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Temperature-Dependence of the Cation Distribution in Ferrimagnetic Spinels

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The cation distribution at some equilibrium temperature in ferrimagnetic spinels can be inferred provided the contributions to the cationic site energies are established. In some compounds, e.g. magnesioferrite, the distribution is strongly dependent on temperature. This is explained by taking into account suitable thermal energy terms in addition to electrostatic or crystal-field octahedral stabilisations. The $Fe_3O_4/Mg_\delta Fe_{3-\delta}O_{4-(\delta-1)/2}$ system is considered and the temperature-dependence in magnesioferrite is discussed. A comparison is made of the theoretical derivation with several experimental data.

1. Introduction

Experimental and theoretical investigations have been carried out by several authors [1-5] on the influence of quenching temperatures on the cation distribution of ferrimagnetic spinels. In fact, some spinel substances, e.g. $Cu^{2+}Fe_2{}^{3+}O_4$, $Mg_\delta{}^{2+}Fe^{3+}{}_{3-\delta}O_{4-(\delta-1)/2}$, $Mg_t{}^{2+}Ni_{1-t}{}^{2+}Fe_2{}^{3+}O_4$, $Ni^{2+}Al_t{}^{3+}Fe_{2-t}{}^{3+}O_4$, etc, are sensitive to their thermal history. The distribution of cations among different oxygen co-ordination lattice sites in equilibrium conditions is due to the magnitude of the cation energies in each of the permissible sublattices, the tetrahedral and the octahedral one.

If Néel's hypothesis of antiparallel alignment between spins of the paramagnetic cations in opposite lattice sites is made, saturation magnetisation data at low temperatures are sometimes successfully used to infer the cation distribution [6]. Such data are not alone sufficient to determine the distribution without further assumptions; if the spinel unit formula contains several paramagnetic cation species or contains paramagnetic cations whose spectroscopic g-factors in one or both sublattices are unknown, and/or the formula contains a very high diamagnetic cation concentration which is responsible for a weakening of the antiferromagnetic superexchange linkages. The first and the third of the above obstacles can be overcome, with suitable assumptions.

A recent investigation [7] on thermodynamic equilibrium conditions in ferrimagnetic crystals containing any number of co-ordination sublattices and cation species led to the determination of the cation distribution, provided the magnitudes of the sublattice cationic energies are known. However, the equilibrium equations do not include explicitly temperature-dependent energy terms.

It is the purpose of this paper to investigate to what degree the cationic energies are relevant to provide a satisfactory picture of the temperature-dependence of the distribution in some simple ferrimagnetic system. By so doing, we wish to extend the results of the previous treatment to a special interesting case.

In order to correlate the mentioned derivations with the present approach, we choose to study the solid solution $Mg_{t\delta}{}^{2+}\ Fe_{1-t}{}^{2+}\ Fe_{2-(\delta-1)t}{}^{3+}\ O_{4-(\delta-1)t/2}$, one of whose end compositions is the well-known temperature-sensitive magnesium ferrite $Mg_\delta{}^{2+}\ Fe_{3-\delta}{}^{3+}\ O_{4-(\delta-1)/2}$. Special emphasis is given to this composition, which is written in a nonstoichiometric form owing to different conclusions drawn by several workers [6, 8, 9]: we thus assume that δ is a suitable number, $1.0 \leq \delta \leq 1.3$.

2. Equilibrium Equations

Fe_3O_4 is known to be a completely inverted spinel, while magnesioferrite is nearly inverted when quenched at low equilibrium temperatures and nearly random when quenched at very high equilibrium temperatures.

By enclosing with round brackets the tetrahedral, and with square brackets the octahedral cations in the spinel formula, the solid solution composition can be written:

$$(\mathrm{Mg}_{x\delta}{}^{2+}\ \mathrm{Fe}_{y}{}^{2+}\ \mathrm{Fe}_{1-x\delta-y}{}^{3+})[\mathrm{Mg}_{(t-x)\delta}{}^{2+}\ \mathrm{Fe}_{1-t-y}{}^{2+}\ \mathrm{Fe}_{1+t+y-(t-x)\delta}{}^{3+}]\mathrm{O}_{4-(\delta-1)t/2} \qquad 0 \leq t \leq 1 . \tag{1}$$

x and y are the tetrahedral fractions per formula of Mg^{2+} and Fe^{2+}, respectively. The equilibrium conditions with respect to cation transfer among the octahedral and tetrahedral sublattices are:

$$(1 - x\delta - y)/x\delta = D[1 + t + y - (t - x)\delta]/(t - x)\delta$$

$$(1 - x\delta - y)/y = E[1 + t + y - (t - x)\delta]/(1 - t - y) \tag{2}$$

$$T_1 = T_2 , \quad p_1 = p_2 ;$$

where

$$D = \exp[(\epsilon_{\mathrm{Mg}}{}^{(1)} - \epsilon_{\mathrm{Mg}}{}^{(2)}) - (\epsilon_{\mathrm{Fe}^{3+}}{}^{(1)} - \epsilon_{\mathrm{Fe}^{3+}}{}^{(2)})]/\mathrm{k}T$$

$$E = \exp[(\epsilon_{\mathrm{Fe}^{2+}}{}^{(1)} - \epsilon_{\mathrm{Fe}^{2+}}{}^{(2)}) - (\epsilon_{\mathrm{Fe}^{3+}}{}^{(1)} - \epsilon_{\mathrm{Fe}^{3+}}{}^{(2)})]\ \mathrm{k}/T. \tag{3}$$

T and p are temperatures and pressures, k is the Boltzmann constant, subscripts and superscripts 1 and 2 refer to quantities related to the tetrahedral and octahedral sites, respectively. The ϵ's are the energies associated with the indicated cations and sublattices.

A first approximation is made by setting $\epsilon_{\mathrm{Fe}^{3+}}{}^{(1)} = \epsilon_{\mathrm{Fe}^{3+}}{}^{(2)}$, which results from crystal-field theory considerations [10, 11]. D and E retain hereafter such modified meanings. The solution of equations 2 will provide x and y as functions of t, the solid solution parameter. An approximate solution is given by*

$$x = [2E + (1 - \mu)t]\delta t/[(2D + \lambda t)(2E + 1 - \mu t) + (1 - t)\delta t]$$

$$y = [2D + (\lambda - \delta)t](1 - t)/[(2D + \lambda t)(2E + 1 - \mu t) + (1 - t)\delta t] \tag{4}$$

with $\lambda = \delta - D(\delta - 1)$, $\mu = 1 + E(\delta - 1)$.

Equations 4 would be greatly simplified if the solid solution range were between $\mathrm{Fe_3O_4}$ and a stoichiometric $\mathrm{MgFe_2O_4}$. The following expressions would then be obtained:

$$x = Et/[E(2D + t) + D(1 - t)],$$

$$y = D(1 - t)/[E(2D + t) + D(1 - t)]. \tag{4'}$$

The two end compositions have the distributions

$$y = (2E + 1)^{-1}, \quad \mathrm{Fe_3O_4} \tag{5}$$

$$x = (\gamma D + 1)^{-1}, \quad \mathrm{Mg}_{\delta}\,\mathrm{Fe}_{3-\delta}\,\mathrm{O}_{4-(\delta-1)/2} \tag{6}$$

with $\gamma = (3 - \delta)/\delta$.

3. Site Stabilisation and Vibrational Energies

Taking advantage of the fact that for the end compositions x and y depend respectively on D and E only, it will be suitable to analyse these two spinels.

$\mathrm{Fe_3O_4}$: with the above outlined approximation, $E \simeq \exp[(\epsilon_{\mathrm{Fe}^{2+}}{}^{(1)} - \epsilon_{\mathrm{Fe}^{2+}}{}^{(2)})/\mathrm{k}T]$. We assume that the octahedral stabilisation energy of a Fe^{2+} ion is of the order of 9 kcal/g atom [12]; at the high solid state reaction temperature of about 1500° K this provides the value $E \simeq 20$ and consequently, $y \simeq 0.025$.

The rather high octahedral stabilisation energy of Fe^{2+} allows us to disregard, in first approximation, the small thermal contribution. By indicating with $S(\mathrm{Fe}^{3+}) = 5/2$, $S(\mathrm{Fe}^{2+}) = 2$ the spin angular momentum quantum numbers and by $g_{(1)}(\mathrm{Fe}^{2+})$, $g_{(2)}(\mathrm{Fe}^{2+})$ and $g(\mathrm{Fe}^{3+}) = 2.00$ the spectroscopic splitting factors of the iron ions, the magnetisation in Bohr magnetons per formula at 0° K is:

$$n_{\mathrm{B}} = 10y + 2[g_{(2)}(\mathrm{Fe}^{2+})(1 - y) - g_{(1)}(\mathrm{Fe}^{2+})y] . \tag{7}$$

Also the relation $g_{\mathrm{eff}}\,(2 + y) = n_{\mathrm{B}}$ holds. We assume the value $g_{\mathrm{eff}} = 2.06$, as found by Bickford [13] by means of ferromagnetic resonance measurements at 120° K.

The $g_{(2)}$ (Fe^{2+}) value cannot be much different, owing to the almost inverse distribution of $\mathrm{Fe_3O_4}$: by setting $g_{(2)}$ $(\mathrm{Fe}^{2+}) = 2.1$, we obtain $g_{(1)}$ $(\mathrm{Fe}^{2+}) = 4.0$ and $n_{\mathrm{B}} = 4.1$, in agreement with experimental measurements [14]. It is well known [15] that $\mathrm{Fe_3O_4}$ has a first-order orthorhombic $\rightleftharpoons$ cubic transition at 119° K: in what follows we shall neglect its implications as far as ferrimagnetic effects are concerned, thus considering the n_{B} values below 119° K as extrapolated from the spinel phase magnetic moments.

$\mathrm{Mg}_{\delta}\,\mathrm{Fe}_{3-\delta}\,\mathrm{O}_{4-(\delta-1)/2}$†: the temperature-independent octahedral stabilisation energy of a Mg^{2+} ion is of the order [16] of 3 kcal/g atom. Considering the limiting value at low quenching temperatures given by Epstein and Frackiewicz [2], we assume $\Delta\epsilon = 3.15$ kcal/g atom. It is now

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*For a similar derivation, see Appendix II of reference 7.

†It is our purpose to avoid further consideration on the nature of nonstoichiometry of the spinel, i.e. whether the latter has to be ascribed to interstitial Mg^{2+} [17] or oxygen deficiency. With the adopted formulae we follow the second approach, although both models deserve consideration.

necessary to rewrite D in the more convenient form:

$$D = \exp \{[(\epsilon_{\text{non-th}}^{(1)} + \epsilon_{\text{th}}^{(1)}) - (\epsilon_{\text{non-th}}^{(2)} + \epsilon_{\text{th}}^{(2)})]/kT\} . \quad (8)$$

All quantities are referred to Mg-ions : the $\epsilon_{\text{non-th}}$ terms are the non-thermal, mainly electrostatic negative energies, while the ϵ_{th} terms are the vibrational positive energies per cation in tetrahedral and octahedral sublattices. At this point it seems natural to consider the ϵ_{th}'s as Debye energies related to Mg^{2+} in each sublattice. Owing to the relatively high quench temperatures of experimental interest and in order to deal with simple algebra, we set:

$$\epsilon_{\text{th}}^{(i)} = 3k\Theta_E^{(i)}/[\exp(\Theta_E^{(i)}/T) - 1] \; / \; i = 1, 2 \quad (9)$$

secluding the zero-point energy amidst the non-thermal contributions and thus assuming the Einstein approximation for the thermal energy.

The difference between thermal energies, even at high temperatures, does not exceed a few kcal/g atom, but it may be a relevant contribution when the electrostatic and other non-thermal energy differences $\Delta\epsilon$ are small, as in the present case.

In the previous Fe_3O_4 case, the contribution of the stabilisation energy is much larger, so that we may disregard the thermal contributions.

In MgO, with NaCl structure, the Mg-ions are octahedrally co-ordinated with a cation-anion distance of 2.10 Å [18]. In the magnesium ferrite, the octahedrally co-ordinated Mg-ions are 2.05 Å apart, the tetrahedrally co-ordinated ones 1.90 Å apart from the anions with the average lattice parameter $a_0 = 8.39$ Å and $u = 0.381$ [19]. The Debye temperature of MgO is $\Theta_D = 772°$ K [20]. On the basis of the above data, taking into account the considerable emptiness of the spinel unit cell* and the rather small cation-anion tetrahedral distance, the following crude assumptions are made: the vibrational energy associated with an Mg^{2+} ion in a octahedral site is given by 9 with $\Theta_E^{(2)} = 600°$ K, that in a tetrahedral site is given by 9 with $\Theta_E^{(1)} = 1500°$ K.

It is worth noting that the chosen temperatures are within reasonable ranges of the magnitudes found on oxide materials. Summarising, the cation distribution, when $t = 1$, is given by:

$$x(T) = \{\gamma \exp[[\Delta\epsilon - 3k\Theta_E^{(2)}(\exp\Theta_E^{(2)}/T - 1)^{-1} + 3k\Theta_E^{(1)}(\exp\Theta_E^{(1)}/T - 1)^{-1}]/kT] + 1\}^{-1} \quad (10)$$

where $\Delta\epsilon$ is the non-thermal octahedral stabilisation energy.

From the above derivation it follows that $\lim_{T \to \infty} x = (\gamma + 1)^{-1}$: at high temperatures, x will be larger, the larger δ is (nonstoichiometry), as confirmed by comparison between the experimental measurements of references 1, 2 and 5.

In fig. 1 a comparison is made between the cation distribution curve drawn from equation 10 with $\delta = 1.06$ and several experimental measurements from the literature; also plotted are: the curve obtained from Pauthenet and Bochirol's [23] expression† and that obtained from Epstein and Frackiewicz [2]. It is seen that while Pauthenet and Bochirol's curve has the lower values at high temperatures, Epstein and Frackiewicz's curve approaches Kriessman and Harrison's experimental magnetic measurements on $MgFe_2O_4$ and the curve of this work approaches Mozzi and Paladino's X-ray and magnetisation experimental data on $Mg_{1.06}Fe_{1.94}O_{3.97}$.

4. Discussion

Several authors [1, 2, 4, 5] have found good agreement between experimental fractional tetrahedral Mg^{2+} ions, x, versus quenching temperatures, T, and the theoretical distribution equation:

$$(1 - x\delta)(1 - x)/x[2 - (1 - x)\delta] = \exp[(\Theta_0 - x\Theta_1)/\delta T] \quad (11)$$

where Θ_0 and Θ_1 are suitable constants having a temperature dimension. The numerator of the argument in the right-hand side of equation 11 clearly shows a dependence of the energy on the distribution parameter x itself.

Equation 11 represents a particular case of a detailed treatment of the statistical thermodynamics underlying the distribution of cations over the tetrahedral and octahedral sites in a ternary spinel, developed by Callen, Harrison and Kriessman [24] several years ago. By considering the different contributions to the energy these authors indicated the Madelung energy as the most important non-thermal one.

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*Anderson quotes for MgO, $\Theta_D = 930°$ K; furthermore that Θ_D in spinel $MgAl_2O_4$ is less than Θ_D in MgO and in Al_2O_3 [21].

†In their equation, Pauthenet and Bochirol assumed a constant value of the stabilisation energy. See the discussion below.

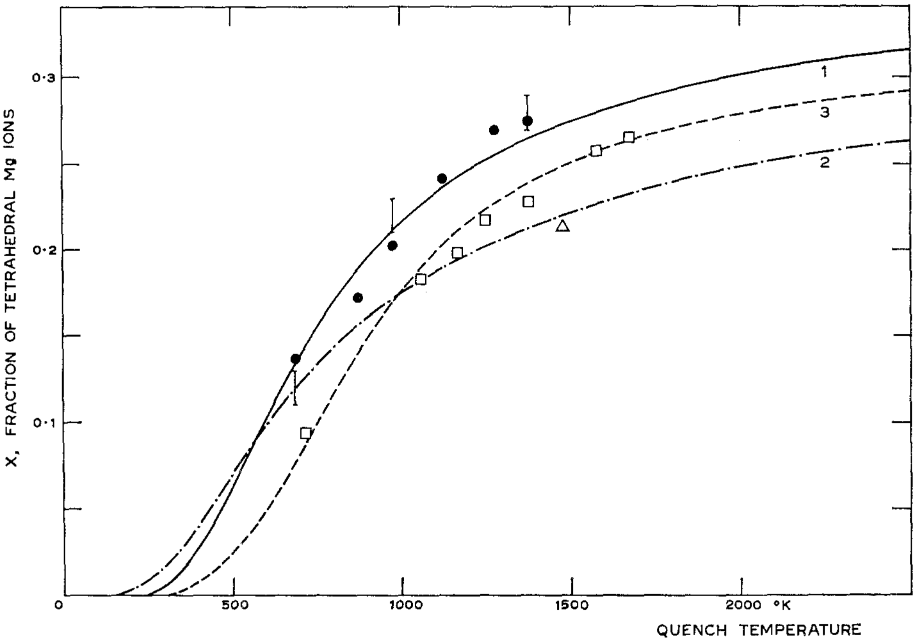

Figure 1 Tetrahedral fraction of Mg-ions versus quenching temperature in $Mg_{\delta}Fe_{3-\delta}O_{4-(\delta-1)\frac{1}{2}}$. Curve 1: theoretical, from this work; curve 2: theoretical, from Pauthenet and Bochirol [23]; curve 3: theoretical, from Epstein and Frackiewicz [2]; I: experimental, X-ray, Mozzi and Paladino [5]; ●: experimental, saturation magnetisation, Mozzi and Paladino [5]; □: experimental, Kriessman and Harrison [1]; △: experimental, Blasse [22].

The thermal contributions were approximated to the high temperature, equipartition limit of the Debye vibrational spectrum and subsequently neglected in the works of references 1, 2, 4 and 5. In an earlier study [25] Verwey, de Boer and van Santen derived a numerical expression of the Madelung energy in a spinel structure as a function of the average cationic charge in the tetrahedral sites for variable magnitudes of the oxygen-parameter, u. The Madelung energy is seen to change appreciably (also by more than 7%) (when the tetrahedral site charge varies strongly) and for certain values of u. In the magnesioferrite case, though, the tetrahedral charge varies from $+2.9$ when $x = 0.1$ to $+2.7$ when $x = 0.3$, and the oxygen-parameter remains constant, $u = 0.381$ [5]; it can be seen that in these conditions the Madelung energy difference is very small, of the order of 0.2%.

Not even the small variation of the lattice parameter from 8.385 Å for $x = 0.12$ to 8.398 Å for $x = 0.28$, as reported by Mozzi and Paladino [5], can give rise to an appreciable influence on the Madelung energy difference. Kriessman and Harrison [4] treated the problem of cation distributions of the system $Mg_tNi_{1-t}Fe_2O_4$. They found out that Θ_1 decreases rapidly to zero as the solid solution approaches the $NiFe_2O_4$ composition, which is an almost inverse and temperature-insensitive spinel [19]. The same trend for Θ_1 was found earlier [1] by the same authors on $Mg_tMn_{1-t}Fe_2O_4$ spinels, as $t \rightarrow 0$.

In our opinion, all the reported facts can be summarised as follows:

(i) Madelung energy differences depend strongly on the distribution when the conditions calculated by Verwey, de Boer and van Santen hold, which implies also that the cationic states must be mainly spherically symmetric.

(ii) When crystal-field energies preponderate over purely electrostatic ones, as for Ni^{2+}, Mn^{3+}, etc, in spinels, the distribution dependence of the energy tends to disappear, owing to the strong cation-lattice interactions.

(iii) When Madelung energy differences are small owing either to small tetrahedral charge variation or to the favourable magnitude of the u-value or to both, other contributions to the energy differences must be taken into account to explain the temperature-dependence of the distribution. The cation distribution problem in magnesioferrite seems to fall within this case.

On the other hand, one is induced to accept the distribution dependence of the energy, owing to the linear behaviour of the numerator of the exponent versus x in equation 11, as was shown in the work of reference 5. In fig. 2 the values of the total (thermal and non-thermal) energy of Mg^{2+} ions calculated by means of equation 10 are plotted versus x values as derived from Mozzi and Paladino's X-ray and magnetic measurements. The latter are derived with the aid of the formula

$$x = [n_B + 5(\delta - 1)]/10\,\delta \qquad (12)$$

where n_B is the saturation magnetisation in Bohr magnetons per molecule extrapolated to 0° K. In the same figure, the theoretical total energy as derived with the adopted values of $\Theta_E^{(1)}$, $\Theta_E^{(2)}$ and $\Delta\epsilon$ is plotted.

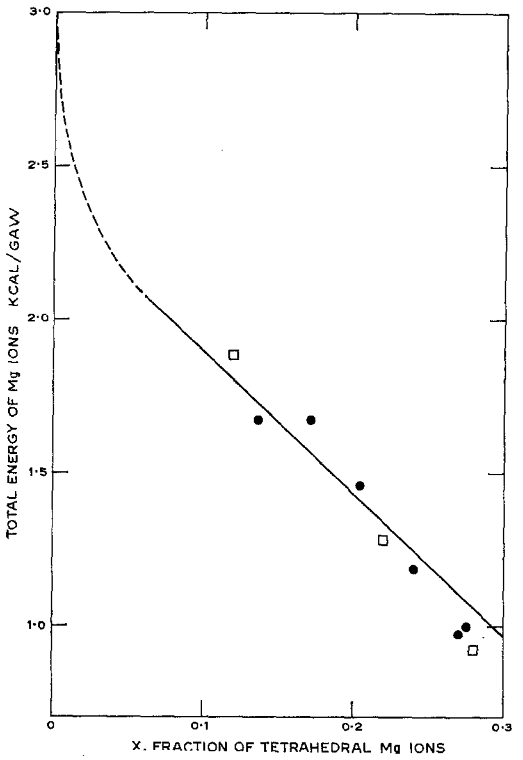

Figure 2 Total (electrostatic + thermal) energy per Mg-ion in $Mg_{1\cdot06}Fe_{1\cdot94}O_{3\cdot97}$ versus fractional tetrahedral Mg, x. Continuous line: theoretical curve, as derived from this work; ●: derived from experimental magnetic measurements (Mozzi and Paladino [5]) through equation 11; ☐: derived from experimental X-ray measurements (Mozzi and Paladino [5]) through equation 11.

We would like to attract the attention of the reader to the linearity of the curve in the range of experimental interest. It could seem at first sight that the total energy of Mg^{2+} ions depends directly on the distribution, but equation 10 demonstrates that this dependence occurs via the temperature. The steep increase of the theoretical curve in the vicinity of $x = 0$ is not physically explained, at present.

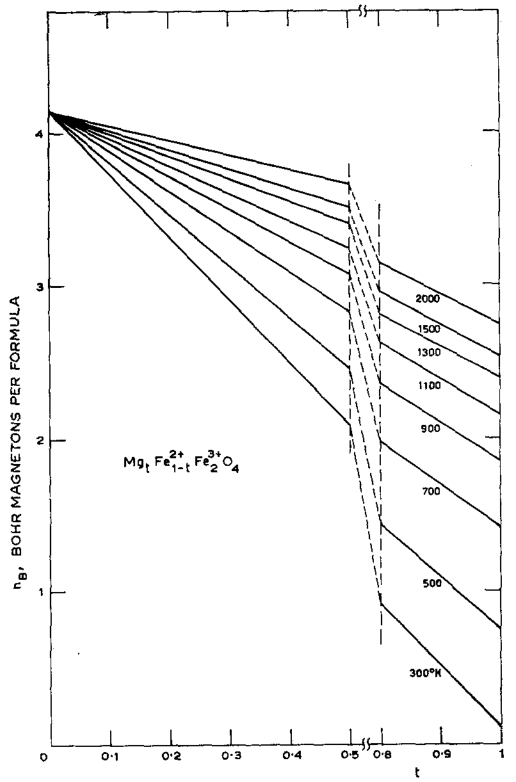

Figure 3 Theoretical magnetisation curve of the system $Fe_3O_4/MgFe_2O_4$ for different quench temperatures as derived from this work.

5. The System $Fe_3O_4/MgFe_2O_4$

As a natural derivation of the previous treatment and by means of equations 4′ and 10, the magnetisation versus composition for different quench temperatures is derived as:

$$n_B = 4.2(1 - t) + 10\,x - 2.2\,y \qquad (13)$$

In fig. 3 the values of n_B extrapolated to 0° K for the system $Mg_tFe_{1-t}Fe_2^{3+}O_4$ are plotted as a function of t for several equilibrium cation temperatures. It can be seen that owing to the insensitivity of Fe_3O_4 to thermal treatment, n_B is less and less dependent on temperature of equilibrium as the composition approaches that of magnetite.

6. Conclusions

A very simple model seems to explain satisfactorily the experimental facts about temperature-dependence of cation distribution in magnesioferrite.

The addition of thermal contributions to the energy seems necessary when other cationic energies are small.

A criticism of the method can be made on the basis of the difficulty of achieving cation thermal energies referred to different sublattices, as Debye or Einstein characteristic temperatures are determined on bulk compositions. It is felt nonetheless that the present study can indicate a reasonably direct way to distinguish between the energy contributions responsible for cation distributions.

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