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A thermodynamic model of Fe–Cr spinels

Abstract A new thermodynamic model for multi-component spinel solid solutions has been developed which takes into account thermodynamic consequences of cation mixing in spinel sublattices. It has been applied to the evaluation of thermodynamic functions of cation mixing and thermodynamic properties of Fe_3O_4–$FeCr_2O_4$ spinels using intracrystalline cation distribution in magnetite, lattice parameters and activity-composition relations of magnetite–chromite solid solutions. According to the model, cation distribution in binary spinels, $(Fe_{1-x}^{2+}\ Fe_x^{3+})[Fe_x^{2+}Fe_{2-2y-x}^{3+}Cr_{2y}]O_4$, and their thermodynamic properties depend strongly on Fe^{2+}–Cr^{3+} cation mixing. Mixing of Fe^{2+}–Fe^{3+} and Fe^{3+}–Cr^{3+} can be accepted as ideal. If Fe^{2+}, Fe^{3+} and Cr are denoted as 1, 3 and 4 respectively, the equation of cation distribution is $-RT\ \ln(x^2/((1-x)(2-2y-x))) = \Delta G_{13}^* + (1-2x)W_{13} + y(W_{14}-W_{13}-W_{34})$ where ΔG_{13}^* is the difference between the Gibbs energy of inverse and normal magnetite, W_{ij} is a Margules parameter of cation mixing and ΔG_{13}^*, J/mol $= -23,000 + 13.4\ T$, $W_{14} = 36$ kJ/mol, $W_{13} = W_{34} = 0$. The positive nonconfigurational Gibbs energy of mixing is the main reason for changing activity–composition relations with temperature. According to the model, the solvus in Fe_3O_4–$FeCr_2O_4$ spinel has a critical temperature close to 500°C, which is consistent with mineralogical data.

Introduction

Oxide spinels, being dominant minerals of the upper mantle of the Earth and accessory minerals in rocks of

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the Earth crust, are regarded as important petrogenetic indicators. They have found many practical uses as magnetic materials, refractories, semiconductors, etc. That is why spinels are of specific interest for petrologists and material scientists and a great deal of work has been devoted to investigating the thermodynamic properties of these minerals.

In the spinel structure, cations occupy tetrahedral and octahedral holes in a dense cubic packing of oxygen anions. The structural formula of a simple spinel, AB_2O_4, can be written as $(A_{1-x}B_x)[A_xB_{2-x}]O_4$ where A and B are di- and trivalent cations (2-3 spinels) or di- and quadrivalent cations (2-4 spinels), x is an inversion parameter equal to 0 in normal spinels, $A[B_2]O_4$, and to 1 in inverse spinels, $B[AB]O_4$ (here and elsewhere tetrahedral and octahedral cations are enclosed in parentheses and brackets respectively; the former notation can be omitted). Thermodynamic properties of spinels depend on intracrystalline cation distribution which is described by thermodynamic models of these minerals. Developing such models for simple, binary and multicomponent spinels is necessary for the understanding and correct expression of their thermodynamic properties, in particular the activity–composition relations, required for the application of thermodynamics in petrology and material science.

Proposed thermodynamic models of spinels are based on the assumption of the random arrangement of cations in every sublattice which determines the configurational entropy S_c and its contribution to the activity of components. The main difference between them is in expression of the dependence of the enthalpy, H, or the nonconfigurational Gibbs energy, G^*, on inversion parameters and composition. The dependence of the enthalpy of simple spinels on x was taken as linear (Neel 1950; Navrotsky and Kleppa 1967) and nonlinear, described by means of regular solution parameters (Kurepin 1975b). By means of lattice energy calculations O'Neill and Navrotsky (1983) substantiated the nonlinear, quadratic dependence of H on x in simple spinels, which was used for developing the thermodynamic

model for binary spinels (O'Neill and Navrotsky 1984). These models were extended to multicomponent Cr spinels (O'Neill and Wall 1987). A key feature of the following spinel models was the formulation of the nonconfigurational Gibbs energy, G^*, of binary or multicomponent spinels by Taylor series expansion in composition and ordering variables (Sack 1982; Nell and Wood 1989; Sack and Ghiorso 1991a, b). However, there are inconsistences between spinels and their models, in particular, between calculated and experimentally determined cation distribution in magnetite, binary and multicomponent spinels. For instance, according to the model of chromian spinels by Sack and Ghiorso (1991a), magnetite is more inverse than random at all temperatures that is not consistent with experimental data. These authors concluded that the EMF-measurements (Wu and Mason 1981) overestimated the degree of randomization in Fe_3O_4. Nevertheless subsequent EMF-measurements (Matteus and Jacob 1992) and Moessbauer (Wissman et al. 1998) have confirmed the conclusions of Wu and Mason (1981) about random cation distribution in Fe_3O_4 at high temperatures. This shows the necessity for improving thermodynamic models for spinels.

According to the above-mentioned thermodynamic models, normal and inverse simple spinels are components of simple, binary and multicomponent spinels; the nonconfigurational mixing properties of spinels are the consequence of mixing these components. An alternative to this approach is the consideration of mixing properties as a consequence of cation mixing in spinel sublattices. Urusov (1983) proposed describing the non-ideality of this cation mixing in simple spinels by a regular model and calculated Margules parameters and site preference energies using available data. This approach was used by Kurepin (1988b) for the analysis of thermodynamic properties of binary spinels and is used in the present work for developing a new thermodynamic model of Fe–Cr spinels. Consideration of cation mixing in sublattices instead of mixing spinel end-members makes this development much simpler. This model is consistent both with equilibrium and cation distribution data for Fe_3O_4–$FeCr_2O_4$ spinels. It can be used for developing similar models of spinels of more complicated compositions, which is necessary for thermodynamic modeling in petrology and material science.

Thermodynamic models of cation mixing

A distinguishing feature of these models is the application of a regular model of mixing to every tetrahedral and octahedral cation sublattice.

Simple spinels

With a random distribution of cations in sublattices of a mixed spinel, $(A_{1-x}B_x)[A_xB_{2-x}]O_4$, the configurational entropy is

$$S_c(Sp) = -R(x \ln x + (1-x) \ln(1-x) + x \ln(x/2) + (2-x) \ln(1-x/2)). \quad (1)$$

The nonconfigurational entropy, $S^*(Sp)$, is represented by the vibrational entropy; spinels with transition metal cations can have additional electronic and magnetic contributions. The nonconfigurational Gibbs energy, $G^*(Sp) = H(Sp) - S^*(Sp)$, can be considered (Fig. 1) as a sum of the Gibbs energy of a normal spinel, $G(NSp)$, the energy of intracrystalline cation distribution, $G^*_{cd}(Sp)$, and the energy of cation mixing in spinel sublattices, $G^*_{cm}(Sp)$:

$$G^*(Sp) = G(NSp) + G^*_{cd}(Sp) + G^*_{cm}(Sp). \quad (2)$$

The change of the nonconfigurational Gibbs energy as a result of intracrystalline cation exchange between tetrahedral and octahedral sites is

$$G^*_{cd}(Sp) = x\Delta G^{**}_{AB} \quad (3)$$

where ΔG_{AB}^{**} is the energy of the reaction $(A) + [B] = (B) + [A]$, being equal to the difference between octahedral site preference energies for cations A and B. The energy of cation mixing in a tetrahedral and octahedral sublattice of a spinel can be expressed in regular approximation by means of Margules parameters $W_{(AB)}$ and $W_{[AB]}$ respectively:

$$G^*_{cm}(Sp) = x(1-x)W_{(AB)} + x(1-0.5x)W_{[AB]}. \quad (4)$$

The condition $\partial G(Sp)/\partial x = 0$ at a minimum of $G(Sp) = G^*(Sp) - TS_c(Sp)$ gives the following equation of equilibrium intracrystalline cation distribution:
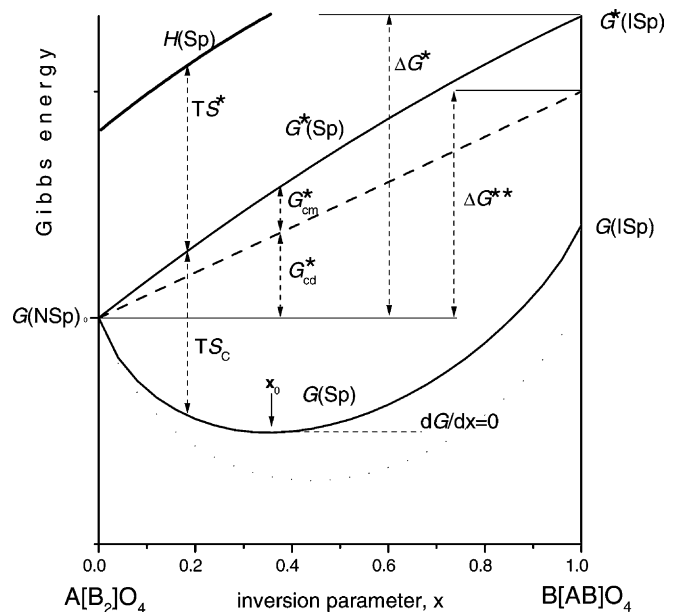

Fig. 1 Simple spinel: thermodynamic functions of disordering

$$-RT\ln(x^2/(1-x)/(2-x)) = \Delta G_{AB}^{**} + (1-2x)W_{(AB)}$$
$$+ (1-x)W_{[AB]}. \tag{5}$$

On the basis of the energetic theory of the heat of mixing (Urusov 1977), the Margules parameter of tetrahedral cation mixing, $W_{(AB)}$, can be accepted as a half $W_{[AB]}$ because of the differences in coordination numbers and in interatomic distances of tetrahedral and octahedral cations in spinels (Urusov 1983). As G_{cm}^* of an inverse spinel $B[AB]O_4$ is 0.5 $W_{[AB]}$,

$$\Delta G_{AB}^{**} = \Delta G_{AB}^* - 0.5W_{[AB]}. \tag{6}$$

Substituting this relation into Eq. 5 and accepting $W_{(AB)} = 0.5\ W_{[AB]}$ we obtain the equation of cation distribution proposed earlier (Kurepin 1975b, 1988a):

$$-RT\ln(x^2/(1-x)/(2-x)) = \Delta H^* - T\Delta S^* + (1-2x)W \tag{7}$$

where parameter $W = W_{AB}$ reflects non-linear, quadratic dependence of $G^*(Sp)$ on x.

Binary spinels

Let us consider a binary spinel solid solution, $AB_{2-2y}B'_{2y}O_4$, of the series AB_2O_4–AB'_2O_4 with the molar fraction of the second component being equal to y. With regard to the distribution of cations between tetrahedral and octahedral sites, its structural formula is

$$(A_{1-x1-x2}B_{x1}B'_{x2})[A_{x1+x2}B_{2-2y-x1}B'_{2y-x2}]O_4.$$
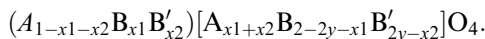
The sum of $G(NSp)$ and G_{cd}^* can be expressed using the Gibbs energy of normal spinels, $A[B_2]O_4$ and $A[B'_2]O_4$, and the differences between the Gibbs energy of inverse and normal spinels, ΔG^{**}:

$$G(NSp) + G_{cd}^* = (1-y)G(A[B_2]O_4) + yG(A[B'_2]O_4)$$
$$+ x_1\Delta G^{**}(AB_2O_4)$$
$$+ x_2\Delta G^{**}(AB'_2O_4) \tag{8}$$

G_{cm}^* is the energy of mixing of cations i and j in tetrahedral and octahedral sites:

$$G_{cm}^* = \sum_i \sum_j W_{(ij)}X'_iX'_j + 2\sum_i \sum_j W_{[ij]}X_iX_j. \tag{9}$$

The configurational Gibbs energy is

$$G_c = RT\left(\sum_i X'_i \ln X'_i + 2\sum_i X_i \ln X_i\right). \tag{10}$$

Insofar as the Gibbs energy of mixing can be represented as a sum of configurational and nonconfigurational contributions, ΔG_c^M and ΔG^{*M} respectively, we can express activity of a component i, $a(i)$, as a product of corresponding configurational, $a^o(i)$, and nonconfigurational, $\gamma(i)$, contributions into activity:

$$a(i) = a^o(i)\gamma(i). \tag{11}$$

At all values of y, x_1 and x_2, the change of G_{cd}^* with x_1 is determined by the energy of the cation exchange reaction, $(A) + [B] = (B) + [A]$, i.e. $\Delta G_{cd}^* = \Delta x_1 \Delta G^{**}$. The same is attributed to a changing x_2. As a consequence, G_{cd}^* being an additive function does not contribute to the activity of the components and therefore $\gamma(i) = \gamma_{cm}(i)$.

If some sublattice of a component in its standard state is occupied by different atoms, this component has the configurational entropy. This case is foreseen by the general expression for configurational contribution to the activity of components, $a^o(i)$ (Kurepin 1975a). If the population of sublattices of a solid solution and its component in the standard state is expressed by structural formulas $(A_aB_b...)[M_mN_n...]...$ and $(A_{a0}B_{b0}...)[M_{m0}N_{n0}...]...$ respectively, the contribution of configurational entropy into activity of this component is

$$a^o((A_{ao}B_{bo}...)[M_{mo}N_{no}...]...)$$
$$= \left(\frac{a}{a_o}\right)^{a_o}\left(\frac{b}{b_o}\right)^{b_o}...\left(\frac{m}{m_o}\right)^{m_o}\left(\frac{n}{n_o}\right)^{n_o}$$

Contribution of G_2^* to the relative partial Gibbs energy, $\Delta\bar{G}^*$, of some spinel component, $A[B_2]O_4$ for instance, can be represented as a sum of those functions for its separate constituents:

$$\Delta\bar{G}_2^*(A[B_2]O_4) = \Delta\bar{G}^*(A) + 2\Delta\bar{G}^*([B]) \tag{13}$$

where $\Delta\overline{G}_{(i)}^* = \sum_j W_{ij}X_{ij} - \sum_i\sum_j W_{ij}X_iX_j$ according to the regular solution approximation.

Thermodynamic model of the Fe–Cr spinel

A general chemical formula of Fe–Cr spinels is $Fe^{2+}Fe^{3+}_{2(1-y)}Cr_{2y}O_4$ where $y = Cr/(Cr + Fe^{3+})$. End members of this solid solution are simple spinels: magnetite (Fe-Fe$_2$O$_4$) and chromite (FeCr$_2$O$_4$). Properties of normal (NSp) and inverse (ISp) spinels, such as normal (NMt) and inverse (IMt) magnetites, are used further on in our thermodynamic analysis. Let us take the following notation for simplicity: $1 \rightarrow Fe^{2+}$, $3 \rightarrow Fe^{3+}$, $4 \rightarrow Cr^3$ (2 is used for Ni^{2+} in our other works). Cr^{3+} cations have very high octahedral site preference energy and therefore we can neglect tetrahedral Cr^{3+}, while cations Fe^{2+} and Fe^{3+} can occupy both tetrahedral and octahedral sites. This is expressed by the structural formula of Fe–Cr mixed spinel:

$$(Fe^{2+}_{1-x}Fe^{3+}_x)[Fe^{2+}_xFe^{3+}_{2-2y-x}Cr_{2y}]O_4$$
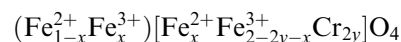
As occupation of tetrahedral sites by Cr cations can be ignored, cationic fractions in tetrahedral sublattice are: $X'_1 = 1-x$, $X'_3 = x$, and those in octahedral sublattice are: $X_1 = x/2$, $X_3 = (2-2y-x)/2$, $X_4 = y$.

As components of Fe–Cr spinel, we can consider normal and inverse magnetite, $(Fe^{2+})[Fe_2^{3+}]O_4$ and $(Fe^{3+})[Fe^{2+}\ Fe^{3+}]O_4$ respectively, chromite $(Fe^{2+})[Cr_2]O_4$ and inverse spinel $(Fe^{3+})[Fe^{2+}Cr]O_4$ with Cr instead of Fe^{3+} in octahedral sites (Fig. 2). Furthermore, we can choose magnetite (Mt) to have an equilibrium cation distribution with inversion parameter x_o, $(Fe^{2+}_{1-xo}Fe^{3+}_{xo})[Fe^{2+}_{xo}Fe^{3+}_{2-xo}]O_4$, and chromite $Fe[Cr_2]O_4$ as components.

Integral thermodynamic properties

The nonconfigurational Gibbs energy $G^*(NSp)$ of a normal binary spinel $(Fe^{2+})[Fe^{3+}_{2-2y}Cr_{2y}]O_4$ can be accepted as a linear function of composition; that is $G_n^*(Sp) = (1-y)\,G(NMt) + y\,G(Chr)$. Change of cation distribution between tetrahedral and octahedral sites gives $G_{cd}^*(Sp) = x\Delta G_{13}^{**}$. The sum $G(NSp) + G_{cd}^*$ for all values of x and y forms a plane in the $x-y-G^*$ diagram (Fig. 2). G_{cm}^* of the Fe–Cr spinel is determined by interactions between cations in tetrahedral and octahedral cation sublattices; that is:

$$G_{cm}^*(Sp) = W'_{(13)}X'_1X'_3 + 2(W_{[13]}X_1X_3 + W_{[14]}X_1X_4 + W_{[34]}X_3X_4). \tag{14}$$

Chromite is a normal spinel. Magnetite is an inverse spinel at room temperature and at higher temperatures it turns into a mixed spinel $(Fe^{2+}_{1-x0}\ Fe^{3+}_{x0})[Fe^{2+}_{x0}\ Fe^{3+}_{2-x0}]O_4$ with inversion parameter x_0. As a mixed spinel it has

$$G^*(Mt) = G(NMt) + x_0\Delta G_{13}^{**} + W'_{(13)}x_0(1 - x_0) + W_{[13]}x_0(1 - x_0/2). \tag{15}$$
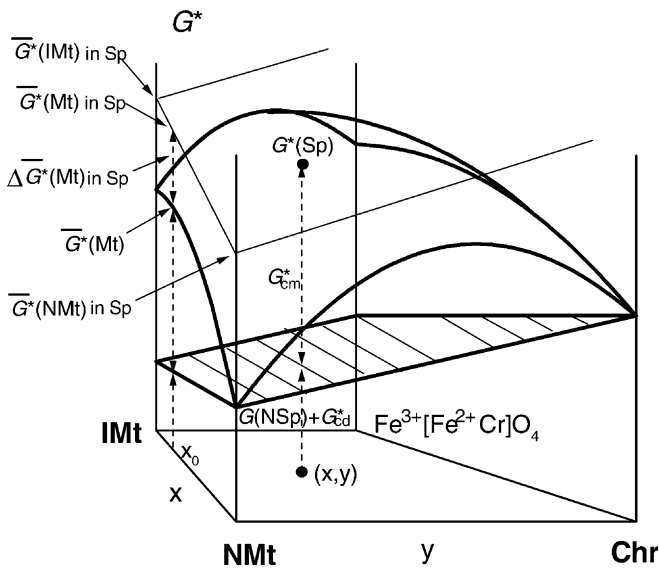

Fig. 2 Fe_3O_4–$FeCr_2O_4$ spinels: nonconfigurational Gibbs energy as a function of composition (y) and inversion parameter (x)

Accepting $W'_{(ij)} = 0.5\ W_{[ij]}$ and $W_{ij} = W_{[ij]}$, we have:

$$G_{cm}^*(Mt) = 0.5W_{13}x_0(3 - 2x_0). \tag{16}$$

The configurational entropy at random distribution of cations in every sublattice is

$$S_c = -R(X'_1\ln X'_1 + X'_3\ln X'_3 + 2(X_1\ln X_1 + X_3\ln X_3 + X_4\ln X_4)) \tag{17}$$

Relative partial thermodynamic properties

The entropic contributions to the activity of magnetite with equilibrium cation distribution and chromite as components of the Fe–Cr spinel are:

$$a^o(Fe_3O_4) = \left(\frac{1-x}{1-x_o}\right)^{1-x_o}\left(\frac{x}{x_o}\right)^{x_o}\left(\frac{x}{x_o}\right)^{x_o}\left(\frac{2-2y-x}{2-x_o}\right)^{2-x_o}, \tag{18}$$

$$a^o(FeCr_2O_4) = (1-x)y^2. \tag{19}$$

$G(NSp)$ and G^*_{cd} as additive functions do not contribute to the activity of the spinel components. The contribution of $G^*_{cm}(Sp)$ to the activity of the components is caused by non-ideal cation mixing. The nonconfigurational Gibbs energy of tetrahedral cation mixing is:

$$G_{cm}^{*\prime} = X'_1X'_3W_{13}/2, \tag{20}$$

and the corresponding partial Gibbs energies of the interaction of tetrahedral cations are:

$$\bar{G}_{1cm}^{*\prime} = X'_3W_{13}/2 - G_{cm}^{*\prime}, \tag{21}$$

$$\bar{G}_{3cm}^{*\prime} = X'_1W_{13}/2 - G_{cm}^{*\prime}. \tag{22}$$

The same parameters at interactions of 1 mol of octahedral cations are:

$$G_{cm}^* = X_1X_2W_{13} + X_1X_4W_{14} + X_3X_4W_{34}, \tag{23}$$

$$\bar{G}_{1cm}^* = X_3W_{13} + X_4W_{14} - G_{cm}^*, \tag{24}$$

$$\bar{G}_{3cm}^* = X_1W_{13} + X_4W_{34} - G_{cm}^*, \tag{25}$$

$$\bar{G}_{4cm}^* = X_1W_{14} + X_3W_{34} - G_{cm}^*. \tag{26}$$

The partial Gibbs energy of cation interactions for magnetite, $(Fe^{2+}_{1-xo}\ Fe^{3+}_{xo})[Fe^{2+}_{xo}\ Fe^{3+}_{2-xo}]O_4$, and chromite, $Fe[Cr_2]O_4$, as components of a spinel is:

$$\bar{G}_{cm}^*(Mt) = (1-x_0)\bar{G}_{1cm}^{*\prime} + x_0\bar{G}_{3cm}^{*\prime} + x_0\bar{G}_{1cm}^* + (2-x_0)\bar{G}_{3cm}^*, \tag{27}$$

$$\bar{G}_{cm}^*(Chr) = \bar{G}_{1cm}^{*\prime} + 2\bar{G}_{4cm}^*. \tag{28}$$

Contributions of the cation mixing to the relative Gibbs energy of components, $\Delta\bar{G}_{cm}^*(i) = RT\ln[\gamma_{cm}(i)]$ as the difference between the partial Gibbs energy of a com-

ponent in spinel, $\overline{G}_{cm}^*(i)$, and the Gibbs energy, $G_{cm}^*(i)$, of this component in its standard state are: $RT \ln[\gamma_{cm}(Mt)]$ $= (1-x_0)$

$$RT \ln [\gamma_{cm}(Mt)] = (1 - x_0)\overline{G}_{1cm}^{*'} + x_0\overline{G}_{3cm}^{*'} + x_0\overline{G}_{1cm}^*$$
$$+ (2 - x_0)\overline{G}_{3cm}^* - x_0(3 - 2x_0)W_{13}/2, \quad (29)$$

$$RT \ln [\gamma_{cm}(Chr)] = \overline{G}_{1cm}^{*'} + 2\overline{G}_{4cm}^*. \quad (30)$$

Thermodynamics of cation distribution and mixing properties of Fe–Cr spinel

Simple spinels

Magnetite

Temperature dependence of cation distribution in magnetite was determined by EMF measurements (Wu and Mason 1981), by measurements of the Seebeck coefficient (Matteus and Jacob 1992) and by Moessbauer measurements (Wissmann et al. 1998; Häggström et al. 1978) (Fig. 3). These data show a gradual transition from an almost inverse ($x \sim 1$) distribution at lower temperatures to a near random one ($x = 2/3$) at 1,400–1,500°C. Moessbauer data by Wissmann et al. (1998) show a considerably smaller inversion degree at higher temperatures than other data show. The dependence $-RT \ln K_D$ where $K_D = x^2/((1-x)(2-x))$ on the inversion parameter of magnetite, x, is ne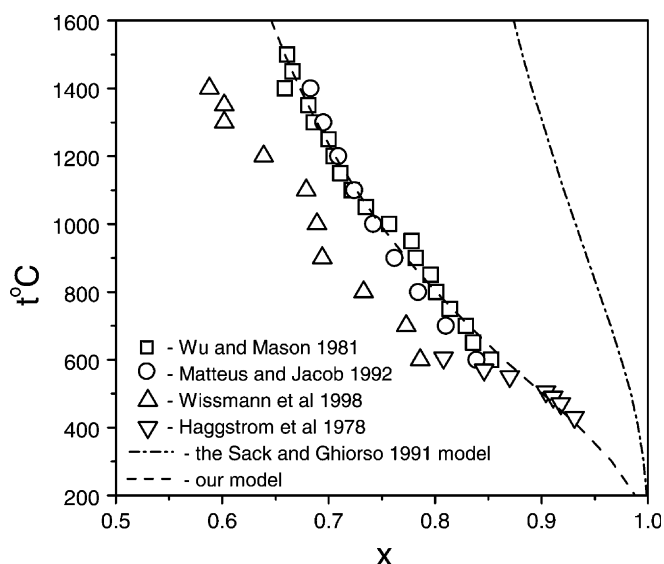arly linear, and all available experimental data reflect the same dependence (Fig. 4). This relation speaks in favour of the proposed by O'Neill and Navrotsky (1983, 1984) model of magnetite as a simple spinel with a large positive value of W_{13}. But in accordance with this model, such spinels like magnetite having a positive or small negative value of ΔH^*, positive value of W and large values of x at high temperatures must transform to normal spinels at cooling (Kurepin 1975b, 1988). According to evaluation of thermodynamic properties of magnetite (O'Neill and Navrotsky 1983, 1984), the temperature of this first order transition to normal spinel is close to 100°C. Since magnetite is an inverse spinel at room temperature and lower, it follows that a model with a large positive value of W_{13} is not valid for a proper description of cation distribution in this mineral.

Values of $-RT \ln K_D$ increase with increasing temperature (Fig. 5). Although there are some discordances between temperature dependences of $-RT \ln K_D$ obtained by different methods, every set of experimental data points at linear dependence what is consistent with a model of magnetite as a simple spinel with $W_{13} = 0$. In particular, the Wu and Mason's 1981 data for 873–1,773 K give

$$x_0 = 1.138 - 3.756e - 4 \times T + 5.688e - 8 \times T^2, \quad (31)$$

$$-RT \ln K_D, J/mol = -23,000 + 13.4T. \quad (32)$$

The latter relation is consistent with data for lower temperatures determined from Häggström et al. (1978). Compilations and assessments of thermodynamic functions of cation distribution in magnetite derived from experimental data using different models are set out in Table 1.
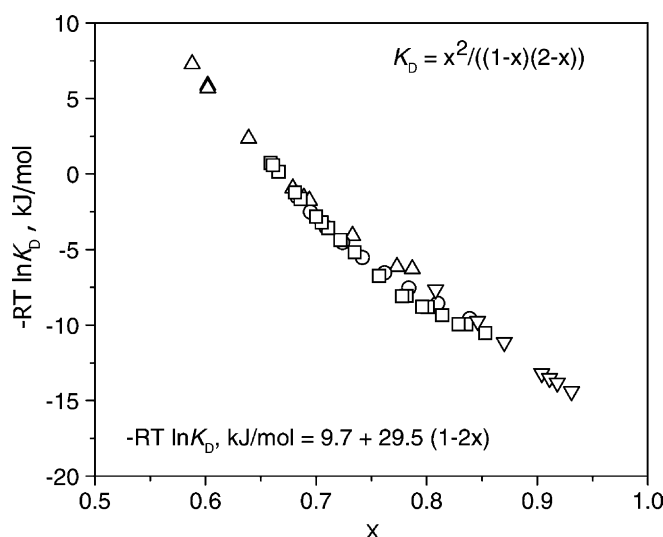

Fig. 3 Magnetite: temperature dependence of inversion parameter, x

Fig. 4 Magnetite: temperature dependence of $-RT \ln(x^2/((1-x)(2-x)))$. Notations as in Fig. 3
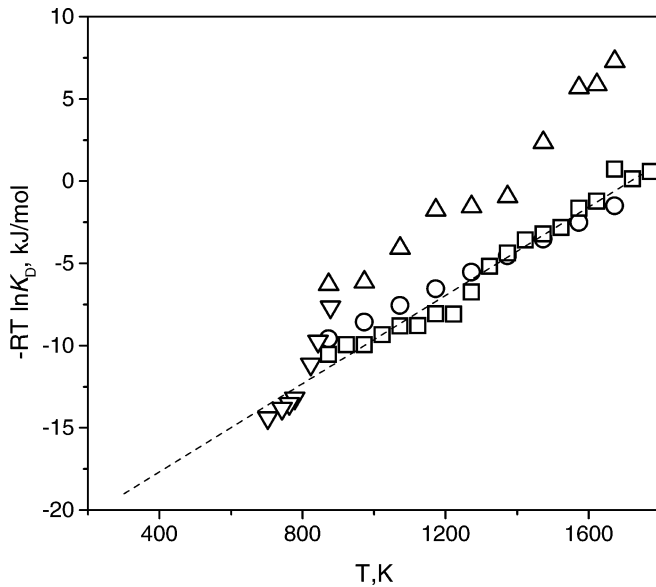
Fig. 5 Magnetite: dependence of $-RT \ln(x^2/((1-x)(2-x)))$ on inversion parameter, x. Notations as in Fig. 3

Fig. 6 Fe_3O_4–$FeCr_2O_4$ spinels: activity–composition relations at 1,500 K according to experimental and calculated data

Chromite

Chromite is a normal spinel at all temperatures due to very high octahedral site preference energy of Cr^{3+}

Fe_3O_4–$FeCr_2O_4$ spinels

Intracrystalline cation distribution data and activity–composition relations can be used for deriving thermodynamic functions of cation mixing in spinels. Many authors studied the high temperature activity–composition relations for Fe_3O_4–$FeCr_2O_4$ (Oleinikov et al. 1968; Schmahl und Dillenburg 1969; Snetlage and Schroecke 1976; Katsura et al. 1975; Petric and Jacob 1982; Perrot 1985). Katsura et al. (1975) determined the activity–composition relations at 1,500 K using the equilibria of spinel with wustite or with iron and taking into account the properties of wustite as a solid solution (Fig. 6). These estimations are considered as the most reliable and were used for the derivation of the thermodynamic functions of cation interaction. Choosing magnetite (Mt) with
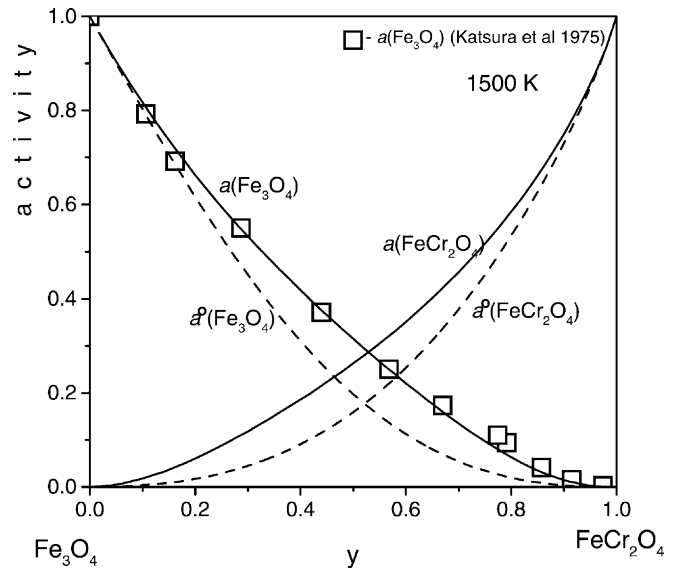
equilibrium cation distribution $(Fe^{2+}_{1-x_0} Fe^{3+}_{x_0})$ $[Fe^{2+}_{x_0} Fe^{3+}_{2-x_0}]O_4$ as a component of high temperature spinel $(Fe^{2+}_{1-x} Fe^{3+}_x)$ $[Fe^{2+}_x \ Fe^{3+}_{2-2y-x} Cr_{2y}]O_4$, we have:

$$a(Mt) = a^o(Mt) \cdot \gamma(Mt), \qquad (33)$$

$$a^o(Mt) = ((1-x)/(1-x_0))^{1-x0}(x/x_0)^{2x0}$$
$$\times \ ((2-2y-x)/(2-x_0))^{2-x0}, \qquad (36)$$

$$RT \ln[\gamma(Mt)] = W_{13}(x_0-x)(x_0-x-y) + W_{14}y(x_0-x)$$
$$- W_{34}y(x_0-x-2y). \qquad (37)$$

Activity–composition data by Katsura et al. (1975) for chromite-magnetite spinels with $0.28 < y < 0.6$ allow us to estimate $W_{14} = 34$ kJ/mol at negligible values of W_{13} and W_{34}.

Cation redistribution in chromite–magnetite spinels lies only in electron exchange between tetrahedral and octahedral sublattices and can take place without delay even at low temperatures. Therefore, we may conclude that cation distribution data obtained at room temperature reflect cation equilibrium at these conditions. Moessbauer measurements (Robbins 1971) showed that

Table 1 Thermodynamic functions of cation distribution in magnetite

Note [a]Evaluated from parameters α, σ and β reported in O'-Neill and Navrotsky (1983, 1984), using the relations: $\Delta \varpi H^* = \alpha + \beta$, $\Delta S^* = \sigma$, $W = -\beta$

Temperature range (°C)	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	W (kJ mol^{-1})	References
	−16.7			Dunitz and Orgel (1957)
	−20.1			Navrotsky and Kleppa (1967)
600–1,500	−23.0	−13.4		Wu and Mason (1981)
600–1,500	9.95[a]		31.2[a]	O'Neill and Navrotsky (1983)
600–1,500	−4.0[a]	−5.76[a]	20.0	O'Neill and Navrotsky (1984)
600–1,400	−18.4	−10.1		Matheus and Jacob (1992)
573–1,400	−23.5	−17.8		Wissmann et al. (1998)

the spinel $(Fe_{1-x}^{2+}Fe_x^{3+})$ $[Fe_x^{2+}Fe_{2-2y-x}^{3+}Cr_{2y}]O_4$ enriched in $FeCr_2O_4$ with $y > 0.63$ is normal ($x \sim 0$). On the contrary, in spinels enriched in Fe_3O_4 with $y < 0.31$, the inversion parameter is decreasing at the same rate as the molar fraction of $FeCr_2O_4$ is increasing. Values of x in spinels of intermediate compositions change considerably with y. For the thermodynamic calculations stated below the values of x in spinels of the middle part of the series are accepted as intermediate between $x = 0.69$ at $y = 0.31$ and $x = 0.05$ at $y = 0.63$ (Fig. 7). The last value of x was adopted arbitrarily taking into account that the fact it must differ from zero.
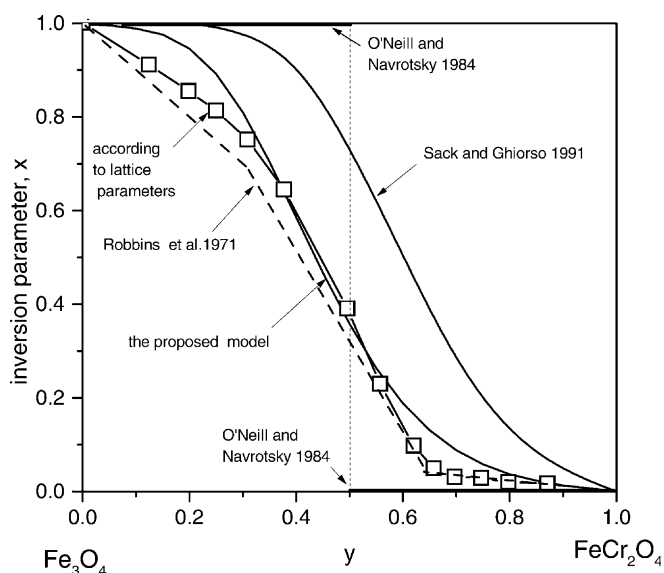

Fig. 7 Fe_3O_4–$FeCr_2O_4$ spinels: compositional dependence of inversion parameter, x

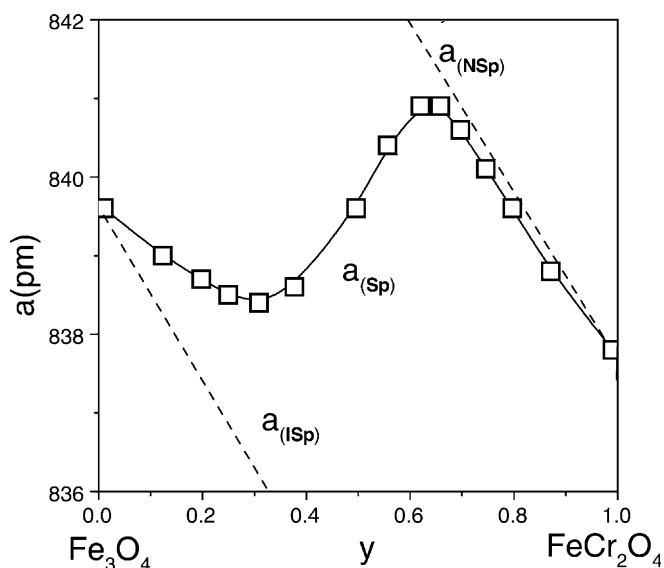**Fig. 8** Fe_3O_4–$FeCr_2O_4$ spinels: compositional dependence of unit cell parameters, a (pm), according to experimental data by Levinstein (1972) (*squares*). Assumed unit cell parameters of inverted and normal spinels are shown by *dash lines*

The compositional dependence for the lattice parameter of magnetite–chromite spinels (Fig. 8) can serve as an additional source of the cation distribution data. The change of lattice parameters of magnetite and chromite at inversion is to make an assessment for this purpose. Zn and Cd ferrites are normal spinel and their lattice parameters are greater by 11.6 and 10.9 pm, respectively, than that of Zn and Cd chromites, which are normal spinels as well (Hill et al. 1983). Adopting an average value of 11.2 pm for the difference between lattice parameters of a ferrite, MFe_2O_4 and a chromite, MCr_2O_4 with the same cation M^{2+}, we can evaluate the lattice parameter for normal magnetite (848.7 pm) using data for chromite (837.5 pm). The obtained difference (9.1 pm) between lattice parameters of normal and inverse magnetite (837.5 and 839.6 pm respectively) can be taken as the difference for other spinels. If the normal and inverse magnetite–chromite spinels obey Vegard's law, then the compositional dependence of their lattice parameters are $a_{(NSp)}$ pm $= 848.7 - 11.2y$ and $a_{(ISp)}$ pm $= 839.7 - 11.2y$. According to experimental data (Levinstein et al. 1972; Wasilewsky 1975) the lattice parameter, $a_{(Sp)}$, of mixed magnetite–chromite spinel decreases with increasing $FeCr_2O_4$ contents in magnetite and increases with increasing Fe_3O_4 content in chromite (see Fig. 8). Using $a_{(Sp)}$ of a mixed binary spinel and corresponding values $a_{(NSp)}$ and $a_{(ISp)}$ we can determine its inversion parameter: $x = (a_{(NSp)} - a_{(Sp)})/(a_{(NSp)} - a_{(ISp)})$. As seen in Fig. 7, this evaluation of the x-y relations is close to the Moessbauer data by Robbins (1971).

According to the considered thermodynamic model, the equation of cation distribution in binary magnetite–chromite spinel is:

$$-RT \ln K_D = \Delta G_{13}^* + (1 - 2x)W_{13} + y(W_{14} - W_{13} - W_{34}). \tag{36}$$

Values of $-RT \ln K_D$ calculated using the x–y relations in magnetite–chromite spinels at room temperature increase with y (Fig. 9). They are close to $\Delta G_{13}^* + y W_{14}$ if we take $W_{14} = \sim 45$ kJ/mol at $\Delta G_{13}^* = -19$ kJ/mol for 298 K according to Eq. 38. If we accept $\Delta G_{13}^* = -15.4$ kJ/mol for 298 K in accordance with the Matteus and Jacob 1992 data on the intracrystalline cation distribution in magnetite, the values of $-RT \ln K_D$ are close to $\Delta G_{13}^* + y W_{14}$ at $W_{14} = \sim 38$ kJ/mol. Recall that $W_{14} = 34$ kJ/mol was determined above from activity–composition data for magnetite–chromite spinels at 1,500 K (Katsura et al. 1975). $W_{14} = 36$ kJ/mol as an intermediate between estimates for 298 K and 1,500 K together with $W_{13} = W_{34} = 0$ and ΔG_{13}^* derived from Wu and Mason 1981 data were used for further calculations.

Integral and partial mixing properties

The nonconfigurational Gibbs energy of mixing, ΔG^{*M}, is caused by non-ideal cation interactions in sublattices:
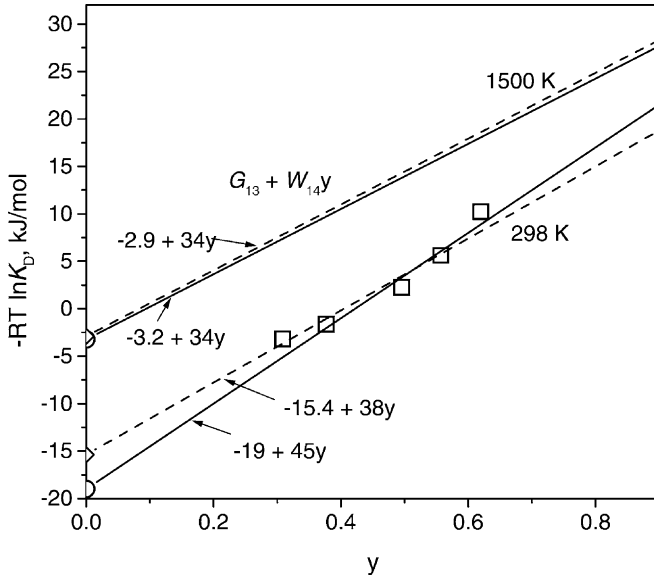
Fig. 9 Fe_3O_4–$FeCr_2O_4$ spinels: values of $-RT \ln K$ (*squares*) calculated on x–y data derived from lattice parameters at room temperature and alternatives to compositional dependence of $\Delta G^*_{13} + yW_{14}$ at 298 and 1,500 K (*lines*). Values of $-RT \ln K$ at $y = 0$ correspond to the ΔG^*_{13}–T dependences derived from Wu and Mason 1981 and Matteus and Jacob 1992 data on high-temperature cation distribution in magnetite (semicircles and triangles respectively)

$$\Delta G_2^{*M} = y(1-y)W \tag{37}$$

where $W = x_0 W_{14}$. The Margules parameter, W, decreases with increasing temperature together with the inversion parameter of magnetite, x_0. Since W is positive, the enthalpy of mixing, ΔH^M, as the main part of ΔG_{cm}^M, is positive as well. It is convenient to represent the entropy of mixing, $\Delta S^M = S_c(Sp) - (1-y) S_c(Mt)$, as

$$\Delta S^M = -\alpha R(y \ln y + (1-y) \ln(1-y)) \tag{38}$$

where the coefficient, α, shows the ratio of ΔS^M (Sp) to ΔS^M of an ideal one-site solid solution. Values of α are close to 2.5 and can be expressed approximately as

$$\alpha = 2.842 - 0.3\tau + y(0.581 - 0.07\tau) \tag{39}$$

where $\tau = T(K)/1{,}000$.

Configurational contributions to the activity of spinel end-members are expressed rather precisely by the equations

$$a^o(Mt) = 1 + \sum_{i=1}^{3}(c_i y^i + c'_i y^i \tau + c''_i y^i \tau^2), \tag{40}$$

$$a^o(Chr) = \sum_{i=1}^{3}(c_i y^i + c'_i y^i \tau + c''_i y^i \tau^2) \tag{41}$$

with coefficients c_i, c'_i and c''_i listed in Table 2. Contributions of G^* to activities are

$$\gamma(Mt) = \exp(x_0 W_{14} y^2/(RT)), \tag{42}$$

Table 2 Coefficients for the composition and temperature dependence of activity of components in Fe–Cr spinels (Eqs. 40 and 41)

i	c_i	c'_i	c''_i
a° (Mt)			
1	−2.13789	0.116851	−2.334 e-2
2	−3.42260	4.35846	−1.33676
3	10.26685	−10.28585	3.129433
4	−5.76615	5.8833	−1.792806
a° (Chr)			
1	3.46102	−0.049259	0.01002
2	−0.94043	1.539447	−0.430968
3	4.160174	−4.236482	1.211461
4	−2.257968	2.71909	−0.782165

$$\gamma(Chr) = \exp(x_0 W_{14}(1-y)^2/(RT)). \tag{43}$$

The comparison of Figs. 6 and 10 shows that temperature changes of $a^o(i)$ are rather small and the considerable increase in the activity of components with decreasing temperature is caused by changing $\gamma(i)$. Fe_3O_4–$FeCr_2O_4$ spinels with accepted thermodynamic properties have a solvus with a critical temperature, T_c, of about 500°C, which is lower if W_{14} exceeds its accepted value (36 kJ/mol). This evaluation of T_c is lower than the experimental determination by Cremer (1969) (~850°C) and the evaluation by Sack and Ghiorso (1991a) (~600°C), but agrees with available mineralogical data. Evans and Frost (1975) found spinels with composition from magnetite to chromite with 75 mol% $FeCr_2O_4$ in serpentinites formed at ~500°C and at moderate pressure. This is evidence of the complete miscibility of Fe_3O_4–$FeCr_2O_4$ at this temperature which is consistent with our results.
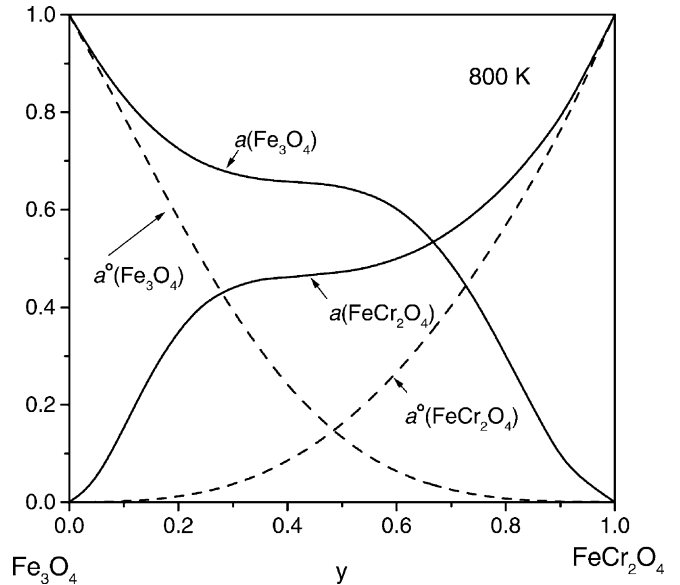

Fig. 10 Fe_3O_4–$FeCr_2O_4$ spinels: activity–composition relations at 800 K according to the proposed model

Conclusions

A new thermodynamic model for multi-component spinel solid solutions has been developed, which takes into account the thermodynamic consequences of cation mixing in every spinel sublattice. The thermodynamic functions of mixing expressed by this model are much simpler than that expressed by previous models. There is a good agreement between thermodynamic functions of cation mixing and thermodynamic properties of Fe_3O_4–$FeCr_2O_4$ spinels evaluated by means of the model using available data for higher and lower temperatures on intra-crystalline cation distribution in magnetite, lattice parameters and activity–composition relations in magnetite–chromite solid solutions. Obtained results show that cation distribution in Fe–Cr spinels and their thermodynamic properties depend strongly on Fe^{2+}–Cr^{3+} cation interactions. The influence of other cation mixing on thermodynamics of spinels is of secondary importance and Fe^{2+}–Fe^{3+} and Fe^{3+}–Cr^{3+} mixing in spinel sublattices can be taken as ideal. Non-ideal Fe^{2+}–Cr^{3+} mixing is the cause of the positive nonconfigurational Gibbs energy of mixing and the temperature dependence of activity–composition relations in Fe–Cr spinels. According to the model, Fe_3O_4–$FeCr_2O_4$ spinels have a solvus with a critical temperature of about 500°C which is consistent with available mineralogical data.

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