The role of volume effects in the Verwey transition in magnetite

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Abstract. Fe^{2+}/Fe^{3+} ordering in magnetite is described in terms of a simple mean-field approach based on an effective interionic Coulomb potential. It is shown that first-order electronic order–disorder transformations, as reported in the literature, can only be reproduced when the dependence of the interionic potential on the unit-cell dimensions is taken into account. In this case the first-order transitions can then be viewed as the result of an interplay between the lattice-deformation energy and the free-energy contribution related to the electronic ordering of the octahedral Fe lattice. Furthermore, the effect of the lattice deformation by hydrostatic pressure on the Verwey transition can be successfully explained to some extent within the context of the same framework. In comparison to experimental data available from the literature, the mean-field approach developed in this paper yields very acceptable results with respect to both qualitative and quantitative aspects, thus opening an interesting new viewpoint on the mechanism of the Verwey transition.

1. Introduction

Since its discovery the Verwey transition in magnetite (Fe_3O_4) has been the subject of numerous investigations. As early as the 1930s Verwey *et al* suggested that the phase transition in magnetite near 125 K, as observed by anomalies in the thermal-expansion and the electric and magnetic properties, consists of an electronic order–disorder transformation at the Fe^{2+}/Fe^{3+} octahedral sublattice [1]. Verwey's interpretation of the phase transition was based on measurements of the conductivity against temperature, showing that the conductivity increases discontinuously by orders of magnitude at the transition. In fact, the low-temperature phase transformation in magnetite became one of the first insulator–metal transitions reported ever. The phenomenon has never lost attention ever since. Lately, for instance, the Verwey transition has often been referred to as an example of charge-ordering phenomena in connection with the colossal magnetoresistance of perovskites [2].

Among many other intriguing issues, the classification (order) of the electronic phase transition at the Verwey transition itself is an interesting topic that has been extensively investigated [3]. In stoichiometric magnetite the Verwey transition is first order. With increasing cation deficiency or with increasing concentration of cation substitutes for the Fe ions at the octahedral lattice sites, however, the transition becomes second order. Honig and co-workers dealt with this aspect of the Verwey transition both experimentally and theoretically [4–6]. Their theoretical investigations consist of a description of the Verwey transition in terms of a mean-field approximation originally advanced by Strässler and Kittel (SK) [7]. The method is capable of describing some qualitative aspects of the Verwey transition in a rather formal and mathematical way. A drawback of the implementation of the SK method by Honig *et al*

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is that the actual mechanism responsible for the electronic order and its collapse at the Verwey temperature is not clearly specified, even when such a precise specification is not required for a more qualitative description of the Verwey transition. So far, a transparent explanation of an ordering mechanism capable of dealing with both first- and second-order electronic phase transitions has not been given in the literature. The present authors recently proposed a model for electronic ordering in magnetite in terms of an effective interionic Coulomb potential [8]. Though offering a successful (semi-) quantitative explanation for the Verwey transition, our approach was, however, unable to deal with problems related to the order of the Verwey transition. We hereby present an extension of our previous treatment that points to the physical mechanisms leading to first-order transitions and how they are suppressed to yield second-order transitions by cation deficiency or cation substitutions.

2. Mean-field model based on an effective interionic Coulomb potential

The basic concept of our model is that the unpaired 3d electrons responsible for the electronic ordering at the octahedral lattice (2^+ electrons) can occupy the sites of two equivalent sublattices (a and b). In the perfectly ordered state one of the sublattices is fully occupied while the other one is fully empty. Driven by the entropy term in the free energy, the 2^+ electrons are distributed statistically over both sublattices with increasing temperature until at the Verwey temperature both sublattices are equally occupied. In a mean-field approach, the (Coulomb) interaction energy of the 2^+ electrons at the respective a and b sublattices can be expressed in terms of the degree of occupation (g) of the a sublattice and two interaction constants (M_1 and M_2) mainly related to the Madelung energy [8]:

$$U_a = -(gM_1 + \alpha(1-g)M_1 + (1-g)M_2 + \alpha g M_2)$$
$$U_b = -((1-g)M_1 + \alpha g M_1 + g M_2 + \alpha(1-g)M_2). \tag{1}$$

The parameter M_1 thereby counts for the interaction of a 2^+ electron with other 2^+ electrons in the same sublattice, whereas M_2 corresponds to the interaction of the electron with the other sublattice. The constant $\alpha = 3/2$ represents the ratio of the ionic charges of the Fe^{3+} and Fe^{2+} ions.

The internal energy of the total ensemble of 2^+ electrons can now be expressed as

$$U = \tfrac{1}{2}N(gU_a + (1-g)U_b) = \beta g^2 - \beta g + \gamma \tag{2}$$

where N is the total number of 2^+ electrons and

$$\beta = N(\alpha - 1)(M_1 - M_2)$$
$$\gamma = -\tfrac{1}{2}N(M_1 + \alpha M_2). \tag{3}$$

The factor 1/2 should be included in (2) to avoid double countings. The variable g varies between $g = 1$ in the ordered state and $g = 1/2$ in the disordered state. By substitution of $g = 1$ into (1) and evaluation of $U_a - U_b$, β/N can be identified as the difference between the a-sublattice and b-sublattice 2^+ electron levels in the perfectly ordered state.

The quantity $r = 2g - 1$ can be viewed as the order parameter of the problem as r varies between $r = 1$ for $g = 1$ and $r = 0$ for $g = 1/2$. By substitution of $g = (r+1)/2$, (2) and (3) then transform into

$$U = \frac{\beta}{4}r^2 + \gamma' \qquad \gamma' = \tfrac{1}{4}N(1+\alpha)(M_1 + M_2) \tag{4}$$

where γ' can be viewed as the internal energy of the total ensemble of 2^+ electrons in the disordered state ($r = 0$), whereas $\beta r^2/4$ counts for the variation of the internal energy upon ordering.

To establish an expression for the Helmholtz free energy $F = U - TS$ as a function of r we must also find an expression for the entropy $S(r) = k \ln W(r)$. Based on similar considerations as the SK method [7], we take for W the number of independent ways to realize a state having gN electrons at the a sublattice and $(1 - g)N$ electrons at the b sublattice:

$$W = \left[\frac{N!}{(N - gN)!(gN)!} \right]^2.$$ (5)

By application of Stirling's formula to (5) and substitution of the result together with (3) and (4) into $F = U - TS$ the Helmholtz free energy for $g \neq 0, 1$ can then be expressed as

$$F = \beta g^2 - \beta g + \gamma - 2NkT(-g \ln g - (1 - g) \ln(1 - g))$$

$$= \frac{\beta}{4} r^2 + \gamma' - 2NkT \left(-\frac{r+1}{2} \ln \frac{r+1}{2} - \frac{1-r}{2} \ln \frac{1-r}{2} \right)$$ (6)

as $N \to \infty$ in the thermodynamic limit.

In thermodynamic equilibrium, r adopts a value r_e for which (6) reaches its lowest minimum on the interval $0 \leqslant r \leqslant 1$. Generally r_e depends on temperature. The procedure of minimizing (6) with respect to r (i.e. solving the equation $\partial F / \partial r = 0$) cannot be carried out completely by algebraic methods but requires a numerical procedure in its final stage. Especially for smaller r-values however, the free energy can be approximated very accurately by a power-series expansion of S in r up to the fourth order, giving

$$S \approx -\frac{Nk}{6} r^4 - Nkr^2 + Nk2 \ln 2$$

and consequently:

$$F \approx \frac{NkT}{6} r^4 + \left(NkT + \frac{\beta}{4} \right) r^2 - NkT2 \ln 2 + \gamma'.$$ (7)

Higher order expansions S and F contain only even terms $(a_{2n} r^{2n})$ with positive coefficients $(a_{2n} > 0)$. An approximate calculation of r_e is now quite straightforward. Depending on T and the sign and magnitude of β, equation (7) yields either one or two (real) solutions to $\partial F / \partial r = 0$:

$$r = 0 \; \forall \; \beta, T \qquad r = \sqrt{-3 \left(1 + \frac{\beta}{4NkT} \right)}; \quad -\frac{4}{3} \leqslant \frac{\beta}{4NkT} \leqslant -1.$$ (8)

The upper solution $r = 0$ represents a disordered state whereas the lower solution represents the (partially) ordered state. The ordered state is only stable when $\beta < 0$, that is when electronic order leads to a decrease of the internal energy U (see equation (4)). A very important observation is that the free energy as expressed by (7) always yields a *second-order* transition at a temperature

$$T_v = -\frac{\beta}{4Nk}$$ (9)

i.e. the order parameter gradually decreases with T until it becomes zero at $T = T_v$, marking the transition to the disordered state. This second-order transition is a direct consequence of the sign of the expansion coefficients a_{2n} in the free-energy expansion. In the ordered regime only the coefficient of the quadratic term is negative while all the others $(2n \geqslant 4)$ are positive. Below T_v, the minimum in the $F(r)$–r curve will therefore gradually move towards $r = 0$ with increasing temperature. As a result, a discontinuous transition from an ordered electron configuration to the disordered state is not possible and, at least within our model, the entropy-driven electronic disordering process does in itself not provide a mechanism for

the observed first-order transitions in magnetite. For an explanation of this type of transition, additional degrees of freedom and their corresponding contribution to the free-energy should be taken into account as well. Furthermore, the interaction constants M_1 and M_2 (i.e. β) should parametrically depend on these additional degrees of freedom, establishing a coupling between the order parameter r and the equilibrium values of the newly introduced degrees of freedom. The lattice parameters evidently provide a set of additional degrees of freedom fulfilling this requirement: directly related to the interionic Coulomb interactions, the interaction parameters explicitly depend on the unit-cell dimensions and symmetry. The experimental observation of both distortions and expansion of the lattice at the Verwey temperature as well as a pronounced dependence of T_v on hydrostatic pressure are indeed strong indications for a coupling between the symmetry and dimensions of the lattice and the electronic order parameter. Incorporating this coupling into our analysis imposes a description in terms of the Gibbs rather than the Helmholtz free energy, i.e. we have to extend equation (7) by adding a term (G_v) related to the lattice deformation and pressure effects. A detailed analysis of the lattice-deformation energy in terms of the actual unit cell dimensions is rather tedious. We therefore adopt a simplified point of view in which we neglect (small) distortions of the crystal axes and we write the lattice-deformation as an expansion of the unit cell volume rather than the different lattice parameters, thereby disregarding the anisotropy of the lattice deformation. This latter approximation is justified because it is known from experiment that near the Verwey transition both the lattice parameters and the unit-cell volume are monotonic functions of T [9]. Furthermore we neglect the effect of thermal expansion, which is only very small near T_v. We define the volume expansion v as the deviation of the unit cell volume from the value for the disordered state at atmospheric pressure p_0. Demanding $\partial G_v / \partial v = 0$ and $v = 0$ at p_0 for the disordered state, it is clear that the lowest order approximation G_v takes the form

$$G_v = \frac{b}{2} v^2 + (p - p_0) v \tag{10}$$

where the quadratic term stands for the deformation energy with b serving as an effective bulk modulus, and the linear term represents the pressure contribution. The effective bulk modulus incorporates the volume dependence of all free energy contributions *not* depending on r or p, including γ' (see equation (4)), which can be considered as additional constants. To make the internal pressure at $p = p_0$ vanish, the first volume derivatives of these contributions cancel in the disordered state, which is in fact also an equilibrium state for $T \geqslant T_v$. The lowest-order variation of the r- and p-independent part of the deformation energy, being described in terms of the deviation (v) from the unit-cell volume in the *disordered* state at $p = p_0$, therefore consists of a quadratic term $1/2bv^2$. When ordering sets in however, the lowest order deformation energy is no longer necessarily a term quadratic in v. Due to the volume dependence of β, an r- and v-dependent variation of the free energy occurs in addition to the term counting for the deformation energy due to r- and p-independent free energy contributions ($1/2bv^2$). In a lowest-order approximation this term is linear in v, and the volume dependence of the interaction constant β is therefore expressed by a (lowest-order) linear term:

$$\beta = \beta_0 + \beta_1 v. \tag{11}$$

Combining (7), (10) and (11), the expression for the free energy becomes:

$$G = \frac{NkT}{6} r^4 + \left(NkT + \frac{\beta_0 + \beta_1 v}{4} \right) r^2 + \frac{b}{2} v^2 + (p - p_0) v \tag{12}$$

where irrelevant constant terms have been left out. For a given value of r the total volume-dependent contribution to the free energy (G_v') consists of a pure deformation part and a part proportional to r^2 related to the coupling of r and v as a result of the volume dependence of

β. Since $b > 0$, v will only be nonzero if the contribution proportional to r^2 is negative and its absolute value larger than the absolute value of the (positive) term related to the elastic deformation, so that a nonzero volume deformation becomes preferable from an energetic point of view if the condition

$$G'_v = \frac{\beta_1 r^2}{4}v + \frac{b}{2}v^2 + (p - p_0)v < 0 \tag{13}$$

holds. Similar to the disordered state, the first volume derivative of G should vanish also in the (partially) ordered state (i.e. $\partial G / \partial v = 0$) to make the internal pressure vanish.

The stationary points of the free-energy expression (12) are represented by

$$r = 0 \qquad r = \sqrt{-3\left(1 + \frac{\beta_0 + \beta_1 v}{4NkT}\right)} \qquad 0 < r \leqslant 1 \tag{14}$$

$$v = -\frac{\beta_1 r^2}{4b} - \frac{(p - p_0)}{b} = v_e + v_p. \tag{15}$$

When v, as expressed by (15), corresponds to a global minimum (i.e. the condition (13) is fulfilled), a volume deformation arises, which consists of a contribution from the electronic ordering v_e and a pressure contribution v_p. Elimination of v from the free-energy expression can be achieved in that case by resubstitution of (15) into (12), leaving an expression for F in terms of r only:

$$G = \left(\frac{NkT}{6} - \frac{1}{32}\kappa\beta_1^2\right)r^4 + \left(NkT + \frac{\beta_0 - \kappa\beta_1(p - p_0)}{4}\right)r^2 \tag{16}$$

where $\kappa = 1/b$. Equation (16) represents a second-order polynomial in r^2. The equilibrium value of r (r_e) corresponds to the global minimum of F on the interval $0 \leqslant r \leqslant 1$ and depends on the sign and magnitude of both polynomial coefficients, which are functions of temperature. Notice that $G = 0$ for the disordered state ($r = 0$). The temperature dependence of these coefficients ($a_4 = (NkT/6 - \kappa\beta_1^2/32)$ and $a_2 = NkT + (\beta_0 - \kappa\beta_1(p - p_0))/4$) leads to a temperature dependence of r_e. Depending on the values of β_0 and β_1 both first- and second-order transitions from an ordered to a disordered state are possible (N.B. If we put $\beta_1 = 0$ and $\beta_0 = \beta$ the free-energy expression (16) reduces to the r-dependent part of equation (7) (i.e. equation (7) without γ' as an irrelevant constant), which yields only second-order transitions. The equilibrium state is not influenced by volume effects in this case). When $\beta_1 \neq 0$, we have $a_4, a_2 < 0$ at $T = 0$ and G reaches its minimum value for $r = 1$, corresponding to a fully ordered state at zero temperature. With increasing temperature both a_4 and a_2 will increase linearly with T and both pass through zero at generally different temperatures. We define T_4 as the temperature at which a_4 passes through zero and T_2 as the temperature for which $a_2 = 0$. The expressions for a_4 and a_2 yield

$$T_4 = \frac{3}{16}\frac{\kappa\beta_1^2}{Nk} \qquad T_2 = -\frac{1}{4}\frac{\beta_0 - \kappa\beta_1(p - p_0)}{Nk}. \tag{17}$$

For $p \geqslant p_0$ two qualitatively different scenarios may occur in connection to the difference between T_4 and T_2. For $T_4 < T_2$ the function $G(r)$ will adopt a global minimum at $r = r_{\min} > 0$ for $T > T_4$ ($a_2 < 0$ and $a_4 > 0$ for $T_4 < T < T_2$ in this case). With increasing T the value of $r_{\min}$ decreases and eventually enters the interval $0 \leqslant r \leqslant 1$, marking the onset of gradual disordering (see figure 1). When $a_2 = 0$ a second-order phase transition takes place, the ordering temperature being equal to $T_v = T_2 = -\beta_0/4Nk$ for $p = p_0$. This scenario is not qualitatively different from the order–disorder transformation in the absence of a volume effect.
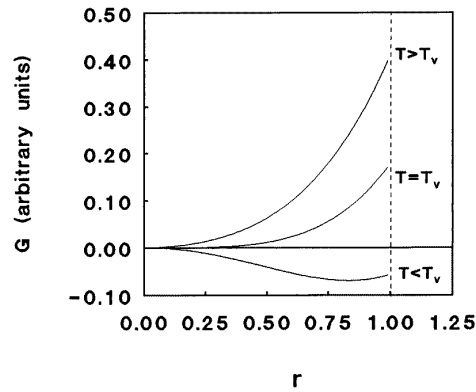
Figure 1. The variation of Gibbs free energy with r at various temperatures in the case of a first-order transition ($T_4 < T_2$).
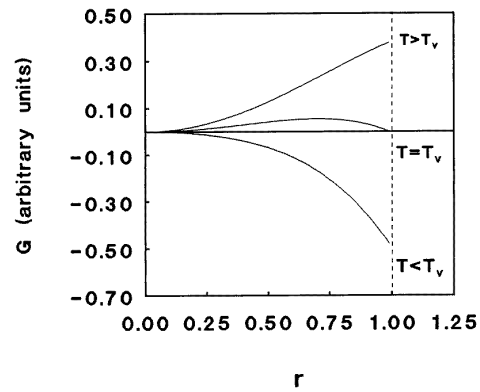
Figure 2. The variation of Gibbs free energy with r at various temperatures in the case of a second-order transition ($T_4 > T_2$).

When $T_2 < T_4$ ($a_2 > 0$ and $a_4 < 0$ for $T_2 < T < T_4$) the situation is entirely different (see figure 2). In this case the function $G(r)$ adopts a global maximum at $r_{max} > 0$ for $T > T_2$. With increasing temperature the value of r_{max} increases. At $T = T_2$, $r = 1$ still corresponds to the minimum free-energy value but with increasing T this minimum value $G_{r=1}$ steadily increases towards zero. At a certain critical temperature $G_{r=1} = G_{r=0} = 0$. In such a case a discontinuous, first-order transition from a fully ordered to a fully disordered state takes place. This scenario resembles the situation in stoichiometric magnetite as revealed by experiments (at $p = p_0$) [6]. A crucial observation is that, according to the analysis presented here, the occurrence of first-order transitions is directly related to the volume effect connected with electronic ordering as a result of volume-dependent interaction constants.

An expression for the Verwey temperature in the case of a first-order transition can be derived in a straightforward way. Putting $r = 1$ in equation (16) and demanding that $G_{r=1}$ vanish ($G_{r=1} = G_{r=0}$) yields for the critical temperature (T_v) at which the first-order transition takes place

$$T_v = \frac{3\kappa\beta_1^2/16 - 6[\beta_0 - \kappa\beta_1(p - p_0)]/4}{7Nk}. \tag{18}$$

At $p = p_0$, in fact, the values of the parameters β_0 and β_1 determine whether the order–disorder transformation will be first or second order, as may be inferred from equation (17). The respective conditions for the phase transition to be first or second order ($T_4 > T_2$ and $T_4 < T_2$) can then be expressed in terms of β_0 and β_1 as follows:

$$\frac{3}{4}\kappa\beta_1^2 + \beta_0 > 0 \qquad \text{first order}$$
$$\frac{3}{4}\kappa\beta_1^2 + \beta_0 < 0 \qquad \text{second order}. \tag{19}$$

3. Qualitative and quantitative verification of the model

The existence of two regimes of respectively first- and second-order transitions in magnetite, related to the cation deficiency or substitute concentration [6], can be explained in terms of the conditions (19). As outlined in a previous paper [8], the effect of cation substitutions at the octahedral lattice or a cation deficiency consists of a (partial) blocking of the electron-exchange mechanism necessary to establish the long-range ordering scheme. The result is that

a fraction of the 2^+ electrons (y) is very strongly localized, thereby limiting the number of 2^+ electrons actually participating in the ordering–disordering process. For low contents of cation substitutions or low cation deficiencies, the interaction parameters decrease linearly with the fraction y of blocked, strongly localized 2^+ electrons:

$$\beta = (1-y)\beta_{y=0} = (1-y)\beta_{0,\,y=0} + (1-y)\beta_{1,\,y=0}v \tag{20}$$

so that the model parameters β_0 and β_1 should be considered as functions of y:

$$\beta_0 = (1-y)\beta_{0,\,y=0} \qquad \beta_1 = (1-y)\beta_{1,\,y=0}. \tag{21}$$

The fraction y is proportional to the oxygen parameter δ or the substitute concentration x ($y = c_\delta \delta$, $y = c_x x$ where c_x depends on the valency of the substituted cations). Considering the dependence of β_1 and β_0 on δ and x, equation (19) incorporates the possibility of a sharp transition from a first- to second-order regime with increasing δ or x when $3/4\kappa\beta_{1,\,y=0}^2$ is only a *little* larger than $|\beta_{0,\,y=0}|$ (recall that $\beta_0 < 0$). As β_1 appears in a quadratic form in (19), whereas β_0 only as a linear term, the term $\frac{3}{4}\kappa\beta_1^2$ will decrease more strongly with δ or x than $|\beta_0|$. As a result critical values of δ and x exist, for which $\frac{3}{4}\kappa\beta_1^2 + \beta_0 = 0$, marking the transition between the two regimes. In the case of magnetite a sharp transition of this nature has been observed indeed in measurements on highly stoichiometric samples.

As in our model $\frac{3}{4}\kappa\beta_1^2$ has to be almost equal to $-\beta_0$ to make the transition from the first- to a second-order regime possible, the value of T_v is, within the context of the model, mainly determined by the value of β_0, as can be verified from equation (19). For low values of x and δ the contributions to T_v linear in x or δ dominate over the quadratic contributions, resulting from the term $3\kappa\beta_1^2/16$ and T_v will depend approximately linearly on x and δ in this case. This observation agrees with experiment [10]. For Ti and Zn substitutions the critical concentration is approximately $x_c \approx 0.012$ and $c_x = 9$ [8]. From these values and combination of (19), (20) and (21) we estimate $\kappa\beta_1^2 \approx -1.49\beta_0$ for pure magnetite.

So far we have seen that the model yields qualitatively correct results. A quantitative check of the applicability of the model is therefore a logical next step. Reproduction of the experimentally observed value of T_v is a key element in such a test. Taking $p = p_0$ and considering $\beta = \beta_0 - \kappa\beta_1^2/4$ ($r = 1$ below T_v), the expression (18) for T_v can be rearranged as

$$T_v = \frac{6}{7}\frac{-\beta}{4Nk} - \frac{3}{7}\frac{\kappa\beta_1^2}{16Nk}. \tag{22}$$

Estimates for β can be obtained from measurements of the electrical transport properties, indicative of a value $\beta/N \approx 0.05$ eV $\pm 10\%$ [8]. Since $\beta = \beta_0 - \kappa\beta_1^2/4$ by definition and for pure magnetite $\kappa\beta_1^2 \approx -1.49\beta_0$, we can estimate $\kappa\beta_1^2 \approx -1.09\beta$. By substitution of this estimate and the experimentally estimated β-values into (22) the model yields for the Verwey temperature $T_v = 107$ K $\pm 10\%$. This result is in fairly good agreement with the experimental value of $T_v \approx 123$ K, even slightly better than the result of $T_v \approx 145$ K $\pm 10\%$ reported in our previous paper [8], which did not include the effects of the lattice deformation.

For a last crucial test of our model we focus on a comparison of the influence of pressure on T_v as predicted by the model, and the experimental data available on this issue. Such a comparison is particularly important, as it indicates whether the parametric dependence of the free energy on the unit cell dimensions is correctly described by the approximate expression (12). As outlined before, the distinction between first- and second-order Verwey transitions for different substitute concentrations appears as a direct consequence of this expression due to the way in which the parametric dependence of G on the unit-cell volume occurs in it. An indication that the volume dependence of G is indeed correctly incorporated into equation (12) would

therefore strongly corroborate the viewpoints outlined in this paper on the Verwey transition and the role of volume effects therein.

Measurements of T_v as a function of hydrostatic pressures even up to 60 kbar have shown that T_v decreases *linearly* with pressure at a rate of $dT_v/dP = -0.27$ K kbar^{-1} for $0 < p < 60$ kbar [11, 12]. Equation (18) indeed predicts a linear relationship between p and T_v. As may be inferred from equation (15), the quantity $-\kappa\beta_1/4$ can be identified as the volume expansion v_e induced by complete electronic ordering ($r = 1$), which corresponds to the discontinuous volume change that occurs when a first-order transition is passed while decreasing temperature ($r = 0 \rightarrow r = 1$). The pressure-induced shift of T_v can be expressed in terms of v_e as

$$\Delta T_v(p) = -\frac{6v_e(p - p_0)}{7Nk}. \tag{23}$$

The value for the relative volume expansion ($\Delta V/V$) induced by the Verwey order in pure magnetite is known from literature: $\Delta V/V = 6 \times 10^{-4}$. As this value is positive equation (23) indeed predicts the experimentally observed decrease of the T_v with increasing pressure. A quantitative reproduction of the experimental data can be obtained as well. By taking N for the number of 2^+ electrons per cubic metre (1.35×10^{28}), substitution of 6×10^{-4} for v_e in equation (23) yields $dT_v/dp = -0.276$ K kbar^{-1}: an excellent agreement with experiment.

4. Conclusions

We have presented a modified mean-field method describing electronic ordering in magnetite in terms of a volume dependent long-range Coulomb interaction. Both first- and second-order electronic phase transitions can be described in terms of the presented method, as well as the experimentally observed transition from a regime of first- to second-order phase transitions with increasing cation deficiency δ or cation substitute concentration x. First-order transitions can be identified as a direct consequence of the relation between the interionic interaction strength and the unit cell dimensions. The linear dependence, predicted by the model, of T_v on δ, x and p is consistent with experiment. The experimental values for T_v and its pressure derivative dT_v/dp are reproduced very well by the model. In general, the outlined analysis in terms of interionic interactions combined with lattice deformation effects provides a unique interpretation of the Verwey transition. The incorporation of the lattice deformations into the model, and its apparent success, offers a new viewpoint.

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