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The influence of a finite bandwidth on the Verwey transition in magnetite

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Abstract. The role of the band structure in the Verwey transition in magnetite (Fe_3O_4) has been analysed within the framework of an exactly solvable two-band model based on an effective interionic Coulomb potential splitting the 3d band of the t_{2g} electrons. The model predicts an instability of the Verwey order below a certain ratio β/W of the Coulomb interaction parameter β and the bandwidth W . This instability can be understood in terms of a clear physical picture showing the impossibility of constructing a self-consistent ordered charge distribution in this case. A resemblance to the Cullen–Callen criterion is evident. It is shown as well that the influence of the band structure on the Verwey temperature vanishes rapidly when β/W increase beyond its critical value. Band-structure effects do provide an explanation, however, for the discontinuity in the Verwey temperature as a function of the concentration of cation dopants or the oxygen stoichiometry, which marks the transition from a first- to a second-order Verwey transition. In this respect, the model reproduces the experimental data quantitatively. Fits obtained by application of the model yield values of 0.037–0.04 eV for the Coulomb gap and 0.012–0.014 eV for the bandwidth. The obtained values of the bandwidth are typical for a strongly localized electron system and support a polaronic band picture.

1. Introduction

Being widely applied as magnetic materials, ferrites are among the most intensively investigated oxides. Magnetite (Fe_3O_4) is a well known representative of the so-called spinel ferrites which are best known for their soft magnetic properties.

As early as the 1920s, the interesting physical properties of magnetite attracted the attention of investigators, leading to the discovery of a temperature-induced phase transition near 120 K, which manifests itself in anomalies in the thermal expansion [1] as well as in the calorimetric [2] and magnetic [3] properties. Soon after its discovery, Verwey suggested, on the basis of measurements of the electrical conductivity, that the phase transition actually originates from an ordering process of the Fe^{2+} and Fe^{3+} ions at the octahedral Fe sublattice in the spinel structure, or equivalently from an ordering of 3d electrons (t_{2g}) at the octahedral sublattice [4, 5]. This viewpoint is now widely accepted and the phase transition, meanwhile known as the Verwey transition, has been the subject of numerous investigations. For a long time the driving mechanism responsible for the transition has been the subject of speculation, although it may be obvious that, because of the nature of the transition, the interionic Coulomb interaction (Madelung energy) is likely to play an important role. Among many interesting other aspects, the thermodynamics of the Verwey transition is in itself remarkable. Not only present in pure but also in lightly doped magnetite, the Verwey transition manifests itself for instance as a first-order transition (pure magnetite and low dopant concentration or cation

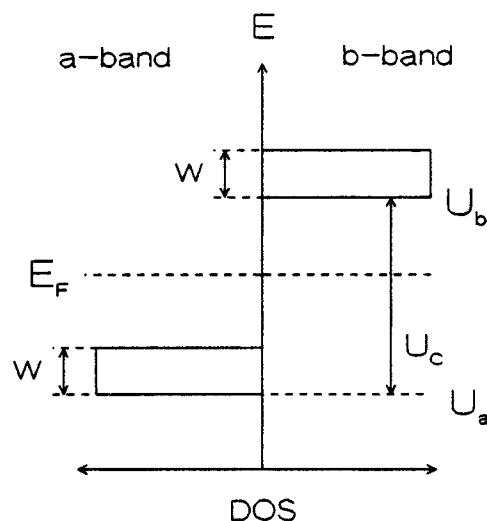


Figure 1. Simplified band structure of magnetite. The two bands correspond to the a and the b sublattices. The bands are separated by a gap due to the interionic Coulomb interaction. At $T = 0$, the lower band is completely filled whereas the upper band is completely empty. The Fermi level lies exactly in between the band minima.

deficiency) as well as a second-order transition (high Ti^{4+} or Zn^{2+} -dopant concentration or cation deficiency) [6]. Various theoretical treatments of the Verwey transition have been presented in the past. Recently the present authors presented a mean-field approach to the Verwey transition based on an effective interionic Coulomb potential [7, 8], explaining and reproducing various aspects of the Verwey transition from both a qualitative as well as a quantitative point of view. Within our mean-field approach, the octahedral Fe sublattice is considered as being split up into two equivalent sublattices a and b. Ordering effects appear as differences in Fe^{2+} occupation of these sublattices. The 3d levels are treated within a simplified scheme of two distinctive levels, each level corresponding to an electron residing at a particular sublattice. Among the aspects correctly reproduced in such an approach are the shift of the Verwey temperature T_V as a result of doping with different transition-metal ions. Also the sharp boundary between a first- and a second-order regime of Verwey transitions, passed upon increasing the doping of magnetite with Zn^{2+} or Ti^{4+} ions, was explained in a satisfactory way by taking into account the effect of structural changes. One aspect of this transition not explained by our model, however, is the sharp discontinuous drop of the Verwey temperature of about 5% upon passing the boundary between the first- and second-order regime. Although the mathematical analysis yields two regimes of qualitatively completely different phase transitions of first and second order respectively, the Verwey temperature follows a continuous curve when the boundary between the two regimes is crossed in our previous approach. It seems obvious that this shortcoming of our model may be related to the description of the octahedral t_{2g} levels in terms of a two-level system. Upon a gradual disordering (second-order transition), the gap between the levels closes and only at $T = T_V$ do both levels coalesce and become equally occupied (i.e. the Fe^{2+} ions are equally distributed over both sublattices). Replacing the two sharp levels by two bands of finite width yields a qualitatively slightly different picture (figure 1). In the case of incomplete ordering, occurring at sufficiently high temperatures, the t_{2g} electrons are partially distributed over both sublattices, and a band overlap may appear when the (Coulomb) gap becomes sufficiently small. The t_{2g} states located within the overlapping

sections of the bands become equally occupied already at $T < T_V$ and the asymmetry of the sublattice occupation will therefore be reduced (in the case of identical bands the states in the overlapping band sections do no longer contribute to this asymmetry at all). A relation between the width of both sublattice bands and the Verwey temperature therefore seems evident. To verify this hypothesis we present an extension of our model based upon a simplified level scheme consisting of two bands of finite width. A major simplification is achieved by the assumption of a uniform density of states for all energies within the two bands, allowing a simple algebraic solution to the model.

2. Theoretical outline

2.1. Description of the model

In the single-electron level scheme of magnetite, the 3d electrons at the octahedral sublattice can be grouped together into ten spin-up electrons and a single spin-down (t_{2g}) electron (per formula unit Fe_3O_4) [9]. The unpaired spin-down electrons correspond to the Fe^{2+} ions and are in fact responsible for the Verwey ordering.

In accordance with previous work [7, 8] the octahedral sublattice is considered as being split up into two *equivalent* sublattices (a and b). A charge density wave can then be viewed as an asymmetric spin-down electron occupation (Fe^{2+} occupation) of these sublattices. We describe the spin-down levels as band states with, however, still a high degree of localization (narrow-band approximation). The interionic Coulomb interaction (which includes the unscreened interaction between a t_{2g} electron and *all* other t_{2g} electrons) can then easily be described within a mean-field formalism [7]. Predominantly because of this interionic Coulomb interaction, the energy levels of the spin-down electrons are split [10]. As a result *two* bands appear, separated by a gap [7], each band being related in real space to one of the sublattices a or b. This approach in terms of ‘sublattice bands’ is justified when the interionic Coulomb interaction (splitting the bands) is large enough compared to the hopping integral. The results of [7] and [8] indeed suggest that the electronic structure of magnetite below T_V can be described successfully in terms of electrons which are thermally excited from one sublattice to another. However, the clearest evidence for a relation between the spatial position of the t_{2g} electrons and their single-electron states and levels comes from magnetic after-effect (MAE) measurements, which show a significant magnetic relaxation below T_V , abruptly collapsing at the Verwey transition [11, 12]. Related to the thermal relaxation of the position of the domain walls, the observed MAE can, in view of the absence of drastic changes in the intrinsic magnetic properties at T_V , only be related to a thermal relaxation of the t_{2g} electron system in terms of a thermally activated change in the position of the t_{2g} electrons. Indeed, the MAE spectra of magnetite can be quantitatively described by the assumption of integral valence sites, i.e. Fe^{2+} and Fe^{3+} ions, related to t_{2g} electrons involved in a process of thermally activated hopping from one site to another [11]. A description of the electronic structure of magnetite based on bands corresponding to electrons residing at only one sublattice therefore seems a good starting point for an analysis of the role of band structure effects in the Verwey transition.

Following Cullen and Callen [13], we furthermore assume that the orbital degeneracy is lifted by the crystal field, such that only one orbital contributes to the part of the t_{2g} band structure relevant for the Verwey transition. Such an approach has been deployed by many authors and proved to be quite useful in describing at least the gross features of the Verwey transition. The success of the approach outlined in [7] and [8] to describe the Verwey transition in both a qualitative and quantitative way, obtained without taking orbital degeneracy into account, suggests that we can indeed refrain from taking orbital degeneracy into consideration.

The density of states of each band can then be taken such that a *completely* filled band contains all t_{2g} electrons (it is shown in appendix A that this is a correct point of view).

Because of the Coulomb gap separating them, the occupations of the two sublattice bands will significantly differ at low temperatures, resulting in a charge-density wave. A simplified two-band level scheme for the spin-down 3d electrons is presented in figure 1. We consider two equivalent bands of equal width W and uniform density of states, identical for both sublattices. The difference between the two band minima, caused by the interionic Coulomb interaction, is indicated as U_C .

When treated within the narrow-band mean-field approximation outlined in [7] and [8], the contribution of the interionic Coulomb interaction to the effective one-electron Hamiltonian can be described as an on-site constant $U_i^{a,b}$ for all t_{2g} electrons at one of the octahedral sublattices (a or b). As a result we have a simple lowest-order perturbation problem for the description of the spin-down electron levels for both sublattices (bands). We define H_0 as the unperturbed Hamiltonian incorporating all interactions except the Coulomb interaction between the unpaired electron and Ψ_0 as an eigenstate of H_0 with eigenvalue E_0 . Considering $U_i^{a,b}$ as perturbation of H_0 we have, in a lowest-order approximation: $(H_0 + U_i^{a,b})\Psi_0 = (E_0 + U_i^{a,b})\Psi_0$. The energy levels E_0 of the spin-down electrons are shifted according to their respective sublattices (a or b) at which they reside over corresponding energy intervals U_i^a or U_i^b , whereas the wavefunctions do not change at all. A gap U_g between the sublattice bands occurs, which is related to the shift of the band minima U_C and the bandwidth W : $U_g = U_C - W$. Of course: $U_C = U_i^b - U_i^a$.

When $U_g > 0$, the lower band is completely filled and the upper band completely empty at zero temperature (consistent with the non-metallic state of magnetite for $T < T_V$). The distribution of the t_{2g} electrons over the a and b sublattices (N_a and N_b) as a function of T can be evaluated easily. In the case of a uniform DOS, D , the number of electrons N in an energy interval $E < E' < E + \Delta E$ at a particular temperature T can be expressed in terms of a simple Fermi–Dirac integral:

$$N = D \int_E^{E+\Delta E} f(E) dE = D[(E - E_F) - kT \log(1 + e^{\frac{E-E_F}{kT}})] \Big|_E^{E+\Delta E} \quad (1)$$

where $f(E)$ represents the Fermi–Dirac distribution and E_F the Fermi level. Taking for N the total number of t_{2g} electrons, the DOS can be expressed as $D = N/W$. For N_a and N_b we then have, by defining the band minimum of the a-sublattice band as $E = 0$ and substitution of the respective band edges of the a- and b-sublattice bands for E and $E + \Delta E$ into (1),

$$\begin{aligned} N_a &= N + \frac{kTN}{W} \log \frac{1 + e^{-E_F/kT}}{1 + e^{(W-E_F)/kT}} \\ N_b &= N + \frac{kTN}{W} \log \frac{1 + e^{(U_C-E_F)/kT}}{1 + e^{(W+U_C-E_F)/kT}}. \end{aligned} \quad (2)$$

The Fermi level can be determined from these equations and the condition $N_a + N_b = N$. After some algebra we have, for all temperatures:

$$E_F = \frac{U_C + W}{2} \quad (3)$$

i.e. an expression which describes a Fermi level exactly in the middle of the gap. Equations (2) and (3) enable us to express the degree of occupation $g = N_a/N$ of the a-sublattice by t_{2g} electrons in terms of U_C , W and T :

$$g = 1 + \frac{kT}{W} \log \frac{1 + e^{-(U_C+W)/2kT}}{1 + e^{-(U_C-W)/2kT}}. \quad (4)$$

The situation $g = 1/2$ corresponds to a disordered state whereas all other values of g between 0 and 1 correspond to a (partially) ordered state with either a majority of the t_{2g} electrons at the a sublattice ($g > 1/2$) or the b sublattice ($g < 1/2$). The quantity $r = |2g - 1|$ may serve as an appropriate order parameter as it varies between $r = 1$ in the fully ordered state and $r = 0$ in the disordered state.

A few remarks on the general validity of equation (4) should be made at this stage. The concept of band states related to an electron residing at a single sublattice is certainly valid at lower temperatures when the Coulomb splitting is sufficiently large. When, due to thermal excitation of electrons to the other band, the Coulomb splitting has decreased sufficiently, a regime of band overlap is finally reached. The states in the overlapping parts of the bands have an equal occupation and they change their nature by adopting an equally mixed a-and b-sublattice character: they no longer contribute to the asymmetric t_{2g} charge distribution over both sublattices. This effect is *numerically* dealt with in a proper way by equations (2) and (4). Although these equations do not specifically count for the change of the electron states in the overlapping band sections, the same degree of occupation is attributed to them, and therefore their net contribution to the charge density wave automatically vanishes. It is conceivable that also the states near the overlapping band sections may undergo some changes and that even when there is still no band overlap but U_C has decreased drastically states of a slightly mixed a or b character may occur. We assume however that, apart from temperatures very close to T_V , the influence of such changes is small in order to maintain a simple solvable model, which still captures some essential features of the Verwey transition however. Equation (4) is thereby considered as a good approximation even at high temperatures. A more exact analysis, for instance in terms of a tight-binding approach, including the variation of the electron states upon disordering, does not even make sense since the geometry of the sublattices, one of the necessary requirements for such an analysis, is still a highly controversial subject at present.

The shift, due to the interelectronic Coulomb interaction, of the band minima of the a and b bands (U_C) can be expressed in terms of g on the basis of previous work [7]:

$$U_C = (2g - 1)\beta \quad (5)$$

where β is a parameter related to the interionic Coulomb splitting $U = \beta$ of both bands in the fully ordered state.

Combination of (4) and (5) shows g as a solution of the equation

$$g = 1 + \frac{kT}{W} \log \frac{1 + e^{-[(2g-1)\beta+W]/2kT}}{1 + e^{-[(2g-1)\beta-W]/2kT}} = F(g). \quad (6)$$

This equation cannot be solved exactly by algebraic methods, but requires a numerical procedure or a graphical solution, the latter being quite elucidating.

An illustration of such a graphical solution for $W = 0.25\beta$ is given in figures 2(a)–(c), showing the function $F(g)$ for $0 < g < 1$ and $\beta > 0$ at three different temperatures, as well as the straight line $f(g) = g$. The intersections of $F(g)$ and $f(g)$ correspond to solutions of equation (6). At $T = 0$ (figure 2(a)) there are three solutions: $g = 0$, $g = 1$ and $g = 1/2$. The solution $g = 1/2$ corresponds to the disordered state while the remaining two solutions are related to equivalent ordered states. They represent the states of lowest free enthalpy below T_V , where ordering decreases the internal energy U [7, 8] and competes with the entropy term in the free enthalpy. The solution $g = 1$ corresponds to a situation where all t_{2g} electrons are at the a sublattice, the b sublattice being completely empty, whereas the solution $g = 0$ represents the reversed situation. The equivalence of both sublattices implies the equivalence of these two ordered-states. From the results reported in [8], it can be shown that in the ordered state the a-band levels are situated at $\Delta = U_C/2$ under the corresponding levels in the fully

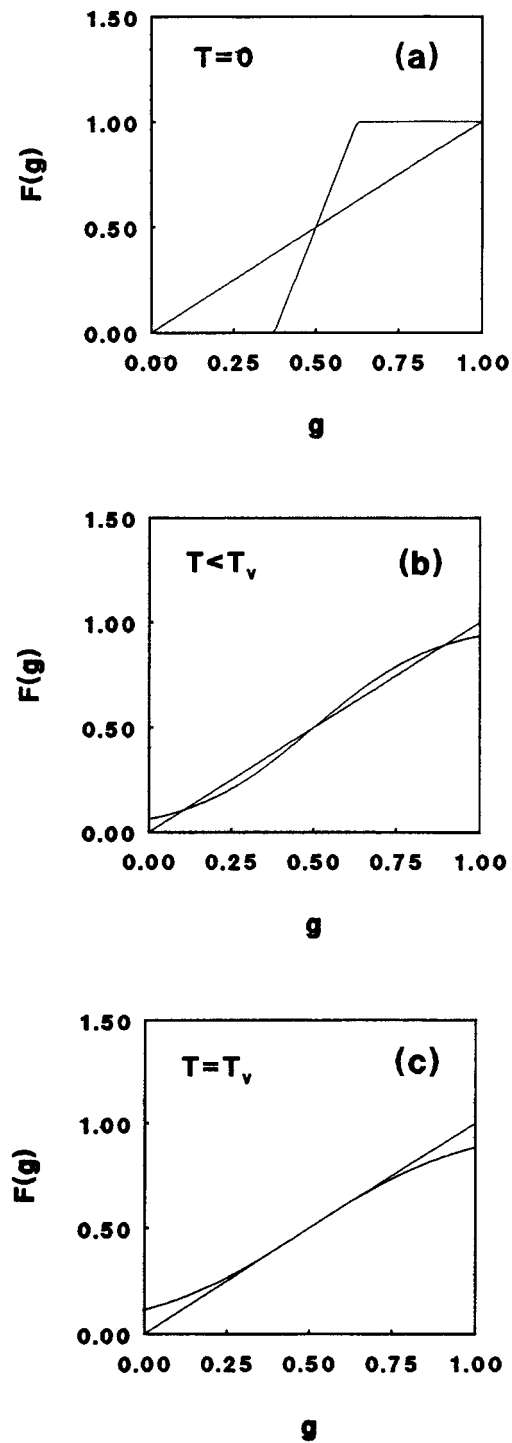


Figure 2. illustration of the graphical solution to equation (6). $F(g)$ is calculated for $a = 4$. At $T = 0$ (a) three solutions appear: two corresponding to an ordered state ($g = 0, g = 1$) and one to a disordered state for $g = 1/2$. With increasing temperature disordering sets in (b) until $g = 1/2$ is the only solution left at $T = T_v$ (c).

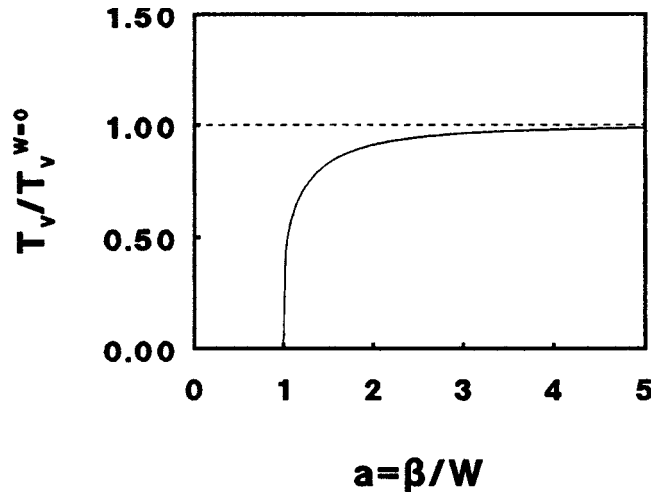


Figure 3. Variation of T_V with a .

disordered state ($g = 1/2$), whereas the b-band levels are lying at $\Delta = U_C/2$ above their corresponding levels for $g = 1/2$ (see figure 1).

At finite temperatures, the positions of the ordered states gradually move closer to $g = 1/2$, the typical characteristic of a process of gradual disordering (figure 2(b)). The Verwey temperature, T_V , can be identified as the temperature for which $g = 1/2$ becomes the only solution, marking the overall collapse of ordering (figure 2(c)). Naturally, $g = 1/2$ remains a solution of (6) for $T > T_V$, representing the disordered state.

Inspection of the basic features of the function $F(g)$ and its development with temperature shows that an ordered state is only possible when the derivative $\partial F(g)/\partial g > 1$ for $g = 1/2$. The Verwey temperature actually marks the temperature for which $\partial F(g)/\partial g = 1$ for $g = 1/2$. This allows us to find an explicit expression for T_V within the context of the model.

For $g = 1/2$ we have

$$\frac{\partial F(g)}{\partial g} = \frac{\beta}{W} \frac{e^{W/2kT} - e^{-W/2kT}}{2 + e^{W/2kT} + e^{-W/2kT}} = 1. \quad (7)$$

With $a = \beta/W$, solving for $\exp(W/2kT)$ yields

$$e^{W/2kT} = \frac{a+1}{a-1} \quad (8)$$

and consequently

$$T_V = \frac{1}{a \log[(a+1)/(a-1)]} \frac{\beta}{2k}. \quad (9)$$

Equations (8) and (9) show that the ratio between the Coulomb-interaction parameter β and the bandwidth in W has a pronounced effect on T_V . For a fixed value of β the Verwey temperature decreases with increasing W (decreasing a), as illustrated by figure 3, showing the relative variation of T_V with a . The reason for this decrease is primarily the occurrence of a bandoverlap at a certain temperature $T < T_V$. Since the bandshift (Coulomb splitting) is related exclusively to the asymmetry in the sublattice occupations, it is clear that the *overlapping* parts of both bands do not contribute to this bandshift, as they represent an equal number of electrons in each sublattice/band, thereby reducing U_C . A band overlap supports in this way the collapse of the Verwey ordering with temperature, an effect becoming stronger with increasing W . The two

level description outlined in the previous work is actually a limiting case of zero bandwidth: for $W \rightarrow 0$ ($a \rightarrow \infty$) the basic result for the two level system, $T_V^0 = \beta/4k$ [7, 8], immediately follows from the band model.

2.2. Stability of the Verwey order

A remarkable feature of figure 3 is the complete disappearance of T_V for $a = 1$ ($T_V \rightarrow 0$ when $a \rightarrow 1$). Apparently, the Verwey ordering becomes unstable when $\beta/W = 1$. A similar effect also occurs in the Cullen–Callen model [13–15]. On the basis of a Hartree approximation including nearest-neighbour Coulomb interactions and a hopping integral, t , Cullen and Callen found in their calculations that the Verwey order disappears below a critical ratio R_c between the (nearest-neighbour) Coulomb interaction parameter U and the bandwidth $W \propto t$: $R_c = U/w = 2.2$ [13]. This observation is known as the Cullen–Callen criterion. It is interesting to observe that by replacing U with β , which represents the Coulomb interaction parameter in our model, we obtain a criterion similar to the Cullen–Callen criterion, predicting a collapse of ordering at $R_c = \beta/W = 1$. The occurrence of this criterion in the present model, however, is not a unique artefact of the rectangular DOS which is assumed for both bands, but can be shown to apply equally well to a wide class of DOS functions taken into consideration. The condition $\beta/W < 1$ means that *if* a stable state exists, the bands overlap at $T = 0$. It is easy to see that, regardless of the actual shape of $D(E)$ and the ratio β/W , the disordered state ($g = 1/2$) is in fact a stable solution in this case. When $\beta/W < 1$, a (partially) ordered state however, with an occupation of the a sublattice $g \neq 1/2$, is possible at $T = 0$ *only* when the set of equations

$$\frac{1}{N} \int_0^{E_F} D(E) dE = g \quad \int_0^{E_F} D(E) dE + \int_{U_C(g)}^{E_F} D(E - U_C(g)) dE = N$$

with $U_C = \beta(2g - 1)$ is solvable for $g \neq 1/2$ and E_F as well. This is only the case for a limited class of functions $D(E)$ (of course not including a rectangular DOS, as may be verified easily). Therefore, the validity of the criterion $\beta/W > 1$ goes even beyond the rectangular DOS assumed in the above. As a result, a relevant viewpoint on the stability of the Verwey order emerges from a few simple concepts. The criterion $\beta/W = 1$ (being to some extent equivalent to the Cullen–Callen criterion) appears as a direct consequence of the impossibility of constructing a self-consistent, ordered charge distribution below a certain ratio of the Coulomb interaction and the bandwidth, even at $T = 0$. It is conceivable that even when the electron states change and adopt a mixed a and b character such a critical ratio still exists within the context of our model. g should then be calculated by integration over both bands, thereby including the a-sublattice occupation of each state as an extra factor in the integrand.

3. Differences between the Verwey transition in the first- and second-order regime: volume and band structure effects

As already mentioned in the introduction, the Verwey transition can manifest itself as a first- or a second-order transition depending on the cation doping of oxygen stoichiometry. The possible origin of the occurrence of these two regimes was outlined in a previous publication [8]. There it was shown that, within an approximation, the first-order transition consists of a discontinuous change from a fully ordered into a fully disordered state, whereas the second-order transition is based on a gradual disordering process. It was pointed out that the physical mechanism distinguishing between first- or second-order transitions is probably related to the dependence

of the interionic Coulomb interaction on the unit-cell dimensions. From this viewpoint a variety of aspects of both the first- and second-order transition could be explained. One pronounced, experimental observation could not be explained however, as discussed in the introduction: the discontinuous drop of the Verwey temperature of at least 5% at the boundary between the first- and second-order regimes.

By including band effects in the analysis of the Verwey transition an explanation for this observation may be given. It is reasonable to assume thereby that the influence of band effects is stronger for second-order transitions than for first-order transitions, especially when the band-gap is large compared to the bandwidth. Below T_V band effects become effective especially in the case of a band overlap, as shown in the previous sections. The first-order transition, being basically a spontaneous change from a highly ordered state into a completely disordered state (still high asymmetry in the band occupations when the transition takes place) is not likely to be associated with any band overlap at all below T_V [8]. Within a gradual (second-order) disordering process, however, the material goes through a stage of band overlap at temperatures near the transition temperature. Using earlier results [8] for the description of the first-order transitions and the model outlined in the previous sections, the experimental values for T_V as a function of the dopant concentration (or equivalently the cation deficiency (d)) can now be reproduced with reasonable accuracy for *both* the first and second-order regime.

For the sake of simplicity, we will totally neglect band effects in the first-order regime, but count for them in the second-order regime. Furthermore, it can be shown that, within the present model, volume effects, related to the electronic ordering (which modify the interionic Coulomb interaction and probably also the bandwidth), do *not* affect the value of the Verwey temperature in the *second-order regime* at all, whereas they do play a role in the first-order regime [8]. Volume effects are in fact related to the volume dependence of β , which may be expressed in terms of the change of the unit-cell volume (v) with respect to the disordered states as $\beta = \beta_0 + \beta_1 v$ [8]. As β determines g at a specific temperature, a coupling exists between g and v so that β can be considered as a function of g as well. In a disordering process of second order, both g and v therefore evolve in a continuous way with temperature when approaching T_V , and the volume dilatation induced by the electronic order becomes smaller and smaller ($|\beta_1 v| \ll |\beta_0|$): i.e. the system approaches the limiting case of zero volume effects where β is a constant. Similar considerations apply to the bandwidth. For temperatures near T_V (both smaller and larger) the system can therefore be considered as being without volume effects, with $\beta = \beta_0$, $W = W_0$ being constants. The Verwey temperature is simply given by equation (9). A more rigorous mathematical proof is given in appendix B. As an illustration of these ideas, figure 4 shows the calculated variation of the order parameter with T in the case of a second-order transition, both with volume affect ($\beta_1 > 0$) taken into account and without ($\beta_1 = 0$). The relation between g and v was calculated from the results of [8] ($W = \text{constant}$ in the calculation). The curves are slightly different from a qualitative point of view. Volume effects enhance the ordering below T_V (the order parameter becomes larger for $T < T_V$ due to volume effects) but T_V is the same for both cases, however.

The expression for T_V in the first-order regime, where volume effects do play a role, reads [8]

$$T_V = \frac{1}{7k} \left(\frac{3}{16} \kappa \beta_1^2 + \frac{6}{4} \beta_0 \right) \quad (10)$$

with κ representing the effective compressibility and β_1 the volume derivative of β being defined per electron (N.B. for convenience, in the present work the parameters β , β_0 and β_1 differ by a minus sign from the corresponding parameters in [8]).

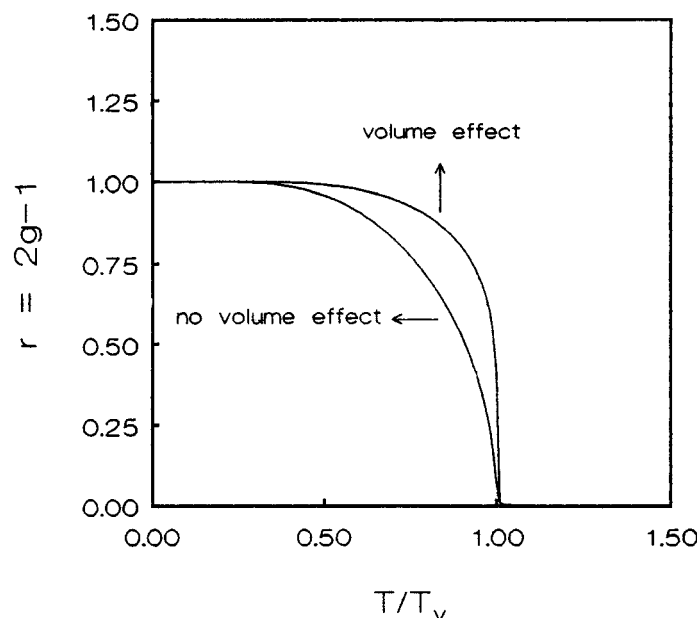


Figure 4. Variation of the order parameter for zero and non-zero value of the parameter β_1 accounting for the variation of the Coulomb interaction with the unit-cell volume. Both curves show the same value for T_V .

The experimental observation of a transition from a first- to a second-order regime for low concentrations (x) of cation dopants requires that $\frac{3}{4}\kappa\beta_1^2$ is slightly higher than β_0 for *undoped* magnetite [8]. Both terms decrease with x , respectively according to a second-order and first-order polynomial in x . A transition from a first- to a second-order regime takes place when $\frac{3}{4}\kappa\beta_1 = \beta_0$. The quadratic term in the polynomial expression for $\frac{3}{4}\kappa\beta_1^2(x)$ is significantly smaller than the linear term ($x \ll 1$). For low dopant concentrations (x) the nature of the variation of both β_0 and β_1^2 with x is therefore approximately still linear. In case of Ti- and Zn-doped magnetites, theory predicts [7], on the basis of trapping of t_{2g} electrons,

$$\beta_1^2(x) = (1 - 9x)^2\beta_1^2(0) \quad \beta_0(x) = (1 - 9x)\beta_0(0). \quad (11)$$

Substitution of these expressions into (10) yields the variation of T_V with x , approximately linear, in perfect agreement with the experimental observation in the first-order regime.

A final issue to be dealt with for a calculation of T_V values of doped (or cation deficient) magnetites is the influence of cation substitutions (deficiency) on the band structure, i.e. the way in which the DOS will evolve upon slight changes in the stoichiometry. If we consider for instance a very high dopant concentration, trapping a significant number t_{2g} of electrons [7], the spatial degrees of freedom of these electrons become considerably reduced and an electronic structure different from that of pure magnetite will be the result. Both the bandwidth as well as the DOS are likely to undergo some changes upon doping, which are, however, rather difficult to describe in a simple model. We will therefore investigate two special (limiting) cases: one in which the bandwidth will be held constant and the effect of cation doping consists of a change of D only (thereby $a = \beta/W$ decreases with increasing cation doping), and the opposite scenario in which D remains constant and W changes proportional to the number of trapped electrons, leaving $a = \beta/W$ a fixed quantity. The model outlined in section 2 is capable of

dealing with both of these cases and the experimental data will be fitted on the basis of both scenarios.

Verwey temperatures were calculated by application of (10) and (11) to the first-order and (9) and (11) to the second-order regime. In the first-order regime we have only $\beta_0(0)$ as an adjustable parameter. The quantity $\kappa\beta_1^2(0)$ can be directly related to $\beta_0(0)$ by combination of equation (11), which describes the variation of β_1 with x in terms of $\beta_1(0)$, and the requirement that at the critical concentration ($x_c = 0.012$) $\frac{3}{4}\kappa\beta_1^2(x_c) = \beta_0(x_c)$ [8]. In the second-order, where equation (9) is used to calculate T_V , we have $a = \beta/W$ as a second adjustable parameter. In the approach where W remains constant as a function of x , $a = a(x)$ differs for each concentration according to

$$a(x) = \frac{1 - 8x}{1 - 8 \times 0.012} a(0.012) \quad (12)$$

where $a(0.012)$ is the value of $a(x)$ at the critical concentration. In the case where W is assumed to be proportional to the number of trapped t_{2g} electrons (i.e. also proportional to β) a remains fixed. The model parameters were fitted to the experimental data in a least squares procedure by *simultaneous* adjustment of $\beta_0(0)$ and a (or $a(0.012)$) to match the data for *both* regimes.

For constant W we find $\beta_0(0) = 0.04$ eV and $a(0.012) = 3.407$ for the best agreement between the calculated and experimental data (see figure 5(a)). A fairly good agreement between theory and experiment is observable. For $W \sim \beta$ we find $\beta_0(0) = 0.04$ eV, $a = 2.864$ (figure 5(b)). The agreement between theory and experiment for the second-order regime is even slightly better in this case than in figure 5(a) (for figures 5(a) and 5(b) the least squares sums differ by approximately 50%). There is a plausible explanation for this improvement as the case of constant W (figure 5(a)) is in fact the least realistic of the two situations considered here. Note that the value for $\beta_0(0)$ found here is the same for both cases, probably because it yields the best reproduction of the data in the first-order regime, for which, neglecting of band effects, $\beta_0(0)$ is the only adjustable parameter.

The value $\beta_0(0) = 0.04$ eV is consistent with experimental results reported in the literature. Estimates of the Coulomb interaction parameter for pure magnetite can be obtained, for instance, from measurements of the thermoelectric force as performed by Kuipers and Brabers [16], giving $\beta \approx 0.05$ eV $\pm 10\%$, whereas data obtained by photoemission spectroscopy indicate an approximately similar value of β [17], which should be taken as half of the gap in the emission spectrum. In the case of pure magnetite β is given by $\beta = \beta_0(0) + \kappa\beta_1^2(0)/4$ [8]. From equation (11) and the condition $\frac{3}{4}\kappa\beta_1^2(0.012) = -\beta_0(0.012)$ we find $\frac{1}{4}\kappa\beta_1^2(0) = 0.37\beta_0(0)$, giving $\beta = 1.37\beta_0(0) = 0.055$ eV, a value consistent with the experimental data reported in [16] and [17].

Estimates for W can be derived straightforwardly from these values. For the situation of constant W we have $W = \beta_0(0.012)/a(0.012) \approx 0.012$ eV and for the case where $W \sim \beta_0$ we find $W(0) = \beta_0(0)/a \approx 0.014$ eV. Note that these are very low values indeed, inherent to a system of highly localized electrons such as magnetite.

The best fitting values of respectively a and $a(0.012)$ mentioned above refer to the ratio between $\beta_0(0)$ and W in pure magnetite. From these results we obtain a value of $a' = \beta/W \approx 4.6$ in the case of a fixed W -value and $a' = \beta/W \approx 3.9$ for $W \sim \beta_0$, corresponding to estimates for the Coulomb bandgap of pure magnetite ($U_g = U_C - W = \beta - W$) of respectively 0.043 and 0.041 eV. It should be kept in mind that the values for both the gap and the bandwidth are subject to a slight uncertainty because the bandwidth in the disordered state may differ somewhat from those in the ordered state (see appendix B).

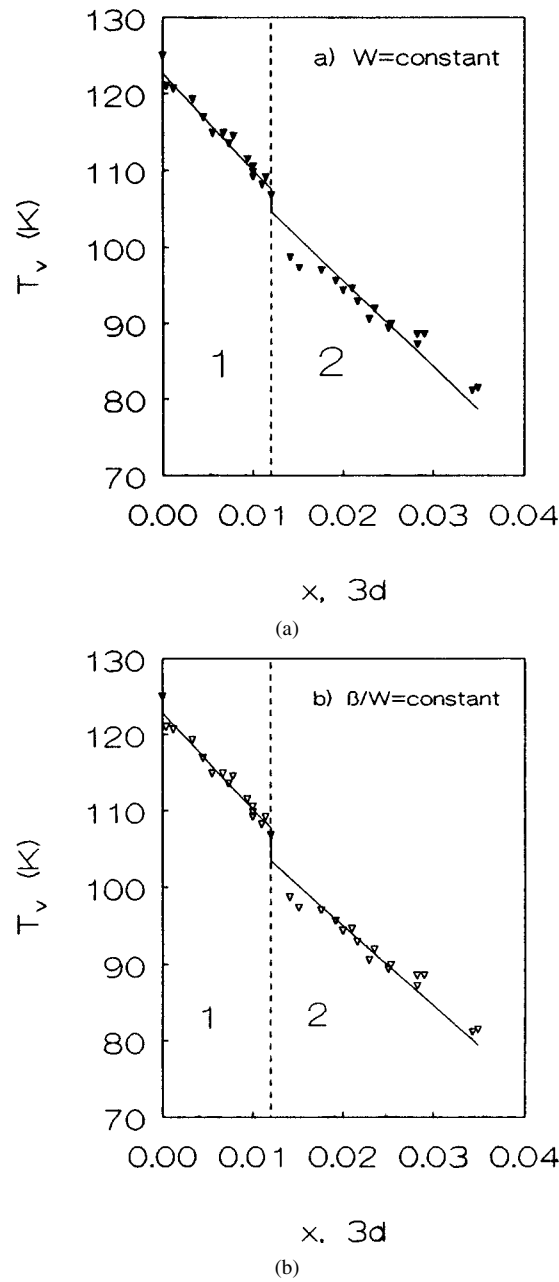


Figure 5. Variation of T_V in the first- and second-order regime. Datapoints correspond to either Zn^{2+} or Ti^{4+} substituted magnetites (x = concentration) or to samples with a cation deficiency $d(\text{Fe}_{3-3d}\text{O}_4)$ having the same effect as Zn^{2+} and Ti^{4+} substitutions. The data were taken from [18]. The drawn lines represent the least-squares fits based on our model for constant W (a) or $W \propto \beta$ (b).

4. Discussion and conclusions

A mean-field approach for the Verwey transition, advanced by the present authors in previous papers [7,8], has been extended by incorporation of a phenomenological treatment of

band-structure effects. The t_{2g} electrons are thereby distributed over two bands, the band minima of which are shifted due to the interionic Coulomb interaction. In this respect the model shows a conceptual similarity to the Stoner model for itinerant ferromagnetism. In both our model for the Verwey transition outlined here and the Stoner model, ordering appears as the result of an asymmetric occupation of two bands which are shifted due to a collective interaction.

A special, exactly solvable case of the model occurs when a rectangular density of states is assumed for both bands. An important observation from the solution to this case is that the ratio $a = \beta/W$ between the interionic Coulomb interaction and the bandwidth has a dramatic effect on the value of the Verwey temperature near $a \approx 1$.

The model has the following properties, which either give a satisfactory explanation to various phenomena related to the Verwey transition or support earlier theoretical concepts.

- (1) Only when $a > 1$ is the Verwey temperature finite. When a becomes unity the Verwey temperature becomes zero, marking the boundary of the stability range of the Verwey ordering. It is shown that this effect applies to a wide class of DOS functions assumed in the calculations and may therefore be considered as a more general property of the band model presented in this paper. In this respect it is crucial that no ordered self-consistent charge distribution at $T = 0$ exists when $a < 1$. A resemblance to the Cullen–Callen criterion is evident. This is particularly interesting because, although frequently used for the interpretation of experimental data, the Cullen–Callen criterion was sometimes criticized and questioned in the past [15]. Our model, however, supports the validity of qualitative considerations based on the Cullen–Callen criterion, irrespective of questions as to whether, for instance, the Hartree approximation which leads to the Cullen–Callen criterion is an appropriate method to deal with the Verwey order [15].
- (2) It can be shown that volume effects, which play a crucial role in the first-order transitions, do not affect the Verwey temperature in the case of second-order transitions. On the other hand, it is plausible that band effects only play an important role in case of the second-order transitions. The model outlined in section 2 can therefore be applied straightforwardly to the second-order regime, while the first-order regime can still be analysed in terms of previous theoretical results. Consistent with experiment, the calculated Verwey temperatures for two limiting cases ($W \propto \beta$ and $W = \text{constant}$) drop by approximately 5% when the boundary between the first- and second-order regime of the Verwey transition is passed. Fairly good agreement between theory and experiment for both cases is achieved by adjustment of the parameters accounting for the interionic Coulomb interaction and the bandwidth. It is remarkable that the precise form of the density of states used in the calculation is apparently of minor importance for the reproduction of the experimental data. The value for the Coulomb interaction parameter, obtained from the fit of the model parameters to the experimentally observed variation of T_V with x , is consistent with experiment. The value for the bandwidth obtained from the analysis of the experimental data is extremely small and could be considered as a justification for the use of a two level description for first-order transitions, for instance in pure (undoped and stoichiometric) magnetite [8, 14]. Such small bandwidths also support a *polaronic* band picture which is not accessible by conventional (*ab initio*) electronic structure calculations, which yield much wider bands [19] or even no band splitting at all [20].

The apparent success of the present model to reproduce the values for the Verwey temperature correctly in both the first- and the second-order regime shows that this model meets some basic aspects of the mechanisms controlling the Verwey transition. Generally, we may conclude that the work presented in this paper provides a valuable extension to our previous

mean-field analyses of the Verwey transition [7, 8]. Altogether, many aspects of the Verwey transition in magnetite can now be interpreted fairly well in terms of a simple theory, which apparently captures however the most basic physical concepts behind the Verwey transition.

Appendix A. Number of electron states per volume unit in a single band

Both sublattices a and b are equivalent in a crystallographic sense. Not only do symmetry operators S connect the sites of a single sublattice ($S_{aa} = S_{bb}$) but there also exists a symmetry operator S_{ab} , connecting the a sites to the b sites. Generally, such symmetry operators can be constructed from translations followed by rotation(s). We consider symmetry operators for which $S \neq S^{-1}$, i.e. operators for which S^2 connects three different sites. Multiplication of such operators can be viewed as a propagation through the lattice. In case of an ordered state there is a distinction between the a and the b sublattice and we may define S_{ab} such that $S_{ab}^2 = S_{aa} = S_{bb}$. In the case of a disordered state, the distinction between the a and the b sublattice disappears and we can choose S_{aa} , S_{bb} and S_{ab} such that $S_{aa} = S_{bb} = S_{ab}$.

In general, the crystal Hamiltonian is invariant under a symmetry operation $S_i = R S_{aa,bb}$ consisting of one of the operators $S_{aa,bb}$, connecting two sites of the same sublattice, followed by a subsequent rotation R . The invariance of the Hamiltonian under S_n implies that the (effective) single-electron wavefunctions $\psi_{E,k}$ are eigenfunctions of S_i as well: $S_i \psi_{E,k} = \lambda \psi_{E,k}$. The operators S_{aa} , S_{bb} and S_{ab} can be defined such that they connect sites along a main crystallographic direction c . When periodic boundary conditions are imposed along this direction over large numbers of unit cells N we have

$$S_{i_o}^n \psi_{o,E,k} = \lambda_o^n \psi_{o,E,k} = \psi_{o,E,k} \quad (\text{A1})$$

$$S_{i_d}^{2n} \psi_{o,E,k} = \lambda_d^{2n} \psi_{o,E,k} = \psi_{o,E,k} \quad (\text{A2})$$

for the ordered and the disordered state respectively. n is related to N and to the number of a–b pairs, n_{ab} , per unit cell in the c direction simply by $n = N n_{ab}/2$, basically representing the number of electrons. An analogy to Bloch's theorem exists in that way that equations (A1) and (A2) can only be fulfilled when respectively

$$\lambda_o = e^{i\phi_o} \quad e^{in\phi_o} = 1 \quad \phi_o = \frac{2\pi j}{n} \quad (\text{A3})$$

for the ordered state and

$$\lambda_d = e^{i\phi_d} \quad e^{i2n\phi_d} = 1 \quad \phi_d = \frac{\pi j}{n} \quad (\text{A4})$$

for the disordered state ($j = \text{integer}$). So, the effect of S_i acting on ψ is a phase rotation corresponding to an angle ϕ . Each value of ϕ corresponds to a specific eigenstate of the Hamiltonian.

A single band is related to a full cycle $\Delta\phi = 2\pi$ of the phase angle. It can then be inferred immediately from (A3) and (A4) that in the disordered state the number of eigenfunctions forming a single band is twice the number of electrons i.e. $2n$. In the ordered state however, only n eigenfunctions fill a single band. So, due to electronic ordering the half-filled metallic band splits up into two bands with an equal number of n electron states per band, regardless of the actual geometry of the sublattices (a, b). In the case of a gap between the two bands, the lower band is completely filled and the upper completely empty so that an insulating state emerges.

Appendix B. The influence of volume effects on T_V in the case of a second-order transition

In section 2, the expression for T_V is derived from the condition $\partial F(g)/\partial g|_{g=1/2} = 1$. In the corresponding analysis of T_V , the Coulomb-interaction parameter as well as the bandwidth were supposed to be constant. However, when volume effects are taken into consideration in the description of the Verwey temperature, this is no longer the case. Volume effects connected with the Verwey transition arise from the coupling between g and the volume, established by the volume dependence of the interionic Coulomb interaction and the bandwidth. As a consequence, β will generally depend as well on g in this case.

It is most convenient then to express β as a series expansion around $g = 1/2$:

$$\beta = \beta(g) = \beta_0 + \sum_{n=1}^{\infty} \beta_n (g - \frac{1}{2})^n \quad (\text{B1})$$

so that the expression for $U_C = \beta(2g - 1)$ becomes

$$U_C = \left(\beta_0 + \sum_{n=1}^{\infty} \beta_n (g - \frac{1}{2})^n \right) (2g - 1) = \sum_{n=0}^{\infty} \beta'_n (g - \frac{1}{2})^{n+1} \quad (\text{B2})$$

where $\beta'_n = 2\beta_n$ for $n \geq 0$. Usually only the lowest order terms are relevant, leading to a continuous variation of β with g [8].

The bandwidth W can also be written as a series expansion in g around $g = 1/2$. Symmetry requires that this expansion contains only even terms:

$$W(g) = \sum_n w_{2n} (g - \frac{1}{2})^{2n} \quad (\text{B3})$$

where $n \geq 0$. The reason for the absence of odd terms in this series is the fact that there are two equivalent ordering modes ($g = g_0 \leq 1/2$ and $g = 1 - g_0 \geq 1/2$) which should correspond to the same value of W at a given value of the order parameter $r = |2g - 1|$. Due to the absence of a linear term in (B3), the influence of changes in the band structure vanishes rapidly with increasing disorder.

For an analysis of the Verwey temperature similar to the one outlined in section 2, we introduce a new function $F'(g, \beta(g))$, obtained by substitution of $\beta(g)$ and $W(g)$ in the expression for F (equation (6)). As a function of g , F' behaves qualitatively similar to the function F , since only the lowest-order terms in (B2) and (B3) are relevant in the vicinity of T_V , leading to a monotonic variation of β with g . T_V can therefore again be obtained from the condition $\partial F'/\partial g|_{g=1/2} = 1$. For $g = 1/2$, $\partial W/\partial g$ vanishes because of (B3) so that we have

$$\left. \frac{\partial F'}{\partial g} \right|_{g=1/2} = \frac{1}{2W} \frac{e^{W/2kT} - e^{-W/2kT}}{2 + e^{W/2kT} + e^{-W/2kT}} \left. \frac{\partial U_C}{\partial g} \right|_{g=1/2}. \quad (\text{B4})$$

It can be seen immediately from (B2) that when $g = 1/2$:

$$\left. \frac{\partial U_C}{\partial g} \right|_{g=1/2} = 2\beta_0 \quad (\text{B5})$$

as all terms for $n > 0$ arising from U_C vanish. This result yields, when substituted into (B4), exactly equation (7) with $\beta = \beta_0$, which directly leads to equation (9) for T_V . Equation (9) was derived without taking any volume effects into account. Therefore, T_V is not affected by volume effects in the case of a second-order transition and is determined solely by the value for β in the disordered state (β_0) and the ratio between the Coulomb interaction and the bandwidth (W_0) in the disordered state (a).

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