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THERMODYNAMIC PROPERTIES AND CATION DISTRIBUTION OF $CdFe_2O_4 + Fe_3O_4$ SOLID SOLUTIONS AT 1073 K

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ABSTRACT

The thermodynamic properties of $CdFe_2O_4 + Fe_3O_4$ spinel solid solutions were determined at 1073 K using the solid electrolyte galvanic cell

$Fe_2O_3 + Fe_3O_4|O^{2-}|Fe_2O_3 + Cd_xFe_{3-x}O_4$

The activity values obtained in this study exhibit negative deviation from the ideal solution model. An analysis of Gibbs free energy of mixing of the spinel solid solution provides information on the distribution of cations between the tetrahedral and octahedral sites of the spinel lattice. This is the basis for the estimation of Gibbs free energy of formation of pure cadmium ferrite from the respective oxides

$\Delta G^0_{CdFe_2O_4} = 1770 - 1.41T$ cal mole^{-1}

Finally, the Cd + Fe + O phase diagram at 973 K is suggested.

INTRODUCTION

The thermodynamic properties of zinc ferrite–magnetite solid solutions are known. Contrary to this system, the thermodynamic properties of $CdFe_2O_4 + Fe_3O_4$ solid solutions have not yet been investigated. The formation of this type of solid solution has been reported [1], and it is interesting to compare the thermodynamic properties of this system with those of $ZnFe_2O_4 + Fe_3O_4$ solid solutions. The Goldschmidt ionic radius of Cd^{+2} (0.92 Å) is larger than the corresponding radius of zinc ion (0.69 Å), and it is possible to follow the change in the thermodynamic properties of the solution when a larger ion is incorporated into the spinel lattice. Moreover, it is known that the thermodynamic properties of spinel solid solutions are connected with the cation distribution [2–4]. Interpretation of the results from this point of view enables the unknown Gibbs free energy of formation of $CdFe_2O_4$ from the respective oxides to be estimated.

EXPERIMENTAL

Materials

The CdO powder used in this study was obtained from CIECH, Poland, the Fe_3O_4 powder from Cerac Inc., and the Fe_2O_3 powder from Merck. Cadmium ferrite ($CdFe_2O_4$) was synthesized by heating pressed pellets containing an equimolar mixture of CdO and Fe_2O_3 for 1 week in air at 1223 K. This method of preparation is analogous to that reported by Sakairi et al. [5]. Formation of the compound was confirmed by X-ray diffraction analysis. The spinel solid solutions were prepared by heating a fine mixture of $CdFe_2O_4$ and Fe_3O_4 in the required ratio in small evacuated silica capsules for 7 days at 1173 K. Since the volume of a capsule was very small, the extent of decomposition of the pellet of the ferrite solid solution to establish an oxygen pressure in the capsule should be negligible. After the heat treatment, the capsules were quenched in water. The formation of solid solutions was confirmed by X-ray diffraction analysis. The $Fe_2O_3 + Fe_3O_4$ reference electrode was prepared by mixing the respective powders. Before mixing, the Fe_2O_3 powder was preheated in air at 1273 K.

Oxygen potential measurements

An EMF cell of the type

$$Fe_2O_3 + Fe_3O_4|ZrO_2 + CaO|Fe_2O_3 + Cd_xFe_{3-x}O_4 \qquad \text{I}$$

was used for oxygen potential measurements. Under the condition that the mutual solubility of the solid solution and Fe_2O_3 is very small, the overall cell reaction is

$$Fe_3O_4 \rightarrow Fe_3O_{4\,s.s.} \qquad (1)$$

and the EMF of the cell is directly related to the activity of Fe_3O_4 in the spinel solid solution by

$$\ln a_{Fe_3O_4} = -\left(\frac{FE}{RT}\right) \qquad (2)$$

where $F = 23063$ cal V^{-1} $mole^{-1}$, E is the EMF in volts, R is the gas constant, and T is the absolute temperature.

A schematic diagram of the cell assembly is shown in Fig. 1. It is identical with that used for investigations of $Fe_3O_4 + ZnFe_2O_4$ solid solutions [6]. A solid electrolyte tube was inserted into an alumina crucible filled with $Fe_2O_3 + Fe_3O_4$ powder. The spinel solid solution powder mixed with Fe_2O_3 was sealed inside the CSZ tube by use of an alumina cement. The cell was kept in the constant temperature zone of a resistance furnace under a stream of pure argon. Copper foil was used as the internal getter inside the furnace

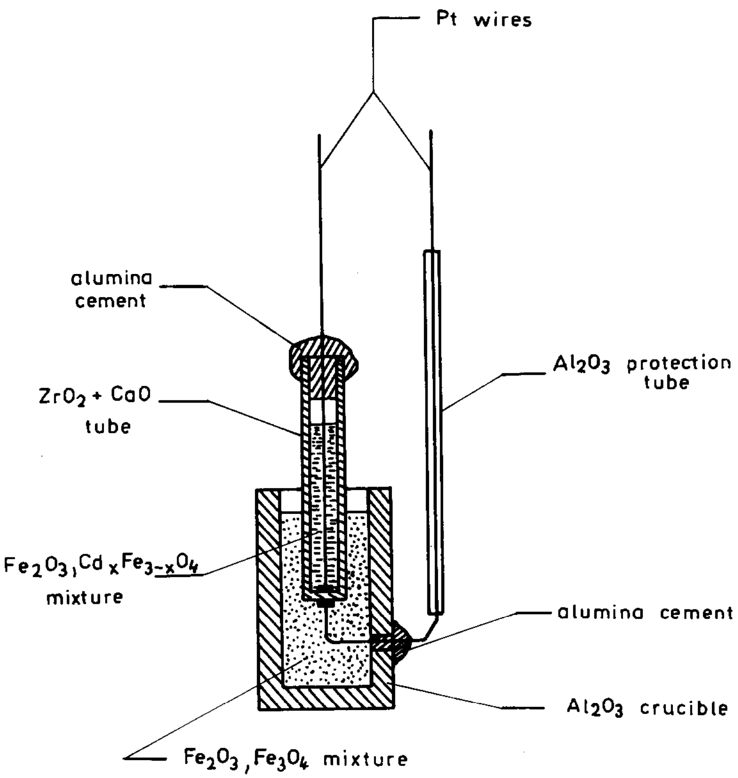

Fig. 1. Schematic diagram of the cell assembly.

tube to maintain the desired oxygen pressure in the gas phase. After constant temperature had been reached the cell was left for 24–48 h to attain equilibrium. The EMF was then recorded by means of a V 534 digital voltmeter (Elwro, Poland). This procedure was repeated for every sample.

RESULTS

The results of EMF measurements produced by cell I at 1073 K are shown in Table 1. Activity coefficients of $CdFe_2O_4$ were calculated by integration of

TABLE 1

Activities and Gibbs free energy of mixing of spinel solid solution at 1073 K

$X_{Fe_3O_4}$	$E(\pm 1$ mV)	$a_{Fe_3O_4}$	$a_{CdFe_2O_4}$	$\Delta G^{M}_{s.s.}$(cal mole^{-1})
0.1	233	0.08	0.90	−740
0.3	140	0.22	0.72	−1459
0.5	110	0.30	0.58	−1850
0.7	75	0.44	0.17	−2345
0.9	23	0.78	0.01	−1459

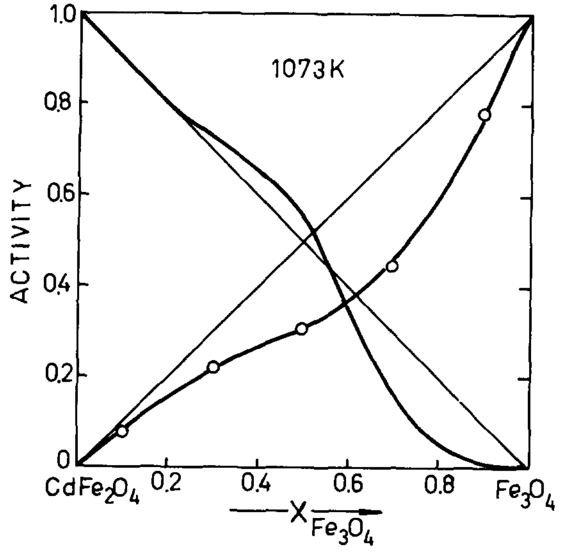

Fig. 2. Activities of magnetite and cadmium ferrite in $Fe_3O_4 + CdFe_2O_4$ spinel solid solutions.

the Gibbs–Duhem equation

$$\ln \gamma_{CdFe_2O_4} = -\int_{1.0}^{X_{CdFe_2O_4}} \left(\frac{X_{Fe_3O_4}}{X_{CdFe_2O_4}} \right) d \ln \gamma_{Fe_3O_4} \tag{3}$$

The activities and corresponding partial free energies of mixing of spinel

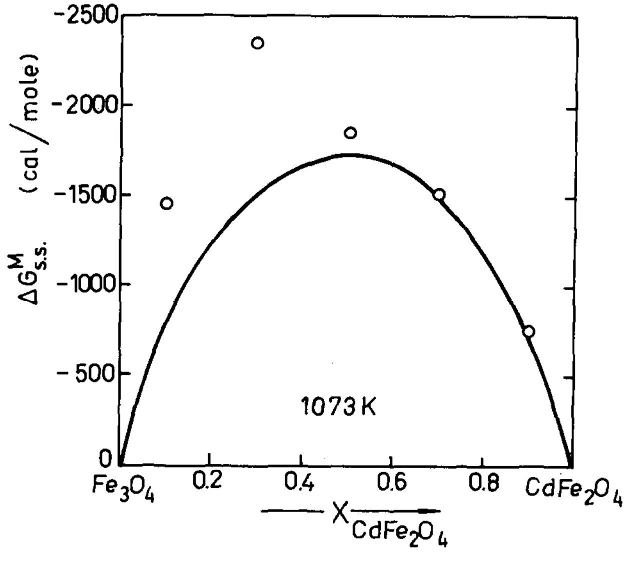

Fig. 3. Integral Gibbs free energies of formation of $Fe_3O_4 + CdFe_2O_4$ spinel solid solutions. ○, Experimental; ————, cation distribution model.

solid solutions were calculated at 1073 K. The free energy change of the reaction

$$4\ Fe_3O_4 + O_2 = 6\ Fe_2O_3 \tag{4}$$

fixing the oxygen potential of the reference electrode was taken from previous work [6]. Numerical results are summarized in Table 1, while the activities of both components and integral free energy of mixing are shown in Figs. 2 and 3.

Estimation of the free energy of formation of cadmium ferrite

The heat of formation of cadmium ferrite was measured by Navrotsky and Kleppa [2] who obtained a value of 1770 cal $mole^{-1}$ at 970 K. The entropy change during cadmium ferrite formation from the respective oxides can be estimated from a knowledge of the cation distribution in pure cadmium ferrite as follows. The measured cation distribution in cadmium ferrite at room temperature is $x = 0.95 \pm 0.02$ [7], where x is the fraction of divalent cation in the tetrahedral site. Accepting the higher limit, i.e. $x = 0.97$, the enthalpy change of exchange reaction can be calculated

$$(Cd^{2+}) + [Fe^{3+}] = [Cd^{2+}] + (Fe^{3+}) \tag{5}$$

which is equal to

$$\Delta H_{ex} = -RT \ln\left\{\frac{(1-x)^2}{x(1+x)}\right\} \simeq 4500 \text{ cal} \tag{6}$$

where ( ) and [ ] denote the tetrahedral and octahedral sites, respectively.

Fixing the value of the enthalpy change as being temperature independent, the cation distribution can be calculated at 1073 K, which is equal to 0.643. Although $CdFe_2O_4$ is a normal spinel at room temperature, the cation distribution at high temperatures may be expected to become closer to random. The configurational entropy of cation mixing can now be calculated using the formula

$$\Delta S^{CM} = -R\left\{x \ln x + (1-x)\ln(1-x) + (1-x)\ln\frac{(1-x)}{2} + (1+x)\ln\frac{(1+x)}{2}\right\} \tag{7}$$

and is equal to 3.16 cal deg^{-1} $mole^{-1}$. Therefore, the entropy change of the reaction of ferrite formation from the respective oxides can be estimated from the known entropy change of the reaction of spinel structure formation [3]

$$CdO(\text{r. salt structure}) + Fe_2O_3(\text{corundum structure}) \rightarrow CdFe_2O_4(\text{spinel structure}) \tag{8}$$

for which $\Delta S_f^0 = -1.75 + 3.16 = 1.41$ cal deg^{-1} mole^{-1}. The Jahn–Teller effect is not expected in this case. Consequently, the Gibbs free energy of formation of cadmium ferrite can be expressed as

$$\Delta G^0_{\mathrm{CdFe_2O_4}} = 1770 - 1.41T \text{ cal mole}^{-1} \tag{9}$$

Distribution of cations between the tetrahedral and octahedral sites of the spinel lattice

From the values tabulated earlier [3] and the measured cation distribution in $CdFe_2O_4$ at room temperature, the following equations are obtained

$$(\mathrm{Cd}^{2+}) + [\mathrm{Fe}^{3+}] \rightarrow [\mathrm{Cd}^{2+}] + (\mathrm{Fe}^{3+}) \tag{10}$$

$$\Delta H_{\mathrm{ex}} = 4500 \text{ cal}$$

$$K = \frac{N_{[\mathrm{Cd}^{2+}]}N_{(\mathrm{Fe}^{3+})}}{N_{(\mathrm{Cd}^{2+})}N_{[\mathrm{Fe}^{3+}]}} = 0.12$$

$$(\mathrm{Fe}^{2+}) + [\mathrm{Fe}^{3+}] \rightarrow [\mathrm{Fe}^{2+}] + (\mathrm{Fe}^{3+}) \tag{11}$$

$$\Delta H_{\mathrm{ex}} = -4000 \text{ cal}$$

$$K = \frac{N_{[\mathrm{Fe}^{2+}]}N_{(\mathrm{Fe}^{3+})}}{N_{(\mathrm{Fe}^{2+})}N_{[\mathrm{Fe}^{3+}]}} = 6.53$$

where N is the ionic fraction of cation i on each site. By definition

$$\Sigma N_{(\mathrm{i})} = 1.0 \tag{12}$$

and

$$\Sigma N_{[\mathrm{j}]} = 1.0 \tag{13}$$

while from mass balance requirements

$$2N_{[\mathrm{Cd}^{2+}]} + N_{(\mathrm{Cd}^{2+})} = X_{\mathrm{CdFe_2O_4}} \tag{14}$$

and

$$2N_{[\mathrm{Fe}^{2+}]} + N_{(\mathrm{Fe}^{2+})} = X_{\mathrm{Fe_3O_4}} \tag{15}$$

Cation distributions at 1073 K were calculated while solving the above equations for different compositions X of the spinel solid solutions. The results obtained are summarized in Table 2. The entropy of mixing of the spinel solid solution is obtained by subtracting the mole fraction weighted sum of cation mixing entropy of two pure component spinels from the cation mixing entropy of the solid solution

$$\Delta S^{\mathrm{M}}_{\mathrm{s.s.}} = \Delta S^{\mathrm{CM}}_{\mathrm{s.s.}} - \left(X_{\mathrm{Fe_3O_4}} \Delta S^{\mathrm{CM}}_{\mathrm{Fe_3O_4}} + X_{\mathrm{CdFe_2O_4}} \Delta S^{\mathrm{CM}}_{\mathrm{CdFe_2O_4}} \right) \tag{16}$$

where the Temkin ideal cation mixing contribution $\Delta S^{\mathrm{CM}}_{\mathrm{s.s.}}$ to the total

TABLE 2

Calculated cation distribution, entropy, enthalpy and Gibbs free energy of mixing of spinel solid solution at 1073 K

$X_{CdFe_2O_4}$	$[Cd^{2+}]$	$[Fe^{2+}]$	$[Fe^{3+}]$	(Cd^{2+})	(Fe^{2+})	(Fe^{3+})	$\Delta S^M_{s.s.}$ (cal deg^{-1} mole^{-1})	$\Delta H^M_{s.s.}$ (cal mole^{-1})	$\Delta G^M_{s.s.}$ (cal mole^{-1})
0	0	0.4453	0.5547	0	0.1094	0.8906	0	0	0
0.2	0.0160	0.3655	0.6185	0.1680	0.0690	0.7630	0.908	−252	−1226
0.4	0.0415	0.2797	0.6788	0.3170	0.0405	0.6425	1.214	−373	−1676
0.6	0.0750	0.1895	0.7355	0.4500	0.0210	0.5290	1.204	−380	−1669
0.8	0.1225	0.0960	0.7815	0.5550	0.0081	0.4369	0.796	−240	−1094
1.0	0.1786	0	0.8214	0.6428	0	0.3572	0	0	0

entropy of the spinel solid solution is given by

$$\Delta S^{\mathrm{CM}}_{\mathrm{s.s.}} = -R\left\{\sum N_{(i)} \ln N_{(i)} + 2\sum N_{[i]} \ln N_{[i]}\right\} \tag{17}$$

Similarly, the heat of mixing of the spinel solid solution due to cation rearrangement can be calculated from octahedral site preference energies

$$\Delta H^{\mathrm{M}}_{\mathrm{s.s.}} = \Delta H^{\mathrm{M}}_{\mathrm{total}} - \left(X_{\mathrm{Fe_3O_4}} \Delta H^{\mathrm{M}}_{\mathrm{Fe_3O_4}} + X_{\mathrm{CdFe_2O_4}} \Delta H^{\mathrm{M}}_{\mathrm{CdFe_2O_4}}\right) \tag{18}$$

where the total heat of mixing is

$$\Delta H^{\mathrm{M}}_{\mathrm{total}} = 2\left\{N_{[\mathrm{Cd}^{2+}]}(4500) + N_{[\mathrm{Fe}^{2+}]}(-4000)\right\} \tag{19}$$

The Gibbs free energy of mixing is given by

$$\Delta G^{\mathrm{M}}_{\mathrm{s.s.}} = \Delta H^{\mathrm{M}}_{\mathrm{s.s.}} - T\Delta S^{\mathrm{M}}_{\mathrm{s.s.}} \tag{20}$$

Calculated values of $\Delta G^{\mathrm{M}}_{\mathrm{s.s.}}$ are shown in Fig. 3 and compared with experimental results obtained at 1073 K.

Phase equilibria at 973 K

Gibbs triangle representation of phase equilibria in the system Cd + Fe + O is shown in Fig. 4. Suggested phase relations are based on the available

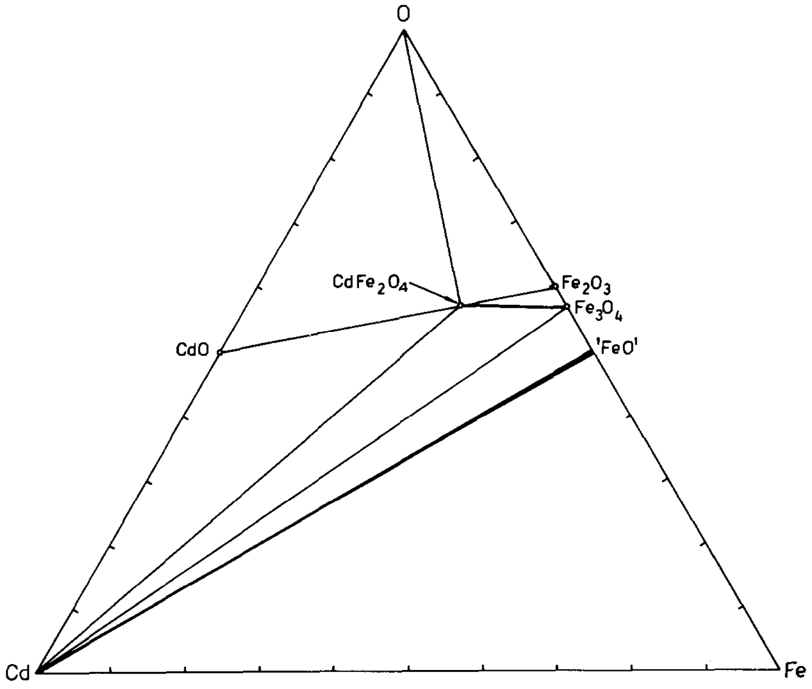

Fig. 4. Suggested phase relations in the system Cd + Fe + O at 973 K.

literature information as well as on the results of this study. According to Hansen and Anderko [8], solid iron and liquid cadmium are immiscible. Information about the FeO + CdO phase diagram is missing, but calculation of the heat of mixing of ionic crystals with NaCl-type structure based on the Born formula [9] yields the regular solution parameter $b = 13$ kcal mole^{-1}. This value indicates a strong tendency towards immiscibility at the temperature of interest ($2b/RT > 4$). Thus, it was assumed that a solid solution in this system does not exist.

From a practical point of view, a more useful representation of phase relations as a function of the oxygen partial pressure at 973 K is shown in Fig. 5. Lines for the equilibria between various phases were derived from literature data [10], except those corresponding to equilibria between spinel solid solution and pure oxides, which were calculated from the reactions

$$4\ Fe_3O_{4\,s.s.} + O_2 \rightarrow 6\ Fe_2O_3 \qquad (21)$$

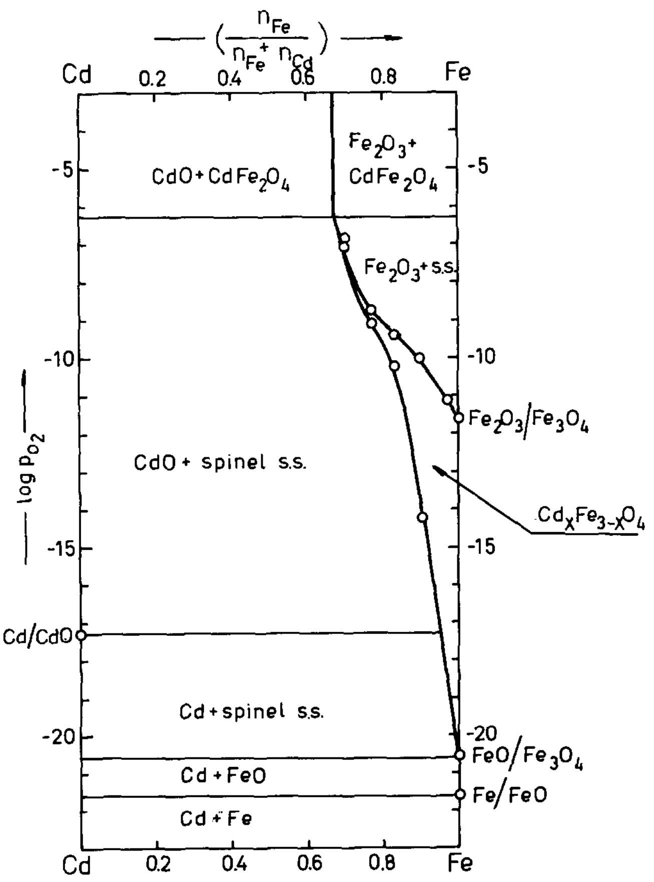

Fig. 5. Phase equilibria in the system Cd + Fe + O as a function of oxygen partial pressure ($p_{\text{total}} = 1$ atm) at 973 K.

and

$$6\ CdFe_2O_{4\,s.s.} \rightarrow 6\ CdO + 4\ Fe_3O_{4\,s.s.} + O_2 \tag{22}$$

Activities and Gibbs free energy of formation of cadmium ferrite were taken from this study. Values of activities determined at 1073 K were converted to 973 K using the regular solution model (i.e. $\ln \gamma_1/\ln \gamma_2 = T_2/T_1$), which is assumed to be a satisfactory approximation for the purpose of the phase diagram calculation.

CONCLUSIONS

The measured activity of Fe_3O_4 and that obtained by graphical integration activity of $CdFe_2O_4$ show negative deviation from Raoult's Law. This deviation is larger than obtained for $Fe_3O_4 + ZnFe_2O_4$ solid solution. An analysis of the free energy of mixing of the $Fe_3O_4 + CdFe_2O_4$ spinel solid solution shows reasonable agreement between the measured and calculated integral free energy of mixing on the basis of a cation mixing model. An increasing discrepancy between the calculated and measured values of $\Delta G^{M}_{s.s.}$ is observed at the Fe_3O_4-rich side. This kind of deviation could be explained by a redox reaction as, for example, in the case of $Fe_3O_4 + CuFe_2O_4$ spinel solid solutions [11]. However, this kind of reaction is improbable in the $Fe_3O_4 + CdFe_2O_4$ system. It seems that another kind of interaction is responsible for this effect. Observed deviation from ideal mixing is negative and it can be assumed that a kind of short-range ordering takes place in the solution. Such a process may have occurred due to the change of coulombic interaction between ions resulting in clustering of an electric nature as mentioned by Blasse [12]. On the other hand, this approach has some limitations. From the point of view of the crystal field theory, the octahedral site preference energies of Cd^{2+} and Fe^{3+} ions are zero; values being accurate to -2.5 kcal. As the site preference energy of the Cd^{2+} ion was adjusted to the measured cation distribution in pure $CdFe_2O_4$, it cannot be excluded that calculated exchange enthalpy included other energetic effects like, for example, Madelung energy, which in turn may affect the results of the model calculations. It should be mentioned that thermodynamics alone cannot resolve this problem. Phase equilibria investigations are necessary to provide information on the phase diagram. It is possible, for example, that the solubility of Fe_2O_3 in solid solution cannot be neglected.

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