

Role of temperature-dependent O-*p*–Fe-*d* hybridization parameter in the metal-insulator transition of Fe₃O₄: a theoretical study

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Abstract. We propose a simple tight-binding based model for Fe₃O₄ that captures the preference of ferrimagnetic over ferromagnetic spin configuration of the system. Our model is consistent with previous theoretical and experimental studies suggesting that the system is half metallic, in which spin polarized electrons hop only among the Fe B sites. To address the metal-insulator transition (MIT) we propose that the strong correlation among electrons, which may also be influenced by the electron-phonon interactions, manifest as the temperature-dependence of the O-*p*–Fe-*d* hybridization parameter, particularly Fe-*d* belonging to one of the Fe B sites (denoted as $t_{\text{FeB-O}}^{(2)}$). By proposing that this parameter increases as the temperature decreases, our density-of-states calculation successfully captures a gap opening at the Fermi level, transforming the system from half metal to insulator. Within this model along with the corresponding choice of parameters and a certain profile of the temperature dependence of $t_{\text{FeB-O}}^{(2)}$, we calculate the resistivity of the system as a function of temperature. Our calculation result reveals the drastic uprising trend of the resistivity profile as the temperature decreases, with the MIT transition temperature located around 100 K, which is in agreement with experimental data.

1. Introduction

Transition-metal oxides have attracted a lot of attention of researchers in both fundamental condensed-matter and applied physics area and are intensely studied in last decades. This is due to their interesting properties that could lead to promising technological applications such as superconductivity [1], giant magnetoresistance [2, 3, 4] and metal-insulator transition [5, 6]. Among them, Fe₃O₄, a ferrimagnet with $T_C \simeq 860$ K with a saturation magnetization of 0.6 Tesla (~ 471 emu/cm³) [7], is considered as an important material owing to its technological applications to be a new generation soft magnet. This material has been predicted theoretically and observed experimentally to be a half-metal [8, 9, 10], making it be prospective for spintronic devices [11, 12, 13].

Fe₃O₄, belonging to the $Fd3m$ symmetry group, crystallizes in cubic spinel inverse structure with lattice constant of $a = 8.396$ Å where oxygen anions form a close-packed face-centered-cubic (fcc)



sublattice with iron cations located in interstitial sites [14]. One-third of Fe atoms are tetrahedrally coordinated with four oxygen ions as Fe^{3+} at tetrahedral sites (A sites) and the remaining two-third of the Fe atoms consist of a 1:1 mixture of Fe^{2+} and Fe^{3+} that are octahedrally coordinated with six oxygen ions at octahedral sites (B sites). At $T_V \simeq 120$ K, the system experiences metal-insulator transition (MIT) known as Verwey transition [15]. At this transition, the structure distorts from cubic symmetry [16]. In addition, charge ordering (CO) occurs at B sites [17, 18], thus increasing the resistivity by two orders of magnitude.

In this work, using an effective model that explores only the dynamics of the electrons, we aim to show how the MIT occurs in Fe_3O_4 , and explain the mechanism underlying it. For this purpose, we construct a tight-binding based Hamiltonian [19] and then calculate the density of states, the electronic energy, and the resistivity of the system. We adjust our model parameters so as to capture the preference of ferrimagnetic over ferromagnetic ordering. Further, within the model, we search for reasonable temperature dependence of a certain parameter that could lead to the occurrence of MIT. We find that temperature-dependent parameter of a particular hybridization between O $2p$ and Fe $3d$, which we denote as $t_{\text{FeB-O}}^{(2)}$, plays the key role in the MIT of Fe_3O_4 . The increase of $t_{\text{FeB-O}}^{(2)}$ as temperature decreases remarkably also leads to a CO transition that occurs slightly below the MIT temperature. We argue that this temperature dependence of $t_{\text{FeB-O}}^{(2)}$ results from strong correlations due to electron-electron as well as electron-phonon interactions involved in the Verwey structural transition. Our results show that the mechanisms of MIT and CO transition in Fe_3O_4 have the same origin, and it may be connected to the Verwey structural transition.

2. Model

Hinted by the indication of half-metallic behavior [8, 9, 10] and charge ordering [17, 18] occurring only at Fe ions at B sites or B layers, and to simplify our calculations, we define the unit cell of our model by selecting the presumably most important layer in the actual unit cell of Fe_3O_4 , as marked with the orange rectangle in figure 1. With this effective two-dimensional unit cell, we propose a tight-binding based Hamiltonian as follows:

$$H = \sum_{\mathbf{k}} \eta_{\mathbf{k}}^\dagger [H_0(\mathbf{k})] \eta_{\mathbf{k}} - J_H \sum_{i,j} \mathbf{S}_j^{(i)} \cdot \mathbf{s}_j^{(i)} + U \sum_{i,j} n_{j\uparrow}^{(i)} n_{j\downarrow}^{(i)}, \quad (1)$$

where $\mathbf{k}$ denotes $\mathbf{k}$ -point in the Brillouin zone, i is index of Fe sites in a unit cell, while j is index of unit cells in the entire system. The first term of the Hamiltonian represents the kinetic part, whereof $\eta_{\mathbf{k}}^\dagger$ is a row vector whose elements are the creation operators associated with the basis orbitals used in the calculation, and $\eta_{\mathbf{k}}$ is its Hermitian conjugate containing the corresponding annihilation operators. $[H_0(\mathbf{k})]$ is a matrix in momentum space. The second term represents the magnetic interactions between spins of the Fe ions and spins of the itinerant Fe electrons in the e_g orbital. The third term describes the local Coulomb repulsive interactions between two Fe electrons occupying the same e_g orbitals.

The $[H_0(\mathbf{k})]$ matrix shown in equation (1) is constructed through tight-binding approximation out of twenty two atomic orbitals forming our Hilbert space. Here, each of four oxygen atoms contributes two p orbitals, and each of three iron atoms contributes one upper e_g orbitals. We order these basis states as follows: $|\text{OAp}_{x\uparrow}\rangle, |\text{OAp}_{x\downarrow}\rangle, |\text{OAp}_{y\uparrow}\rangle, |\text{OAp}_{y\downarrow}\rangle, |\text{OBp}_{x\uparrow}\rangle, |\text{OBp}_{x\downarrow}\rangle, |\text{OBp}_{y\uparrow}\rangle, |\text{OBp}_{y\downarrow}\rangle, |\text{OCp}_{x\uparrow}\rangle, |\text{OCp}_{x\downarrow}\rangle, |\text{OCp}_{y\uparrow}\rangle, |\text{OCp}_{y\downarrow}\rangle, |\text{ODp}_{x\uparrow}\rangle, |\text{ODp}_{x\downarrow}\rangle, |\text{ODp}_{y\uparrow}\rangle, |\text{ODp}_{y\downarrow}\rangle, |\text{FeA}e_{g\uparrow}\rangle, |\text{FeA}e_{g\downarrow}\rangle, |\text{FeB}_1e_{g\uparrow}\rangle, |\text{FeB}_1e_{g\downarrow}\rangle, |\text{FeB}_2e_{g\uparrow}\rangle, \text{ and } |\text{FeB}_2e_{g\downarrow}\rangle$. These basis states form a 22×22 matrix in momentum space whose structure is arranged in four 11×11 blocks corresponding to their spin directions as

$$[H_0(\mathbf{k})] = \begin{bmatrix} H_0(\mathbf{k})_\uparrow & \mathbf{O} \\ \mathbf{O} & H_0(\mathbf{k})_\downarrow \end{bmatrix}, \quad (2)$$

where $\mathbf{O}$ is a 11×11 -size zero matrix, and

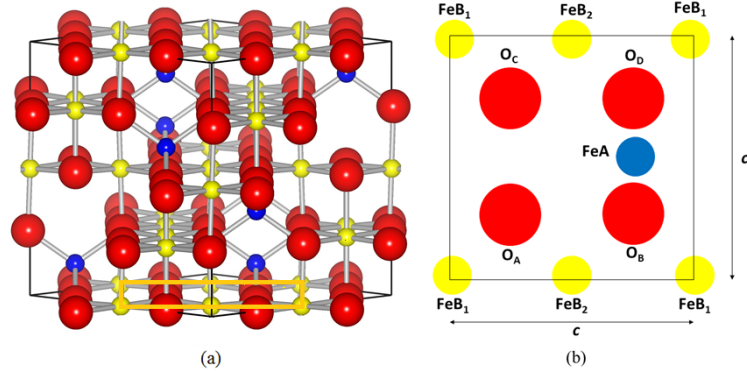


Figure 1. (a) Actual crystal structure of Fe_3O_4 of which the two-dimensional block marked with the orange rectangle is taken to be the effective unit cell of the model. (b) Detail of the model unit cell.

$$H_0(\mathbf{k})_{\uparrow(\downarrow)} = \begin{bmatrix} \epsilon_{\text{O}_A} & 0 & 0 & -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & -2t_{\text{O-O}}^{(1)} \cos \beta & -t_{\text{O-O}}^{(2)} e^{-i\delta} & 0 & 0 & -t_{\text{FeB-O}} e^{i\delta/2} & 0 \\ 0 & \epsilon_{\text{O}_A} & -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & -2t_{\text{O-O}}^{(1)} \cos \beta & 0 & 0 & -t_{\text{O-O}}^{(2)} e^{i\lambda} & 0 & 0 & -t_{\text{FeB-O}} e^{-i\lambda/2} \\ 0 & -2t_{\text{O-O}}^{(1)} \cos \alpha & \epsilon_{\text{O}_B} & 0 & -t_{\text{O-O}}^{(2)} e^{-i\delta} & 0 & 0 & -2t_{\text{O-O}}^{(1)} \cos \beta & -t_{\text{FeA-O}} e^{-i\beta/2} & 0 & -t_{\text{FeB-O}} e^{i\delta/2} \\ -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & 0 & \epsilon_{\text{O}_B} & 0 & -t_{\text{O-O}}^{(2)} e^{i\lambda} & -2t_{\text{O-O}}^{(1)} \cos \beta & 0 & -t_{\text{FeA-O}} e^{-i\beta/2} & -t_{\text{FeB-O}} e^{-i\lambda/2} & 0 \\ 0 & -2t_{\text{O-O}}^{(1)} \cos \beta & -t_{\text{O-O}}^{(2)} e^{i\delta} & 0 & \epsilon_{\text{O}_C} & 0 & 0 & -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & 0 & -t_{\text{FeB-O}} e^{-i\delta/2} \\ -2t_{\text{O-O}}^{(1)} \cos \beta & 0 & 0 & -t_{\text{O-O}}^{(2)} e^{-i\lambda} & 0 & \epsilon_{\text{O}_C} & -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & 0 & -t_{\text{FeB-O}} e^{i\lambda/2} & 0 \\ -t_{\text{O-O}}^{(2)} e^{i\delta} & 0 & 0 & -2t_{\text{O-O}}^{(1)} \cos \beta & 0 & -2t_{\text{O-O}}^{(1)} \cos \alpha & \epsilon_{\text{O}_D} & 0 & -t_{\text{FeA-O}} e^{i\beta/2} & -t_{\text{FeB-O}} e^{-i\delta/2} & 0 \\ 0 & -t_{\text{O-O}}^{(2)} e^{-i\lambda} & -2t_{\text{O-O}}^{(1)} \cos \beta & 0 & -2t_{\text{O-O}}^{(1)} \cos \alpha & 0 & \epsilon_{\text{O}_D} & 0 & -t_{\text{FeA-O}} e^{i\beta/2} & 0 & -t_{\text{FeB-O}} e^{i\lambda/2} \\ 0 & 0 & -t_{\text{FeA-O}} e^{i\beta/2} & -t_{\text{FeA-O}} e^{i\beta/2} & 0 & 0 & -t_{\text{FeA-O}} e^{-i\beta/2} & -t_{\text{FeA-O}} e^{-i\beta/2} & \epsilon_{\text{FeA}} & 0 & 0 \\ -t_{\text{FeB-O}} e^{-i\delta/2} & 0 & 0 & -t_{\text{FeB-O}} e^{i\lambda/2} & 0 & -t_{\text{FeB-O}} e^{-i\lambda/2} & -t_{\text{FeB-O}} e^{i\delta/2} & 0 & 0 & \epsilon_{\text{FeB}} & -t_{\text{FeB-FeB}} \cos \alpha \\ 0 & -t_{\text{FeB-O}} e^{i\lambda/2} & -t_{\text{FeB-O}} e^{-i\delta/2} & 0 & -t_{\text{FeB-O}} e^{i\delta/2} & 0 & 0 & -t_{\text{FeB-O}} e^{-i\lambda/2} & 0 & -2t_{\text{FeB-FeB}} \cos \alpha & \epsilon_{\text{FeB}} \end{bmatrix}, \quad (3)$$

where $\alpha = k_x c/2$, $\beta = k_y c/2$, $\delta = (k_x + k_y)c/2$ and $\lambda = (k_x - k_y)c/2$. Here, ϵ , t and $c = a\sqrt{2}/2$, with $a = 8.396 \text{ \AA}$ [14], indicate the on-site energy, hybridization parameter and lattice parameter of the model, respectively, while the subscripts indicate the corresponding atoms.

We treat the second and the third terms of the Hamiltonian in equation (1) as a self-consistent local self-energy matrix $[\Sigma_{\text{loc}}(z)]$ that depends on the angles representing the relative direction between the electron spin and the spin of the Fe ion at the corresponding site. The elements of this 22×22 matrix are all zero, except for the blocks

$$\begin{aligned} \begin{bmatrix} \Sigma_{9,9} & \Sigma_{9,20} \\ \Sigma_{20,9} & \Sigma_{20,20} \end{bmatrix} &= \begin{bmatrix} -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeA}} + U \langle n_{\text{FeA}\downarrow} \rangle & -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeA}} e^{-i\phi_{\text{FeA}}} \\ -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeA}} e^{i\phi_{\text{FeA}}} & -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeA}} + U \langle n_{\text{FeA}\uparrow} \rangle \end{bmatrix}, \\ \begin{bmatrix} \Sigma_{10,10} & \Sigma_{10,21} \\ \Sigma_{21,10} & \Sigma_{21,21} \end{bmatrix} &= \begin{bmatrix} -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeB}_1} + U \langle n_{\text{FeB}_1\downarrow} \rangle & -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeB}_1} e^{-i\phi_{\text{FeB}_1}} \\ -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeB}_1} e^{i\phi_{\text{FeB}_1}} & -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeB}_1} + U \langle n_{\text{FeB}_1\uparrow} \rangle \end{bmatrix}, \\ \begin{bmatrix} \Sigma_{11,11} & \Sigma_{11,22} \\ \Sigma_{22,11} & \Sigma_{22,22} \end{bmatrix} &= \begin{bmatrix} -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeB}_2} + U \langle n_{\text{FeB}_2\downarrow} \rangle & -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeB}_2} e^{-i\phi_{\text{FeB}_2}} \\ -\frac{J_H S \hbar}{2} \sin \theta_{\text{FeB}_2} e^{i\phi_{\text{FeB}_2}} & -\frac{J_H S \hbar}{2} \cos \theta_{\text{FeB}_2} + U \langle n_{\text{FeB}_2\uparrow} \rangle \end{bmatrix}. \end{aligned} \quad (4)$$

Here, the second term, i.e. the spin-spin interaction term, is treated following Furukawa's implementation [20] of the dynamical mean-field theory (DMFT) [21]. Whereas, the third term of the Hamiltonian, i.e. the Hubbard U term, is treated within the mean-field approximation, where $\langle n_{\text{FeA}\uparrow} \rangle$, $\langle n_{\text{FeB}_1\uparrow} \rangle$, $\langle n_{\text{FeB}_2\uparrow} \rangle$, $\langle n_{\text{FeA}\downarrow} \rangle$, $\langle n_{\text{FeB}_1\downarrow} \rangle$, and $\langle n_{\text{FeB}_2\downarrow} \rangle$ are the averaged occupation values of the electrons in Fe ions with spin up and down. In order to make sure that our choice of parameters leads to the preference of ferrimagnetic (up-up-down) over ferromagnetic (up-up-up) configurations of the spins of the Fe ions in each unit cell, we perform our calculations under each different spin configuration. For ferrimagnetic configuration, we set $\theta_{\text{FeA}} = \pi$ and $\theta_{\text{FeB}_1} = \theta_{\text{FeB}_2} = \phi_{\text{FeA}} = \phi_{\text{FeB}_1} = \phi_{\text{FeB}_2} = 0$, while for ferromagnetic

configuration, $\theta_{\text{FeA}} = \theta_{\text{FeB}_1} = \theta_{\text{FeB}_2} = \phi_{\text{FeA}} = \phi_{\text{FeB}_1} = \phi_{\text{FeB}_2} = 0$.

3. Method

We solve the model by applying the DMFT algorithm as used in reference [22] to calculate the Green function and the corresponding physical quantities of interest. The total electronic energy of the system can be calculated as

$$E = \int \omega \text{DOS}(\omega) f(\mu, T, \omega) d\omega - U(\langle n_{\text{FeA}\uparrow} \rangle \langle n_{\text{FeA}\downarrow} \rangle + \langle n_{\text{FeB}_1\uparrow} \rangle \langle n_{\text{FeB}_1\downarrow} \rangle + \langle n_{\text{FeB}_2\uparrow} \rangle \langle n_{\text{FeB}_2\downarrow} \rangle). \quad (5)$$

Here, $f(\mu, T, \omega)$ is Fermi-Dirac distribution function with μ indicating the chemical potential of the system. We also calculate the conductivity tensor as

$$\sigma_{\alpha\beta}(T) = \frac{\pi e^2}{\hbar c} \int d\nu \frac{(f(\mu, T, \nu))(1 - f(\mu, T, \nu))}{T} \frac{1}{N} \sum_{\mathbf{k}} \text{Tr}[v_{\alpha}(\mathbf{k})][A(\mathbf{k}, \nu)][v_{\beta}(\mathbf{k})][A(\mathbf{k}, \nu)]. \quad (6)$$

Here, $[v_{\lambda}(\mathbf{k})] = \partial[H_0(\mathbf{k})]/\partial k_{\lambda}$ denotes the Cartesian component of the velocity matrix and $[A(\mathbf{k}, \nu)] = ([G(\mathbf{k}, \nu + i0^+) - G(\mathbf{k}, \nu - i0^+)])/(2\pi i)$ denotes the spectral function matrix. In order to restore the proper physical unit, the dimensional prefactor $\pi e^2/(\hbar c)$ is introduced since the rest of the expression was derived by setting $e = \hbar = 1$. As we are interested to explore the temperature dependence of resistivity, we define the resistivity as inverse of the corresponding diagonal element of the conductivity tensor, that is $\rho_{\alpha\alpha} = 1/\sigma_{\alpha\alpha}$. Here, as x and y directions are not completely equivalent in our model, we expect that ρ_{xx} and ρ_{yy} to be slightly different quantitatively, but pretty much the same qualitatively.

4. Results and discussion

Based on some physical considerations, we estimate and set the following parameter values for our calculations: $\epsilon_{\text{O}_A} = \epsilon_{\text{O}_C} = -1.5$ eV, $\epsilon_{\text{O}_B} = \epsilon_{\text{O}_D} = -1.8$ eV, $\epsilon_{\text{FeA}} = 0.5$ eV, $\epsilon_{\text{FeB}} = 0.4$ eV, $t_{\text{FeA-O}} = 1.8$ eV, $t_{\text{FeB-O}}^{(1)} = 0.9$ eV, $t_{\text{O-O}}^{(1)} = 0.4$ eV, $t_{\text{O-O}}^{(2)} = 0.3$ eV, $t_{\text{FeB-FeB}} = 0.825$ eV, $t_{\text{FeA-FeB}} = 1$ eV, $U = 4$ eV and $J_H = 1$ eV. As for $t_{\text{FeB-O}}^{(2)}$, we vary this parameter as a function of temperature for the reason we elaborate later. Our calculated densities of states for various temperatures are shown in figure 2 for which the energy value is defined relative to the chemical potential. The inset of figure 2 clearly shows that at low temperatures ($T < 100$ K) the system forms a gap around the chemical potential, indicating that it is in an insulating phase. The bands on the left side of the chemical potential arises from O $2p$ orbitals, while Fe $3d$ orbitals contribute to the bands on the right side of the chemical potential. By setting $t_{\text{FeB-O}}^{(2)}$ to decrease as temperature increases following a certain functional form (to be discussed further later), we can see that the gap gradually disappears turning the system into a metal at high temperatures ($T > 100$ K). This demonstrates that the MIT is driven by the temperature dependence of $t_{\text{FeB-O}}^{(2)}$.

To analyze the origin of the gap and investigate the mechanism of MIT in Fe_3O_4 , we show in figure 3 the projected densities of states contributing to states around the chemical potential at high temperatures, and show how they evolve as temperature decreases. These states come from both Fe at B sites (i.e. Fe B₁ and Fe B₂ in figure 1). It is clearly seen in the figure that the gap forms due to splitting of Fe B₁ and Fe B₂ bands. At high temperatures Fe B₁ and Fe B₂ bands are roughly equally filled, but at low temperatures the Fe B₁ states are filled with more electrons than the Fe B₂ states are, suggesting a charge ordering occurs. Hence, these two bands are responsible for the closing and opening of the gap around the chemical potential, and thus the mechanism of MIT. The redistribution of electrons among the Fe B₁ and Fe B₂ sites occurring around the MIT transition signifies that the MIT arises concomitantly with the formation of CO phase among electrons in Fe B sites.

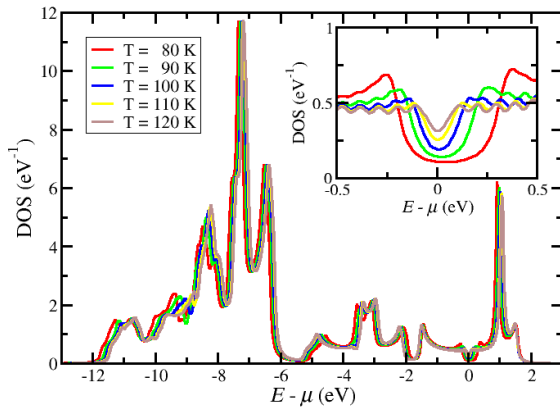


Figure 2. Calculated density of states of Fe_3O_4 . The gap is closed at high temperature, indicating the metal-insulator transition occurs in this system.

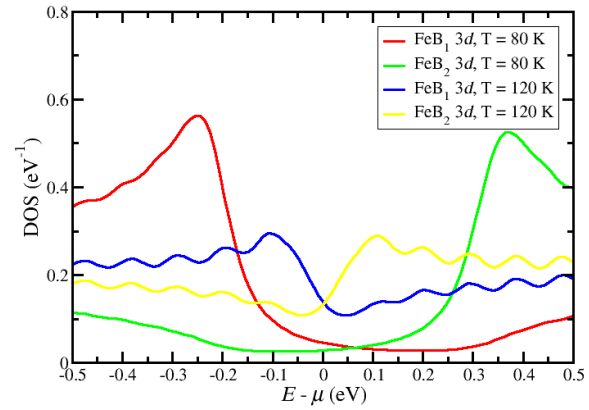


Figure 3. Projected density of states of Fe d bands at low (80 K) and high (120 K) temperatures. The dynamics of these two bands control the formation of the gap.

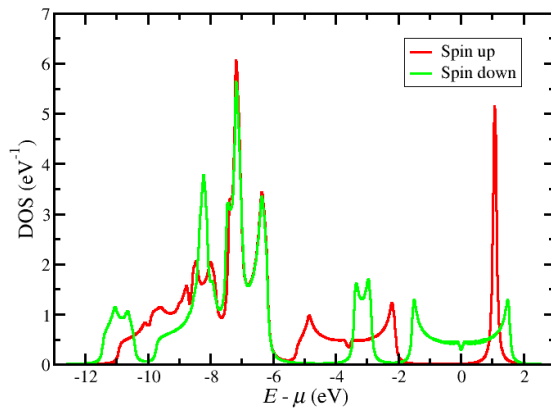


Figure 4. Spin-polarized density of states at $T = 120$ K. The system is half-metal with insulating majority spin channel and metallic minority spin channel.

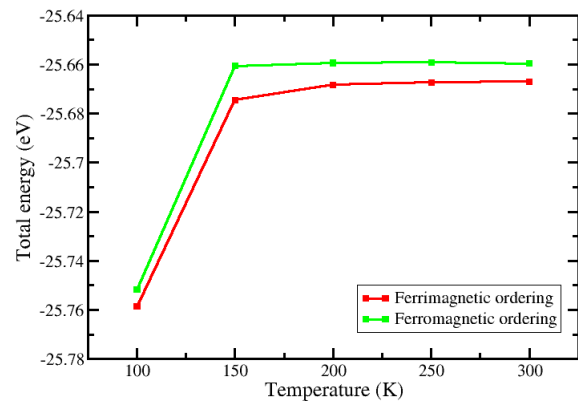


Figure 5. Plot of total electronic energy versus temperature. The system energetically prefers to be in ferrimagnetic spin configuration.

Further, our model also captures the half-metallicity of Fe_3O_4 at high temperatures. As shown in figure 4, the majority (up) spin channel is in insulating state, whereas the minority (down) spin channel has a metallic characteristic. This result confirms the half-metallic nature of Fe_3O_4 which has been observed experimentally [10].

Figure 5 shows the calculated total electronic energy versus temperature for both ferrimagnetic and ferromagnetic spin configurations. It can be seen that the system has lower energy when the Fe spins are in ferrimagnetic configuration compared to that in ferromagnetic configuration. In the ferrimagnetic configuration, for every unit cell in our model the Fe spins at B sites are antiparallel to the spin of Fe at A site. Hence, the two magnetic moments of $5 \mu_B$ from Fe^{3+} at A and B sites are cancelled, leaving the net magnetic moment of $4 \mu_B$ from the remaining Fe^{2+} at B site. This magnetic moment corresponds to the saturation magnetization value of 0.6 Tesla observed in experiment [7].

In order to show the MIT process as observed in experiment, we calculate temperature-dependent resistivity of our Fe_3O_4 model and show the results in figure 6. Within our model, the resistivity calculated along the x direction, ρ_{xx} , has slightly different values from that calculated along the y

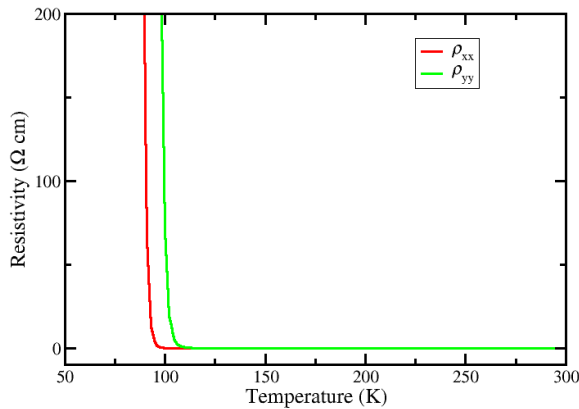


Figure 6. Resistivity as a function of temperature calculated along x and y directions described in the model unit cell. The Verwey transition is located at ~ 100 K.

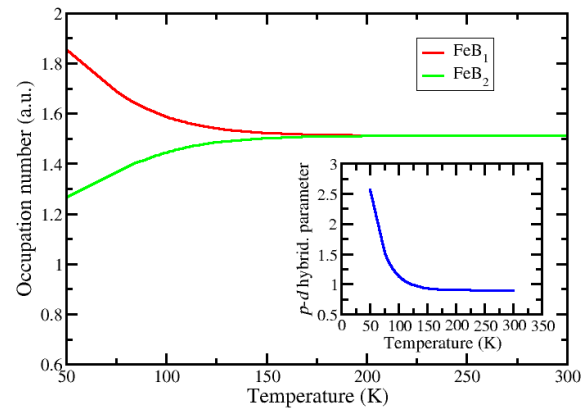


Figure 7. Occupation numbers of electrons at Fe B₁ and Fe B₂ sites as functions of temperature. Inset: the temperature-dependence of $t_{\text{FeB-O}}^{(2)}$.

direction, ρ_{yy} . However, both have exactly the same profile in which an abrupt change indicating the MIT is observed at ~ 100 K, which was initially referred to as Verwey transition [15]. The temperatures about which the abrupt resistivity change occurs is close to the transition temperature T_V obtained from experiment (~ 120 K). As already mentioned before, the transition from metal at high temperatures to insulator at low temperatures is due to charge localization at one of the two Fe B sites (i.e. the B1 sites in this case). This charge localization can be illustrated by the imbalanced occupation numbers of electrons at of Fe B₁ and B₂ sites as the system is brought to low temperatures, as shown in figure 7. This result is consistent with the experimental observation of charge ordering occurring in Fe₃O₄ at low temperatures [17, 18], which according to our model, is responsible for the insulating behavior of the system.

Now we elaborate why and how we propose the temperature dependence of $t_{\text{FeB-O}}^{(2)}$. Within our model that does not incorporate electron-phonon interactions explicitly, the possible abrupt change in conductivity with temperature can only be accommodated if we allow for some parameter(s) to depend on temperature in some manner, presumably due to correlation effects arising from electron-phonon interactions. To find out which parameter(s) having such a temperature dependence, we analyze the projected DOS profiles around the chemical potential as shown in figure 3. From there, we see that the gap can be opened and closed by adjusting the parameter that controls the distribution of states below and above the chemical potential between Fe B₁ and Fe B₂. Hence, we infer that the parameter playing such a role is the hybridization between O 2p to Fe 3d at B₁ sites, i.e. the $t_{\text{FeB-O}}^{(2)}$. Therefore, to properly capture the temperature-dependent physics phenomenologically within our model, we propose that $t_{\text{FeB-O}}^{(2)}$ depends on temperature in the following way:

$$t_{\text{FeB-O}}^{(2)}(T) = Ae^{-\frac{T}{T^*}} + B, \quad (7)$$

where $A \approx 12$ eV, $T^* \approx 25.34$ K and $B \approx 0.9$ eV. The plot of $t_{\text{FeB-O}}^{(2)}(T)$ as a function temperature is shown in the inset of figure 7. Such a temperature-dependent behavior of a hybridization parameter between O p and d orbital of a transition metal element is not a completely new phenomenon as it has been observed experimentally in some other systems [23]. For our model of Fe₃O₄, as discussed above, this temperature-dependence of $t_{\text{FeB-O}}^{(2)}$ leads to MIT as well as CO transition in the system.

5. Concluding remarks

In conclusion, we have developed a theoretical model to investigate the role of temperature-dependent O-*p*-Fe-*d* hybridization parameter in the metal-insulator transition of Fe₃O₄. Our model has successfully explained the transition, capturing the Verwey transition temperature at ~100 K, the ferrimagnetic configuration and the half-metallicity of the system. Our calculation results suggest that the MIT occurs concomitantly with charge ordering among electrons of Fe at B sites. We argue that the temperature dependence of the O-*p*-Fe-*d* hybridization parameter arises as a manifestation of Verwey structural transition felt by the electrons through electron-phonon interactions.

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