Re-examining the Verwey transition in Fe₃O₄

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Motivated by recent structural data questioning the adequacy of the charge order (CO)/disorder picture for the Verwey transition (at \( T = T_V \)) in magnetite, we re-investigate this issue within a new theoretical picture. Using the state-of-the-art LDA+DMFT method, we show that the non-trivial interplay between the \( B \)-site octahedral distortions and strong, multi-orbital electronic correlations in the half-metallic state is a necessary ingredient for a proper quantitative understanding of the physical responses across \( T_V \). While weak CO is found to have very small effects on the low-\( T \) spectral function, the low-\( T \) charge gap and the resistivity jump across \( T_V \) are quantitatively reproduced only upon inclusion of CO in LSDA+DMFT scheme. Our results strongly suggest that the Verwey transition is dominantly driven by multi-orbital electronic correlations with associated JT distortions on the \( B \)-sublattice, and constitutes a non-trivial advance in attempts to understand the physics of Fe₃O₄.

Magnetite is a ferrimagnetic spinel oxide with a high Curie temperature, \( T_c = 858 \) K. Hence, it is viewed as an ideal candidate for room temperature spintronic applications. Being the oldest magnetic material known to humanity, it has nonetheless defied a consistent physical understanding to date. It is believed that the Verwey transition at \( T = T_V \) is associated with an order-disorder transition from a charge ordered (CO) state of \( Fe \) ions on the \( B \) sublattice (with \( Fe^{2.5+δ}Fe^{2.5−δ} \) for \( Fe_B \) ions) to a disordered state (\( Fe^{2.5} \) at all \( Fe_B \) sites) at higher \( T \). One would expect insulating behavior below \( T_V \), as indeed observed. However, a consistent picture of the electronic state and transport has proved to be very controversial. Photoemission (PES) studies lead to conflicting results: Chainani et al. found a finite density of states (DOS) at the Fermi level, in agreement with the predicted metallic behavior in the high-\( T \) cubic phase. This is apparently corroborated by the optical conductivity studies, which reveal clear gap opening below \( T_V \), and significant spectral weight transfer at higher energies at higher \( T \). The “Drude” contribution is estimated to be small, with most of the spectral weight spread out over the incoherent part. However, Park et al. use PES and IPES results to conclude that there is no spectral weight at \( E_F \) above \( T_V \). The gap does not collapse across \( T_V \), but only shrinks by about 50 meV. This would be consistent with a conductivity jump by a factor of 100 across \( T_V \) only if semiconducting behavior is assumed above \( T_V \) as well. Qualitatively similar conclusions have been derived very recently by Schupp et al., who, moreover, use soft X-ray photoemission to determine the bulk electronic structure (PES lineshape). Thus, the Verwey transition is a semiconductor to semiconductor transition, rather than an insulator-metal transition, as thought earlier. Other observations like the small carrier mobility, the unusual \( T \)-dependence of the conductivity, and the mid-infrared peak in optics suggest electronic localisation, but now in both phases.

The existence and nature of the CO state in Fe₃O₄ is equally controversial. New high resolution powder diffraction data find very small charge disproportionation, \(-0.1 < δ < 0.1\), while resonant X-ray scattering studies even concluded the absence of CO below \( T_V \). Thus, contrary to traditional expectation, the electrostatic minimisation required for the CO cannot be the dominant mechanism driving the Verwey transition. On the other hand, the possibility of orbital order (OO), perhaps of a more complex type, has not hitherto been investigated. Recall that \( Fe^{2+} \) is a Jahn-Teller active ion, and, in fact, that the low-\( T \) distortions of the \( O \) octahedra around \( B \) site ions can be viewed as JT distortions. Indeed, a recent LDA+U calculation finds that the local occupation of \( t_{2g} \) orbitals on \( B \) sites follows the octahedral distortion expected from a JT effect. They also find a charge disproportionation close to the experimentally suggested (small) value, but this could probably be washed out by dynamical frustration effects beyond LDA+U in the real system. Observation of the distorted octahedra around \( B \) sites in the refined low-\( T \) structure suggests that orbital correlations and associated JT effects in a fully magnetically polarised situation might be essential ingredients for understanding the Verwey transition.

An important feature is clear from PES, IPES and optical measurements across \( T_V \). Characteristic strong correlation signatures are clearly visible. In particular, the detailed forms of the lineshapes in each phase, as well as the appreciable transfer of dynamical spectral weight over large energy scales across \( T_V \) constitute clinching evidence for a phase transition between two strongly correlated phases accompanied by strong spectral weight transfer (SWT). A direct comparison with LSDA(+U) results clearly shows substantial discrepancy between theory and experiment over the whole energy range.
pointing to the basic inadequacy of LSDA(+U) to describe the actual, correlated electronic structure. This mandates extension of LSDA to include dynamical effects via LSDA+DMFT.

Previous theoretical work has dealt with this problem on two fronts. Various bandstructure calculations indicate a half-metallic state with a gap in the majority density-of-states (DOS). This conflicts, however, with the observed semiconducting resistivity up to $T = 320$ K, and so recent LDA+U work attempts to cure this malady. Moreover, the role of the B-site octahedral distortion has been clarified in the LDA+U work, which suggests that the Verwey transition may be understandable as an orbital order/orbital disorder transition. Experimentally, the situation is far from clear, and theoretically, one expects staggered (Neel) orbital order to be susceptible to strong dynamical frustration (in a way similar to what happens to usual antiferromagnetism on inverse spinels). However, the possibility of more complex orbital ordering patterns, involving more than one tetrahedron, is not ruled out in principle. On the second front, Ihle and Lorenz explicitly considered a scenario involving a phase transition from a CO insulator below $T_V$ to a short-range ordered, “metallic” state above $T_V$. This model gives rise to polaronic band motion above $T_V$ along with polaronic hopping conductivity at higher $T$, in good agreement with observations. However, in light of experiments questioning the relevance (or even existence) of CO, a new starting point may be necessary. Motivated by new structural data and by the LSDA+U work, an order-disorder transition in the $t_{2g}$ orbital sector on the B-sublattice ($Fe^{2+} - Fe^{3+}$), along with concomitant Jahn-Teller distortions, might be an attractive candidate for a consistent understanding of this system. We point out that study of the effects of orbital correlations/JT distortions in geometrically frustrated TM oxides is an enterprise in its infancy: these studies show that the combination of strong correlations in the d shell and geometrical frustration can induce qualitatively new, complex behaviors.

Summarising, the microscopic origin of carrier localisation, and of its modification across $T_V$, remains an open issue. The clarification of this issue should go hand-in-hand with a microscopic understanding of the changes in electronic structure across the transition. Here, we explore this new proposal in detail. We marry the state-of-the-art LSDA with multi-orbital dynamical mean field theory ([MO]DMFT) restricted to the $t_{2g}$ sector (see below). We choose LSDA+[MO]DMFT because though LSDA captures structural effects reliably in the detailed one-electron dispersion(s), it generically fails to yield the correlated, insulating/metallic ground states characterised by appreciable dynamical SWT.

We start with the recent LSDA density-of-states (DOS). This describes a half-metallic ferromagnet, with full spin polarisation over an appreciable energy scale around $E_F$. The total DOS has dominant $Fe(B)$ site contributions, but those coming from $Fe(A)$ sites, as well as O-2p states cannot be neglected either. Strictly speaking the Fe DOS also has contributions coming from $d - p$ hybridisation. In what follows, we include only the $Fe - t_{2g}$ DOS as the bandstructure (LDA) input in our calculation. The doublet $E_g$ orbitals lie about 0.019 eV above the singlet $A_g$ orbital, giving a $t_{2g}$ level splitting, $\Delta_{t_{2g}} = \Delta = 0.019$ eV. The $Fe - e_g$ states, split by the crystal field, lie much higher and can be safely neglected. *Ab initio* estimates yield the intra-orbital Hubbard $U \simeq 3.7 - 4.0$ eV, and, with a Hund coupling, $J_H \simeq 1.0$ eV, the inter-orbital Hubbard interaction, $U' \simeq (U - 2J_H) = 1.7 - 2.0$ eV. Further, $\Delta$ acts like an external field in the orbital sector, sensitively controlling the occupations of the $t_{2g}$ orbitals (orbital polarisation) in much the same way as the magnetisation of a paramagnet is a function of an external magnetic field. In addition, the nearest neighbor Coulomb interaction, $V$, between n.n Fe sites is important in $Fe_3O_4$: its value is not reliably known, but is estimated to be $V \simeq 0.4$ eV. With this, the total many-body Hamiltonian for $Fe_3O_4$ is:

$$H = \sum_{k\alpha\sigma} \varepsilon_k^{ab} c_{k\alpha}^{\dagger a\sigma} c_{k\alpha}^b + U \sum_{i\sigma} n_i^a n_i^\sigma + U' \sum_{iab} n_i^a n_i^b$$

$$+ V \sum_{<i,j>ab} n_i^a n_j^b - J_H \sum_{iab} \mathbf{S}_i^a \cdot \mathbf{S}_j^b + \Delta \sum_{iab} (n_i^a - n_i^b),$$

where $a, b$ label the $t_{2g}$ orbitals.

We use (MO)DMFT to solve this three-orbital model. Further, the iterated perturbation theory (IPT) is used as an “impurity solver”. While not exact, IPT does provide very good agreement with QMC results for the one-band Hubbard model at high-$T$, and with exact diagonalisation as well as very recent dynamical-DMRG results for the one-particle spectral functions. The detailed formulation of (MO)IPT for orbitally degenerate systems has already been developed and used, so we do not repeat the equations here. Since $Fe_3O_4$ is half-metallic, we use the (MO)IPT version developed earlier by us for $Cr_2O_4$ to study the spectral function in the minority spin sector. We extend earlier work to include the effect of $V$ by decoupling it in the Hartree approximation, which is exact as $d \to \infty$.

For $Fe_3O_4$, we start with the high-$T$ cubic structure, with its bandstructure computed by LSDA. In addition to generating multi-orbital Hartree shifts, which statically renormalise the LDA orbital energies by amounts depending upon $U', J_H$ as well as by the occupation of each $t_{2g}$ orbital, the second order diagrams in DMFT explicitly account for the dynamical nature of electronic correlations, leading to drastic shifts in spectral weights and non-trivial changes in the LDA line-shapes. With $U' = 1.7eV, V = 0.4eV$, we derive the correlated spectral function in the high-$T$ phase: the re-
DOS for LDA+DMFT calculations, with the corresponding LDA
the two correlated phases are described by two separate
very different from that used in other works [19], where
for V
values of orbital occupations and the
renormalised val-
phase. For each trial value, we monitor the correspond-
tability of the high-
malised in widely unanticipated ways by multi-orbital in-
these bare LDA parameters do not have a clear physi-
cal meaning when correlations are strong, and are renor-
malised as the initial input, we selfconsistently search for the critical value of $\Delta_c$ which
destabilises the high-T phase, within LDA+DMFT. We
find, as will become clearer below, that the second so-
lution of the DMFT equations becomes more stable for
$\Delta_c = 0.01 eV$. Interestingly, (lower panel of Fig. 4),
the second solution also corresponds to an insulator, but
with a larger gap $O(0.1 eV)$: we point out that the low-T
phase is indeed found to have a larger gap in PES [4].
As for the high-T phase, dynamical multi-orbital corre-
lations drastically modify the LDA(+U) spectra in the
low-T phase as well.

We now compare our LDA+DMFT results with re-
cent published PES [4, 5] and BIS [4] measurements
(BIS was done only for the high-T phase). Remark-
ably, excellent quantitative agreement with the occu-
pied as well as unoccupied parts of the spectrum is
clearly revealed (Fig. 2) over the whole energy range from
$-0.7 eV$ to 1.0 eV. Concomitantly, comparing the two
LSDA+DMFT solutions, we find that the high-T phase
is also insulating with smaller gap ($\Delta^{HT}_0 = 0.051 eV$)
than that for the low-T phase ($\Delta^{LT}_0 = 0.075 eV$). This
is again in agreement with the PES spectra.

Further light on the character of the Verwey transition
is shed by studying the evolution of the full many
body DOS as a function of $\Delta$. In Fig. 3, we show how
the DOS depends on $\Delta$ within LSDA+(MO)DMFT. It
is indeed remarkable that our results resemble the
experimental ones [5] very closely if we plausibly suppose

Motivated by the possible absence of CO in Fe$_3$O$_4$, and
by the LSDA+U work showing up the important role of
the JT distortion in the B-sublattice, we adopt the fol-
lowing strategy to study the Verwey transition. We start
by noticing that, in a strongly correlated system, the
correlated values of structural parameters do not have any
correspondence with bare LDA values anymore; in fact,
these bare LDA parameters do not have a clear physical
meaning when correlations are strong, and are renor-
malised in widely unanticipated ways by multi-orbital in-
teractions. So we adopt a new strategy, where we seek
the instability of the high-T phase as a function of the
B-site JT distortion. We vary the crystal field on the B
sites in small trial steps, starting from its LDA+DMFT
value (and not the bare LDA value) in the high-T cubic
phase. For each trial value, we monitor the correspond-
ing spectral functions, as well as the renormalised val-
ues of orbital occupations and the B-site distortion from
the correlated solution, in a way similar to that done
for V$_2$O$_3$ and VO$_2$ [18]. Our procedure is conceptually
different from that used in other works [19], where
the two correlated phases are described by two separate
LDA+DMFT calculations, with the corresponding LDA
DOS for each phase as inputs into the DMFT calcula-

result is shown in Fig. 1. The (Mott) insulating beha-

FIG. 1: (Color online) Orbital-resolved (upper panels) and
total (lower panel) one electron spectral functions for the two
insulating phases of Fe$_3$O$_4$. Notice the changes in the $A_{1g}$ or-
bital DOS; the $E_g$ orbitals shows small changes, demonstrat-
ing the nearly two-fluid character of the Verwey transition.

FIG. 2: (Color online) Comparison of theoretical
LSDA+DMFT results for the total spectral function in
the high- and low-T phases of Fe$_3$O$_4$ with experimental
results taken from Ref. 5 (for PES) and from Ref. 4 (for BIS).
and disproportionation $\eta$ of CO has proved to be controversial. In any case, if a small correction will result in miniscule changes in the dc resistivity (and fitted previously by an activated hopping term) is also naturally accounted for: assuming this form, $\rho_{dc}(T) \sim \exp(\Delta E/k_B T)$ for both phases at $T_V$ with the appropriate gaps derived above, we find that the resistivity jump across $T_V$ is $r = e^{1.5} \approx 90$. This is very close to the factor of slightly less than 100 as estimated experimentally [20], constituting a further check on our results.

In conclusion, in line with very recent experiments, we propose that $B$-site JT distortions in a correlated multi-orbital situation play a crucial role in understanding the changes in electronic structure across the Verwey transition in Fe$_3$O$_4$. In the strongly correlated situation, small changes in the $B$-site octahedral distortions with $T$ give rise to large changes in dynamical spectral weight transfer from low- to high energies as $T$ is raised. The excellent quantitative agreement with the experimental spectral function, as well as with the gap values in both phases and with the resistivity jump across $T_V$ constitutes strong support for our new mechanism involving the role of multi-orbital correlations and associated structural effects in the half-metallic situation.

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1. E. Verwey, Nature 144, 327 (1939).
2. A. Chainani et al., Phys. Rev. B 51, 17976 (1995).
3. L. V. Gasparov et al., Phys. Rev. B 62, 7939 (2000).
4. J.-H. Park et al., Phys. Rev. B 55, 12813 (1997).
5. D. Schrump et al., Europhys. Lett., 70, 789 (2005).
6. J. P. Wright et al., Phys. Rev. Lett. 87, 266401 (2001).
7. J. García et al., Phys. Rev. Lett. 93, 156408 (2004).
8. I. Leonov et al., Phys. Rev. Lett. 93, 146404 (2004).
9. G. Kotliar et al., cond-mat/0511085.
10. A. Yanase and K. Siratory, J. Phys. Soc. Jpn. 53, 312 (1984).
11. V. N. Antonov et al., Phys. Rev. B 64, 134410 (2001).
12. D. Ihle and B. Lorenzo, J. Phys. C 18, L647 (1985).
13. S. Di Matteo et al., Phys. Rev. B 72, 020408(R) (2005).
14. H. Seo et al., Phys. Rev. B 65, 085107 (2002).
15. M. J. Rozenberg et al., Phys. Rev. Lett. 83, 3498 (1999).
16. D. J. García et al., Phys. Rev. Lett. 93, 266401 (2004).