band structure must also be taken into account. The results also show that STS is a valuable technique for the elucidation of changes in the surface electronic properties of materials that undergo metal-insulator type transitions.

IV. CONCLUSION

Using STS the well-ordered (001) and (111) surfaces of Fe_3O_4 are shown to exhibit a ~ 0.2 eV gap in the DOS around E_f , at room temperature. The gap is consistent with a degree of electronic order on the surface of magnetite, at room temperature, far above T_V . It is shown that surface disorder, in terms of steps and nonstoichiometry, alters the electronic signature of magnetite. For spectra of the (111) surface obtained at 140 K a ~ 0.2 eV gap is again resolved, along with discrete spectral features at -0.45 ± 0.1 V in the occupied band and $+0.5 \pm 0.1$ V in the unoccupied band. The enhanced spectral resolution indicates an increased degree of electronic order compared to room temperature. Below T_V a

large band gap does not open up in the DOS, pointing to the Verwey transition at the magnetite surface being of a semiconductor-semiconductor nature, as opposed to a metal-insulator transition. The situation for the bulk may be entirely different. The fact that a gap in the surface DOS does not open up below T_V suggests that ionic charge ordering does not occur at the surface. Increased splitting of the resolved peaks in the occupied and unoccupied d -electron bands is found below T_V . This is consistent with the formation of an increased barrier to electron hopping at the surface. Such a mechanism could offer an explanation for the well-known conductivity drop in bulk magnetite, below T_V , despite the fact that no large opening of the actual band-gap magnitude occurs. However, whether such a conductivity change actually occurs at the surface cannot be ascertained. The increased band splitting also suggest that, while it may not be the driving force, a limited degree of charge disproportionation plays an integral part of the Verwey transition at the magnetite (111) surface.

ACKNOWLEDGMENT

The authors would like to acknowledge funding from Science Foundation Ireland (SFI) under Contract No. 00/PI.1/C042.

*Electronic address: jordank@tcd.ie

- ¹A. Yanase and K. Siratori, *J. Phys. Soc. Jpn.* **53**, 312 (1984).
- ²Z. Zhang and S. Satpathy, *Phys. Rev. B* **44**, 13319 (1991).
- ³E. J. W. Verwey and P. W. Haayman, *Physica (Amsterdam)* **8**, 979 (1941).
- ⁴E. J. W. Verwey, P. W. Haayman, and R. Romeyn, *J. Chem. Phys.* **15**, 181 (1947).
- ⁵S. F. Alvarado, M. Erbudak, and P. Munz, *Phys. Rev. B* **14**, 2740 (1976).
- ⁶Yu. S. Dedkov, M. Fonin, D. V. Vyalikh, J. O. Hauch, S. L. Molodtsov, U. Rüdiger, and G. Güntherodt, *Phys. Rev. B* **70**, 073405 (2004).
- ⁷V. I. Anisimov, I. S. Elfimov, N. Hamada, and K. Terakura, *Phys. Rev. B* **54**, 4387 (1996).
- ⁸M. Iizumi and G. Shirane, *Solid State Commun.* **17**, 433 (1975).
- ⁹J. P. Wright, J. P. Attfield, and P. G. Radaelli, *Phys. Rev. B* **66**, 214422 (2002).
- ¹⁰P. W. Anderson, *Phys. Rev.* **102**, 1008 (1956).
- ¹¹F. Walz, *J. Phys.: Condens. Matter* **14**, R285 (2002).
- ¹²J. Garcia and G. Subias, *J. Phys.: Condens. Matter* **16**, R145 (2004).
- ¹³G. Kh. Rozenberg, M. P. Pasternak, W. M. Xu, Y. Amiel, M. Hanfland, M. Amboage, R. D. Taylor, and R. Jeanloz, *Phys. Rev. Lett.* **96**, 045705 (2006).
- ¹⁴M. Mizoguchi, *J. Phys. Soc. Jpn.* **70**, 2333 (2001).
- ¹⁵G. Subias, J. Garcia, and J. Blasco, *Phys. Rev. B* **71**, 155103 (2005).
- ¹⁶D. L. Camphausen, J. M. D. Coey, and B. K. Chakraverty, *Phys. Rev. Lett.* **29**, 657 (1972).
- ¹⁷M. Fonin, R. Pentcheva, Yu. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger, and G. Güntherodt, *Phys. Rev. B* **72**, 104436 (2005).
- ¹⁸A. Chainani, T. Yokoya, T. Morimoto, T. Takahashi, and S. Todo, *Phys. Rev. B* **51**, 17976 (1995).
- ¹⁹J.-H. Park, L. H. Tjeng, J. W. Allen, P. Metcalf, and C. T. Chen, *Phys. Rev. B* **55**, 12813 (1997).
- ²⁰D. Schrupp, M. Sing, M. Tsunekawa, H. Fujiwara, S. Kasai, A. Sekiyama, S. Suga, T. Muro, V. A. M. Brabers, and R. Claessen, *Europhys. Lett.* **70**, 789 (2005).
- ²¹Yu. S. Dedkov, U. Rüdiger, and G. Güntherodt, *Phys. Rev. B* **65**, 064417 (2002).
- ²²D. J. Huang, C. F. Chang, J. Chen, L. H. Tjeng, A. D. Rata, W. P. Wu, S. C. Chung, H. J. Lin, T. Hibma, and C. T. Chen, *J. Magn. Magn. Mater.* **239**, 261 (2002).
- ²³X. W. Li, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid, *Appl. Phys. Lett.* **73**, 3283 (1998).
- ²⁴G. Hu and Y. Suzuki, *Phys. Rev. Lett.* **89**, 276601 (2002).
- ²⁵S. van Dijken, X. Fain, S. M. Watts, and J. M. D. Coey, *Phys. Rev. B* **70**, 052409 (2004).
- ²⁶K. Jordan, G. Mariotto, S. F. Ceballos, S. Murphy, and I. V. Shvets, *J. Magn. Magn. Mater.* **290**, 1029 (2005).
- ²⁷N. Berdunov, S. Murphy, G. Mariotto, and I. V. Shvets, *Phys. Rev. B* **70**, 085404 (2004).
- ²⁸S. F. Ceballos, G. Mariotto, S. Murphy, and I. V. Shvets, *Surf. Sci.* **131–140**, 523 (2003).
- ²⁹G. Mariotto, S. Murphy, and I. V. Shvets, *Phys. Rev. B* **66**, 245426 (2002).
- ³⁰J. A. Stroschio, R. M. Feenstra, and A. P. Fein, *Phys. Rev. Lett.* **57**, 2579 (1986).
- ³¹P. Martensson and R. M. Feenstra, *Phys. Rev. B* **39**, 7744 (1989).
- ³²J. Y. T. Wei, N.-C. Yeh, and R. P. Vasquez, *Phys. Rev. Lett.* **79**, 5150 (1997).