The Compound Energy Model for Ionic Solutions with Applications to Solid Oxides

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The application of the compound energy model to crystalline ionic phases is discussed and compared with the regular solution model. Its application to solutions with reciprocal reactions between cations on different sublattices is discussed with special reference to oxides. Examples are taken from various solutions between spinels, including cases with vacancies and interstitials. Problems connected with the choice of a state of reference for charged components in a multicomponent solution are addressed.

1. Introduction

When considering partially ordered alloys, Gorsky[1] in 1928 proposed a model by assuming that the difference in energy of an atom in two sublattices depends on the average degree of order. His model may thus be characterized as a mean field treatment. In contrast, Borelius[2] in 1934 considered the energy of nearest neighbor pairs and also of larger groups of atoms. This may be regarded as the first bond energy model. Later the same year, Bragg and Williams[3] published their first model, which was an extension of the Gorsky mean field treatment. However, the next year Bethe[4] again considered nearest neighbors and defined the bond energies in very clear terms. He also took into account short-range order, but in the so-called zeroth approximation,[5] his theory gave the same result as the mean field model of Bragg and Williams.

The bond energy model has been developed in many ways over the years and has proved to be an extremely powerful approach. For instance, it has even been applied to ionic melts by assuming that there are two sublattices, one for cations and one for anions.[6,7] In an attempt to find a more general formulation of the

Gibbs energy for ionic melts, Hillert and Staffansson[8] used a purely formal method, which may be regarded as a mean field approximation, and they showed that their model can also be applied to crystalline phases with sublattices. It was later emphasized[9] that their model can be applied directly to cases where atoms of the same element can occupy sites with different numbers of neighbors, whereas the bond energy model requires some drastic modification. It was then proposed to give the model a name emphasizing this difference, and the name compound energy model was chosen because Gibbs energies of stoichiometric compounds play a central role.

The compound energy model provides a particularly convenient formalism for representing the Gibbs energy of solution phases with sublattices. The present report describes how the model can be applied to oxide systems, in particular to spinels where cations can occupy at least two sublattices. For simple cases, a comparison is made with the ordinary regular solution model. Applications to higher order systems are demonstrated by reference to several actual cases, and some problems for multicomponent systems are discussed.

2. Basic Model

The compound energy model[8,9] is based upon the Gibbs energy, $^\circ G_{ij}$, for end-members of the solution, and they are regarded as compounds. The subscripts i and j refer respectively to the constituents on the first and second sublattices. Since they play the

role of components, we may call them component compounds. For one mole of formula units of a phase with two sublattices, the model gives

$$G_m = \sum_i \sum_j y_i' y_j'' {}^\circ G_{ij} - TS_c + {}^E G_m \qquad \text{(Eq 1)}$$

The occupancy of the sublattices is represented by the site fractions, y_i' and y_j'', defined for each sublattice separately. S_c is the ideal entropy of mixing in the two sublattices. ${}^E G_m$ is the excess Gibbs energy.

We shall first consider salt systems with one sublattice for the cations, A, B, C, etc., and one for the anions, X, Y, Z, etc. For each group of four related compounds, one may consider a so-called reciprocal reaction

$$AX + BY = AY + BX \qquad \text{(Eq 2)}$$

and the Gibbs energy of this reciprocal reaction is

$$\Delta^\circ G_{AB:XY} = {}^\circ G_{AY} + {}^\circ G_{BX} - {}^\circ G_{AX} - {}^\circ G_{BY} \qquad \text{(Eq 3)}$$

We shall denote this quantity simply by $\Delta^\circ G$ when there is no risk of misunderstanding.

If we need more parameters in order to describe the properties of a system, we can introduce interaction energies between cations or between anions. Such interactions are generally expected to be smaller. For a quaternary system, we would have
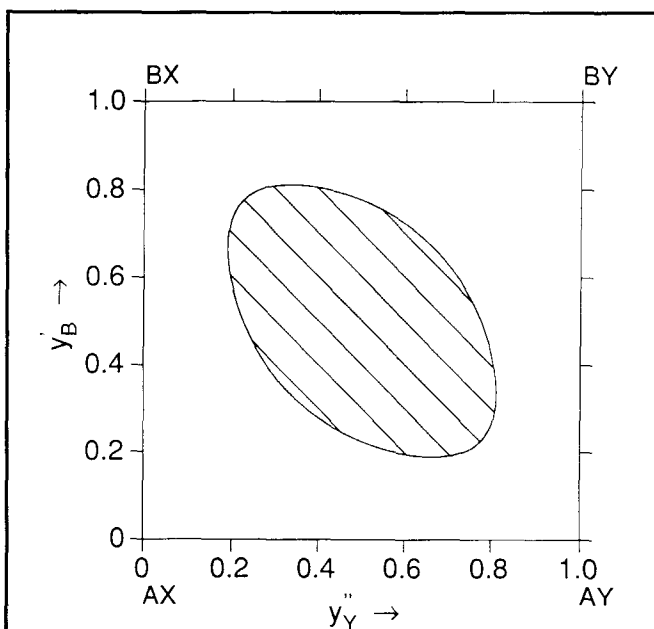
$${}^E G_m = L_{AB:X} y_A' y_B' y_X'' + L_{AB:Y} y_A' y_B' y_Y'' + L_{A:XY} y_X'' y_Y'' y_A'$$
$$+ L_{B:XY} y_X'' y_Y'' y_B' \qquad \text{(Eq 4)}$$

In the notation for interaction energies, we use a colon to separate elements on different sublattices. We can also introduce a "reciprocal" parameter, $L_{AB:XY} y_A' y_B' y_X'' y_Y''$, which plays a role inside the reciprocal system only. If the reciprocal parameter is small, then the model has a strong predictive power because the properties of the quaternary system can then be calculated from the lower order systems and the main role may even be played by the properties of the binary compounds (the end-members).

In a quaternary system, there are four y variables but only two of them are independent because $y_A' + y_B' = 1$ and $y_X'' + y_Y'' = 1$. We could, for instance, use y_B' and y_Y'' as the independent variables, and the composition area would be a square. See Fig. 1. So far we have presumed that all cations have the same valency and all anions have the same. Then solutions may exist over the whole composition square, but if the absolute value of the Gibbs energy of the reciprocal reaction is large, $|\Delta^\circ G| > 4 RT$, a miscibility gap will arise. For positive values of $\Delta^\circ G_{AB:XY}$ in Eq 3, the tie-lines will be parallel to the AX–BY diagonal. For negative values, they will be parallel to the AY–BX diagonal, as shown in Fig. 1.
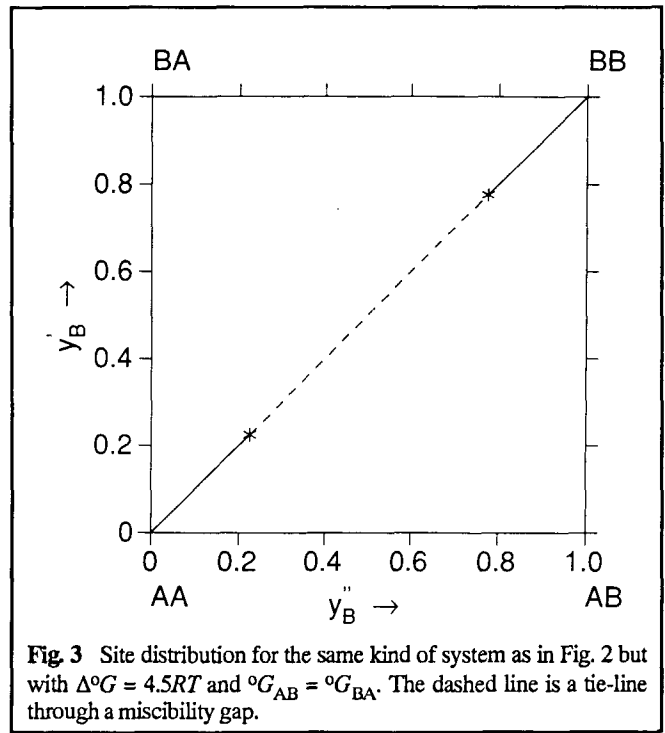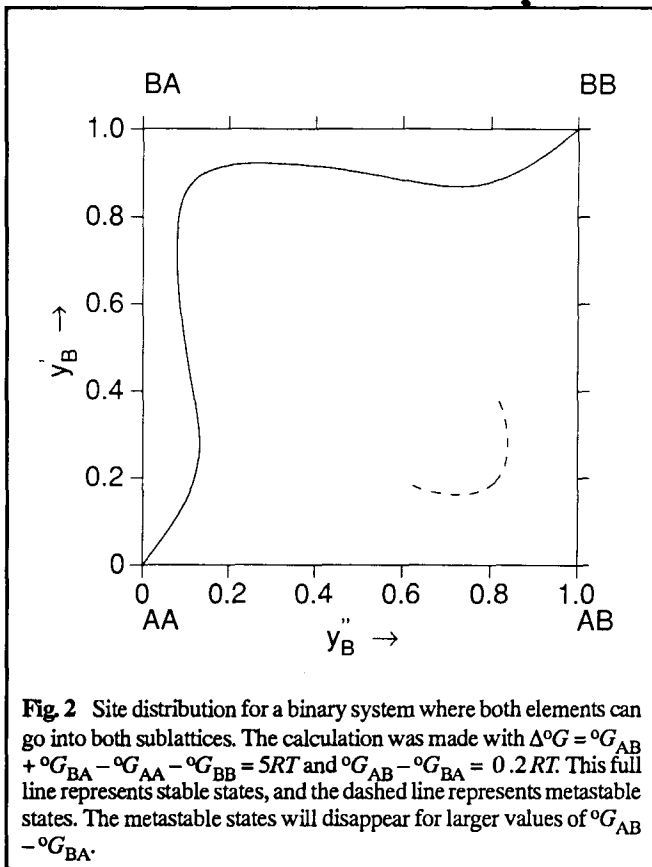
The mixing behavior of the quaternary system depends primarily on $\Delta^\circ G$ and secondarily upon the excess Gibbs energy, ${}^E G_m$. For a system like $(Na, K)_1(Cl, Br)_1$, we indeed expect $\Delta^\circ G \neq 0$ because cations are close to anions and each cation may prefer one anion to another. For this particular case, it is known that NaCl + KBr is more stable than NaBr + KCl, and $\Delta^\circ G$ defined as ${}^\circ G_{NaBr} + {}^\circ G_{KCl} - {}^\circ G_{NaCl} - {}^\circ G_{KBr}$ is thus greater than zero.

3. Application to Metallic Systems

In metallic systems, there are also cases where different elements go to different sublattices. In a quaternary system, one may have a solution phase $(A, B)_a(C, D)_b$ where a and b are the number of sites on each sublattice. The compound energy model can be applied to such cases as well, and the mathematical expressions are the same. Sometimes the same elements can occupy two different sublattices, and in a binary system one may have the phase $(A, B)_a(A, B)_b$. The above expressions can still be applied by identifying X with A, Y with B, y_X'' with y_A' and y_Y'' with y_B'. However, in this case, one can vary the composition only by taking various proportions of A and B, and we can use the mole fraction of B, x, as the only composition variable. We thus have an analytical relation between the two independent site fractions:

$$a y_B' + b y_B'' = (a + b)x \qquad \text{(Eq 5)}$$

and for each value of x one has to find the y_B' and y_B'' values that give the minimum Gibbs energy. Such information is often called "site distribution." One would thus find that all possible alloys fall on a curve between the AA and BB corners. By numerical calcu-

Fig. 1 Composition square for a reciprocal system showing a miscibility gap at some temperature. This miscibility gap is caused by a negative value of $\Delta^\circ G = {}^\circ G_{AY} + {}^\circ G_{BX} - {}^\circ G_{AX} - {}^\circ G_{BY} = -4.5RT$.

Fig. 2 Site distribution for a binary system where both elements can go into both sublattices. The calculation was made with $\Delta^\circ G = {}^\circ G_{AB} + {}^\circ G_{BA} - {}^\circ G_{AA} - {}^\circ G_{BB} = 5RT$ and ${}^\circ G_{AB} - {}^\circ G_{BA} = 0.2\,RT$. This full line represents stable states, and the dashed line represents metastable states. The metastable states will disappear for larger values of ${}^\circ G_{AB} - {}^\circ G_{BA}$.

Fig. 3 Site distribution for the same kind of system as in Fig. 2 but with $\Delta^\circ G = 4.5RT$ and ${}^\circ G_{AB} = {}^\circ G_{BA}$. The dashed line is a tie-line through a miscibility gap.

lations with negative $\Delta\,{}^\circ G_{AB:AB}$, defined as ${}^\circ G_{AB} + {}^\circ G_{BA} - {}^\circ G_{AA} - {}^\circ G_{BB}$ in accordance with Eq 3, one will find two lines, both of a hyperbolic shape, one approaching the BA corner, the other approaching the AB corner. For $a = b = 1$, the first one will represent stable equilibria and the second one metastable equilibria if ${}^\circ G_{AB} > {}^\circ G_{BA}$. See Fig. 2. For positive $\Delta^\circ G_{AB:AB}$ values, the alloys will fall on a straight line, the AA–BB diagonal, but at low temperatures there will be a miscibility gap in the middle. See Fig. 3. In order to avoid confusion, the tie-line is here shown with a dashed line.

4. Solutions Between Silicates

In modelling silicates, it is often possible to regard Si-O aggregates as single species occupying their own sublattice. Sometimes the cations occupy two different sublattices even in a simple silicate, as for example enstatite, $MgSiO_3$, which should thus be written as $(Mg)_1(Mg)_1(Si_2O_6)_1$. A solution with $FeSiO_3$ should be described with the formula $(Mg, Fe)_1(Fe, Mg)_1(Si_2O_6)_1$ and may be treated as a reciprocal system. Mg and Fe are both divalent, and all points in the composition square will represent neutral compositions. However, the composition can only vary by the use of different mixtures of $MgSiO_3$ and $FeSiO_3$, and the situation will be similar to the one described in Fig. 2. Experimentally one has observed hyperbolic curves indicating large negative values of $\Delta^\circ G_{MgFe:FeMg}$, indicative of a strong tendency for Mg to prefer the first (M1) sublattice and for Fe to prefer the second one

Fig. 4 Site distribution for $(Fe,Mg)_1SiO_3$ orthopyroxene. The experimental data are from Ref 11.
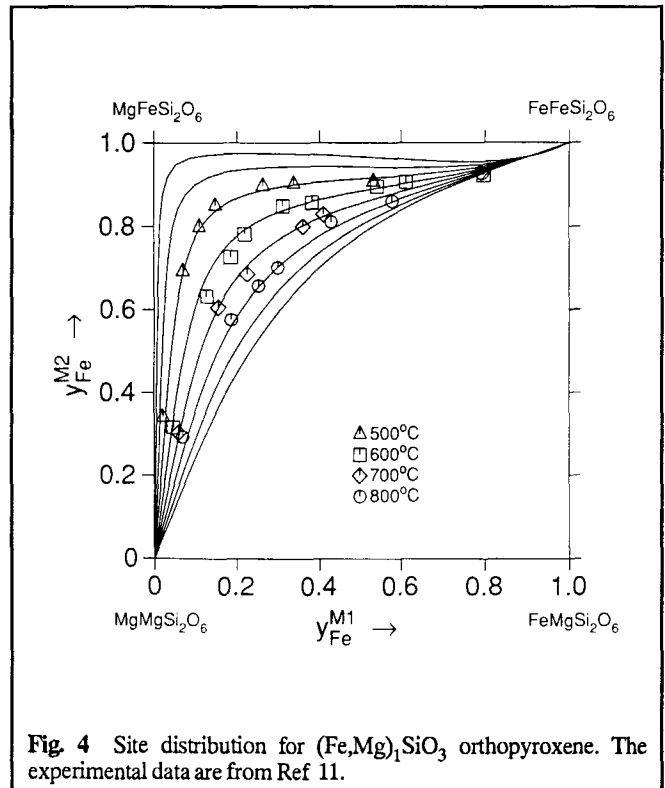
(M2). The experimental curves can be roughly described using constant negative values of $\Delta^\circ G_{MgFe:FeMg}$ and of ${}^\circ G_{MgFeSi_2O_6} - {}^\circ G_{FeMgSi_2O_6}$. However, the curves are slightly
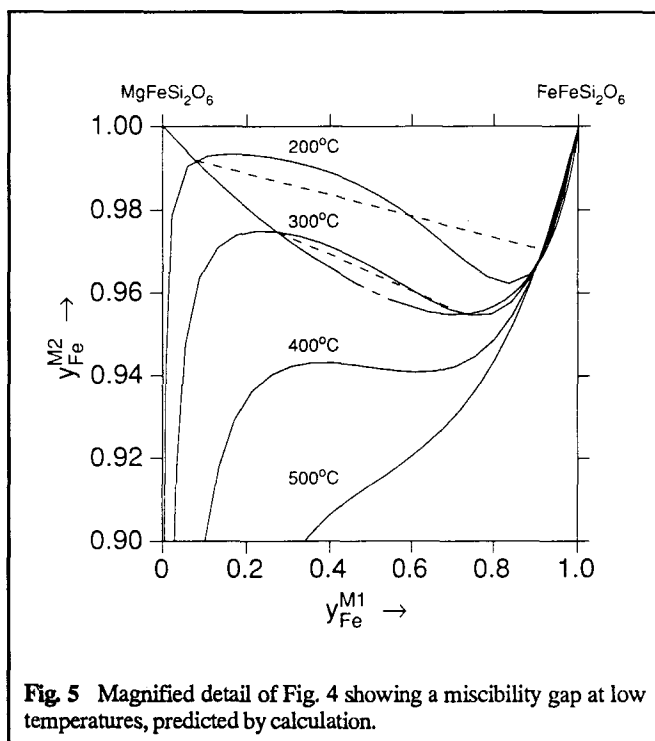
Fig. 5 Magnified detail of Fig. 4 showing a miscibility gap at low temperatures, predicted by calculation.

Fig. 6 The neutral line in a reciprocal system formed by mixing two salts of different valencies.

asymmetric, and Jansson[10] found that a more accurate representation of the data required the introduction of two binary interaction energies. His result is presented in Fig. 4.

The interaction energies used in Fig. 4 were positive and will thus give rise to a miscibility gap at low temperatures. This was found by a more careful calculation. See Fig. 5, which is a magnification of the upper part of Fig. 4. The tie-lines are shown as dashed lines.

5. Systems With a Neutral Line

In all cases discussed so far, all points inside the composition square represent possible compositions although not necessarily stable states of equilibrium. The situation is different if the ions have different valencies. We shall now denote ions with the lowest valency by A, B, C, and D and by X and Y and ions with a higher valency by E and F and by Z. We shall first consider a system obtained by mixing two salts with different valencies but the same structure, $(A^{+1})_1(X^{-1})_1$ and $(E^{+2})_1(Z^{-2})_1$. That solution may be represented by the formula $(A^{+1}, E^{+2})_1(X^{-1}, Z^{-2})_1$, and there are four component compounds AX, AZ, EX, and EZ. However, the compounds EX and AZ cannot exist because they are electrically charged. In spite of this fact, the previous model can still be used if the condition of electroneutrality is added. For all situations of physical interest, the quantities $^oG_{EX}$ and $^oG_{AZ}$ only appear in a neutral combination, in this case $^oG_{EX} + {}^oG_{AZ}$, and all such solutions will fall on a neutral line in the composition square. One may still work with all four ^oGs but give one of the charged compounds or a charged combination of them the value 0 (or any other arbitrary value).

As a consequence, there are only three independent parameters that are of physical significance, but they may be selected in a
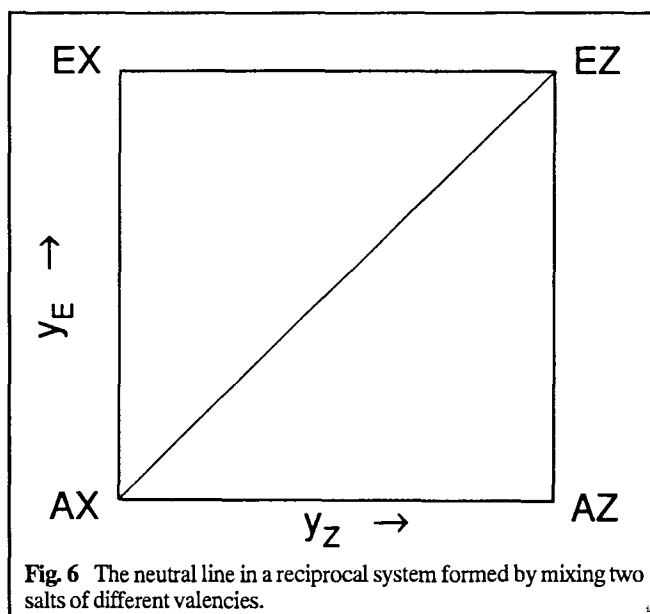
number of ways. A very convenient way is to take the Gibbs energies of the two end-points of the neutral line, in this case $^oG_{AX}$ and $^oG_{EZ}$, and the Gibbs energy of the reciprocal reaction, $\Delta^oG_{AE:XZ}$, which determines the shape of the Gibbs energy curve along the neutral line.

Since one is only interested in the neutral line, one may rewrite the Gibbs energy expression by introducing the condition of electroneutrality, in our case

$$1 \times y_A + 2 \times y_E = 1 \times y_X + 2 \times y_Z \qquad \text{(Eq 6)}$$

which given $y_A + y_E = 1$ and $y_X + y_Z = 1$ simplifies to

$$y_E = y_Z \qquad \text{(Eq 7)}$$

The neutral line will thus be the AX-EZ diagonal in this case. See Fig. 6. By denoting y_E with x, we get from Eq 1 and 4

$$
\begin{aligned}
G_m &= (1-x)^2 \, {}^oG_{AX} + (1-x)x {}^oG_{AZ} + x(1-x){}^oG_{EX} \\
&\quad + x^2 \, {}^oG_{EZ} - TS_c + L_{AE:X}(1-x)^2 x + L_{AE:Z}(1-x)x^2 \\
&\quad + L_{A:XZ}x(1-x)^2 + L_{E:XZ}x^2(1-x) \\
&= {}^oG_{AX} + x[({}^oG_{EZ} - {}^oG_{AX}) + (\Delta^oG + L_{AE:Z} + L_{A:XZ})] \\
&\quad - x^2[(\Delta^oG + L_{AE:X} + L_{A:XZ}) + (L_{AE:X} + L_{A:XZ} \\
&\quad - L_{AE:Z} - L_{E:XZ})] + x^3(L_{AE:X} + L_{A:XZ} - L_{AE:Z} \\
&\quad - L_{E:XZ}) - TS_c \qquad \text{(Eq 8)}
\end{aligned}
$$

It is interesting to note that there are only four combinations of parameters in this expression, $^oG_{AX}$, $({}^oG_{EZ} - {}^oG_{AX})$, $(\Delta^oG + L_{AE:X} + L_{A:XZ})$, and $(L_{AE:X} + L_{A:XZ} - L_{AE:Z} - L_{E:XZ})$. Thus, only four can be evaluated from experimental information, and within the
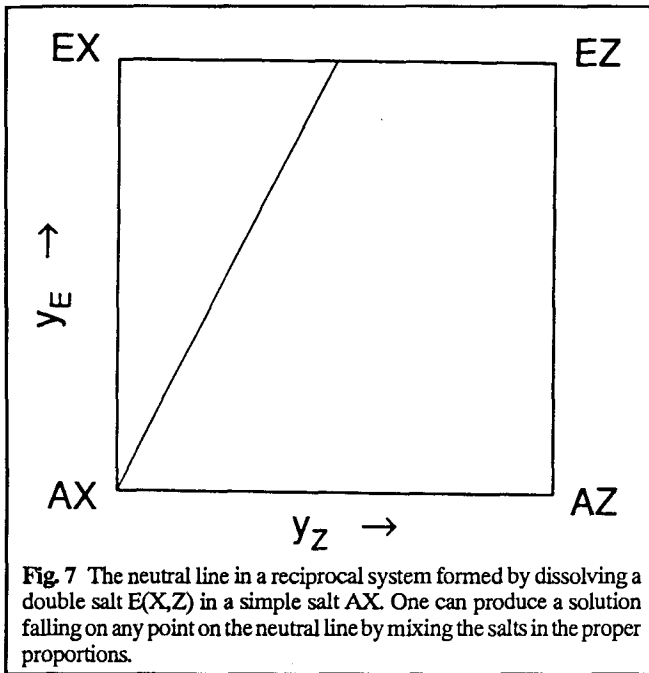
Fig. 7 The neutral line in a reciprocal system formed by dissolving a double salt E(X,Z) in a simple salt AX. One can produce a solution falling on any point on the neutral line by mixing the salts in the proper proportions.

limitations of the model, only four are required for a description of the properties.

With an ordinary subregular solution model for a binary (AX)-(EZ) system, one would get

$$G_m = (1-x)\,^{\circ}G_{AX} + x\,^{\circ}G_{EZ} + x(1-x)(L_1 + xL_2) - TS_c$$

$$= \,^{\circ}G_{AX} + x(^{\circ}G_{EZ} - \,^{\circ}G_{AX} + L_1) - x^2(L_1 - L_2)$$

$$- x^3 L_2 - TS_c \qquad (Eq\ 9)$$

This result is identical with the result of the compound energy model if we identify L_1 with $(\Delta\,^{\circ}G + L_{AE:X} + L_{A:XZ})$ and L_2 with $-(L_{AE:X} + L_{A:XZ} - L_{AE:Z} - L_{E:XZ})$ and if we use the proper expression for the entropy, S_c, taking into account the individual contributions from the sublattices.

6. Solution of a Double Salt in a Simple Salt

It is also possible that only one of the component compounds falls on the neutral line. Consider for example the system $(A^{+1}, E^{+2})_1(X^{-1}, Z^{-3})_1$, for which the condition of electroneutrality gives a different line. See Fig. 7.

$$1 \times y_A + 2 \times y_E = 1 \times y_X + 3 \times y_Z \qquad (Eq\ 10)$$

$$y_E = 2y_Z \qquad (Eq\ 11)$$

Here it is possible to dissolve only a balanced mixture of EX and EZ into AX because EX and EZ are both charged and neither can exist by itself. Instead, a double salt, $E_1X_{0.5}Z_{0.5}$, which appears at the upper end of the neutral line, may exist. According to our model, its Gibbs energy is

$$G_{d.s.} = 0.5\,^{\circ}G_{EX} + 0.5\,^{\circ}G_{EZ} - RT\ln 2 + 0.25L_{E:XZ} \qquad (Eq\ 12)$$

where the $RT\ln 2$ term arises from the ideal entropy of mixing of X^{-1} and Z^{-3}. By introducing the condition of electroneutrality and denoting y_E by x, we get on the neutral line

$$G_m = (1-x)(1-x/2)\,^{\circ}G_{AX} + (1-x)(x/2)\,^{\circ}G_{AZ} +$$

$$x(1-x/2)\,^{\circ}G_{EX} + x(x/2)\,^{\circ}G_{EZ} - TS_c + L_{AE:Z}(1-x)$$

$$x(x/2) + L_{AE:X}(1-x)x(1-x/2) + L_{A:XZ}(1-x)$$

$$(1-x/2)(x/2) + L_{E:XZ}x(1-x/2)(x/2)$$

$$= \,^{\circ}G_{AX} + x[G_{d.s.} + \,^{\circ}G_{AX} + RT\ln 2 - 0.5(\Delta\,^{\circ}G$$

$$+ 0.5L_{E:XZ} - 2L_{AE:X} + L_{A:XZ})] + x^2[0.5(\Delta\,^{\circ}G$$

$$+ 0.5L_{E:XZ} - 2L_{AE:X} - L_{A:XZ}) - 0.25(2L_{AE:X} - 2L_{AE:Z}$$

$$- L_{E:XZ} + L_{A:XZ})] + 0.25x^3(2L_{AE:X} - 2L_{AE:Z} - L_{E:XZ}$$

$$+ L_{A:XZ}) - TS_c \qquad (Eq\ 13)$$

Again we find that only four combinations of parameters appear, and they can be identified with parameters in a subregular solution model for a binary system, provided that the correct expression is used for the entropy, S_c, taking into account the individual contributions from the sublattices.

7. Solution of Two Double Oxides

Let us now consider an oxide phase with two sublattices for the cations. We can then have a double oxide $A_1C_1O_1$ if the cations are monovalent. A solution between two such double oxides may be represented by the formula $(A, B)_1(C, D)_1O_1$ if A and B can only go into the first sublattice and C and D only into the second one. The properties can be represented directly by the basic model.

It is more interesting to consider the case of different valencies, found for instance in solutions of spinels, $(A^{+2}, E^{+3})_1(B^{+2}, F^{+3})_2(O^{-2})_4$. The condition of electroneutrality will be

$$2 \times y_A + 3 \times y_E + 2 \times 2y_B + 3 \times 2y_F = 8 \qquad (Eq\ 14)$$

$$y_E = 2y_B \qquad (Eq\ 15)$$

This is the same type of relation we found in the previous section, and the equations derived there will apply if we substitute B for Z and F for X, except that the entropy will be different because we now have two sites in the second sublattice and a triple oxide, $E_1B_1F_1O_4$, will play the same role as the double salt. According to our model, its Gibbs energy is

$$^{\circ}G_{t.o.} = 0.5\,^{\circ}G_{EB} + 0.5\,^{\circ}G_{EF} - 2RT\ln 2 + 0.25L_{E:BF} \qquad (Eq\ 16)$$

For simplicity, we have here omitted oxygen from the notation.

8. Simple Spinel

The simple spinel is a very common kind of double oxide with two different sublattices for the cations. However, usually both

cations can go into both sublattices. For a simple spinel $A_1E_2O_4$, where A is divalent and E is trivalent, we should then write the formula as $(A^{+2}, E^{+3})_1(A^{+2}, E^{+3})_2(O^{-2})_4$. The diagram will look as the previous one (see Fig. 8), and we can use the expression derived for the double salt, Eq 13, by substituting A for Z and E for X and by using $2RT \ln 2$ instead of $RT \ln 2$.

It should be realized that all points on the neutral line now represent the stoichiometric composition $A_1E_2O_4$ but with different distributions of A^{+2} and E^{+3} on the two cation sublattices. The point representing the minimum of Gibbs energy for any one temperature and pressure is the only point available for experimental studies. There are cases where that point is close to the AE corner. They are called normal spinels, and we may use the notation

$$G_{nAE} = {}^\circ G_{AE} \qquad \text{(Eq 17)}$$

Other cases are close to the other end-point of the neutral line, $(E^{+3})_1(A^{+2}, E^{+3})_2(O^{-2})_4$, and they are called inverse spinels. We may use the notation

$$G_{iAE} = 0.5 {}^\circ G_{EE} + 0.5 {}^\circ G_{EA} - 2RT \ln 2 + 0.25 L_{E:AE} \qquad \text{(Eq 18)}$$

Formally, the properties of the simple spinel can be represented with Eq 13, which contains eight parameters, ${}^\circ G_{AE}$, ${}^\circ G_{EA}$, ${}^\circ G_{AA}$, ${}^\circ G_{EE}$, $L_{AE:A}$, $L_{AE:E}$, $L_{A:AE}$, and $L_{E:AE}$. However, we have seen that there are only four independent parameters on the neutral line, and with our notation they may be written as G_{nAE}, G_{iAE}, $(\Delta^\circ G + 0.5 L_{E:AE} - 2 L_{AE:E} - L_{A:AE})$, and $(2 L_{AE:E} - 2 L_{AE:A} - L_{E:AE} + L_{A:AE})$. Furthermore, we have seen that only one point in the reciprocal system is available for experimental studies, and thus one can hope to measure only its position and Gibbs energy value for that condition. Thus, normally it will be possible to evaluate only two parameters. In this situation, one could either use some theoretical estimate of various quantities or one would have to reduce
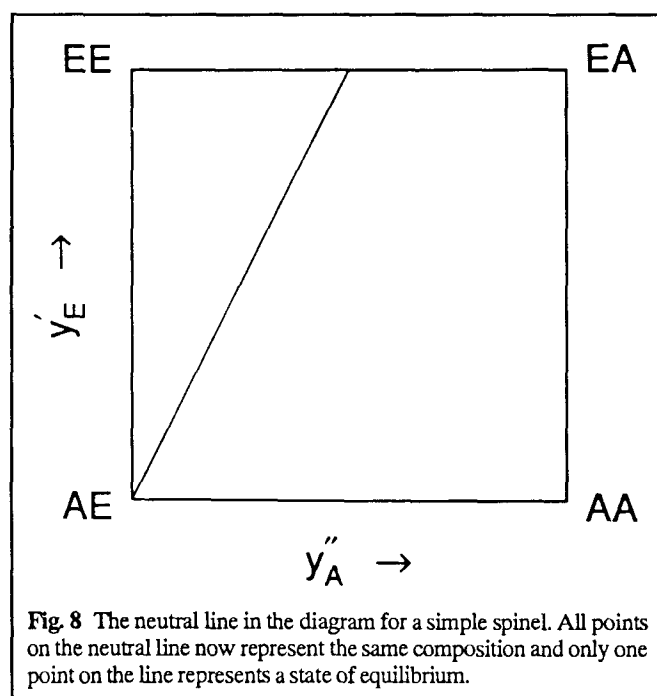
the number of parameters. The first simplification should be to set the last combination of parameters to zero, which may seem natural in view of the fact that there are twice as many cations on the second sublattice. It may thus be reasonable to assume that the interaction between A and E on the second sublattice should result in an L value twice as large as for an interaction on the first sublattice. Equation 13 will thus yield the following expression if we retain y'_E instead of x.

$$G_m = G_{nAE} + y'_E[G_{iAE} - G_{nAE} + 2RT \ln 2 - 0.5(\Delta^\circ G$$

$$+ 0.5 L_{E:AE} - 2L_{AE:E} - L_{A:AE})] + 0.5(y'_E)^2[\Delta^\circ G$$

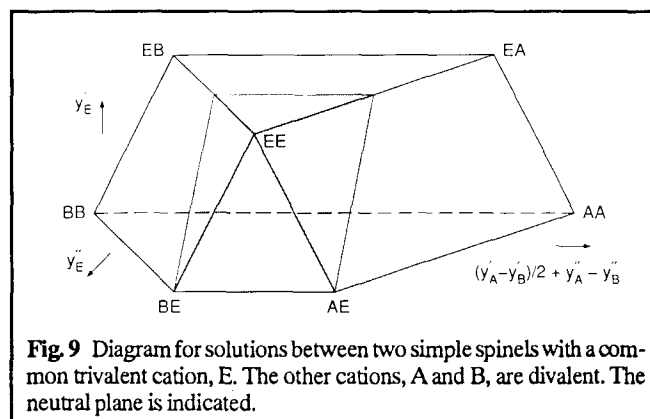$$+ 0.5 L_{E:AE} - 2L_{AE:E} - L_{A:AE}] - TS_c \qquad \text{(Eq 19)}$$

By retaining y'_E we here emphasize that this variable cannot be controlled by varying the composition, which was the case for Eq 13. Instead we must find the equilibrium value of y'_E, which minimizes the Gibbs energy.

The second simplification should be to put $(\Delta^\circ G + 0.5 L_{E:AE} - 2L_{AE:E} - L_{A:AE})$ equal to zero, which may seem less natural because it is in contradiction with the previous statement that $\Delta^\circ G$ is the most important parameter. However, we are now considering interactions between cations in an oxide where the primary interaction is between cations and oxygen. Previously we considered interactions between cations and anions.

Another alternative would be to increase the experimental information by extending the study to various temperatures. It may then be possible to evaluate one more parameter, either one of those now put to zero or a temperature dependence in G_{nAE} or G_{iAE}.

Suppose one has evaluated two parameters, G_{nAE} and G_{iAE}, assuming that $(\Delta^\circ G + 0.5 L_{E:AE} - 2L_{AE:E} - L_{A:AE})$ and $(2L_{AE:E} - 2L_{AE:A} - L_{E:AE} + L_{A:AE})$ are zero. In order to make calculations with the compound energy model, one should then give the eight parameters such values that the four conditions are satisfied. On the neutral line all such sets of parameter values will give the same result. Without any further assumption regarding the simple spinel, one may thus simply put $\Delta^\circ G$ and all L s equal to zero. With this choice we would have

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Fig. 8 The neutral line in the diagram for a simple spinel. All points on the neutral line now represent the same composition and only one point on the line represents a state of equilibrium.

Fig. 9 Diagram for solutions between two simple spinels with a common trivalent cation, E. The other cations, A and B, are divalent. The neutral plane is indicated.

$$^{o}G_{AE} = G_{nAE} \qquad \text{(Eq 20)}$$

$$^{o}G_{EA} + {}^{o}G_{EE} = 2^{o}G_{iAE} + 4RT \ln 2 \qquad \text{(Eq 21)}$$

$$^{o}G_{AA} + 2^{o}G_{EE} = G_{nAE} + 2G_{iAE} + 4RT \ln 2 \qquad \text{(Eq 22)}$$

$$^{o}G_{EE} - {}^{o}G_{EE} = 0 \qquad \text{(Eq 23)}$$

Here we have arbitrarily chosen $^{o}G_{EE}$ as a reference for the charged compounds. It can be given the value zero or any arbitrary value. Furthermore, it is easy to see that this set of expressions is based on the choice
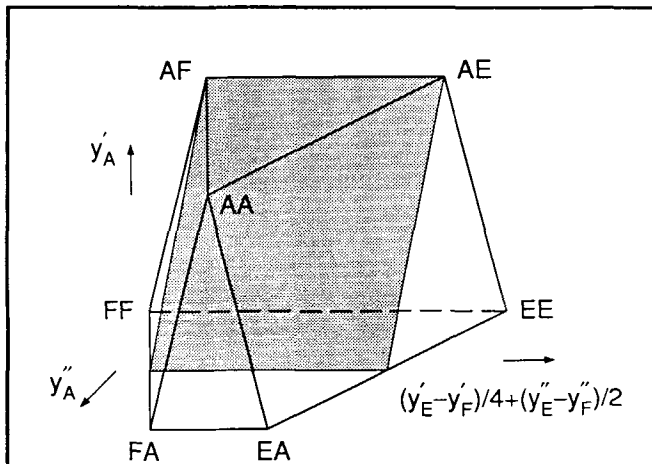
Fig. 10 Diagram for solutions between two simple spinels with a common divalent cation, A. The other cations, E and F, are trivalent. The neutral plane is indicated.

$$\Delta^{o}G_{AE:AE} = {}^{o}G_{AE} + {}^{o}G_{EA} - {}^{o}G_{AA} - {}^{o}G_{EE} = 0 \qquad \text{(Eq 24)}$$

9. Solution Between Two Spinels With a Common Cation

A solution between two simple spinels with a common trivalent cation, $A_1E_2O_4$ and $B_1E_2O_4$, will be described with the formula $(A^{+2}, B^{+2}, E^{+3})_1(A^{+2}, B^{+2}, E^{+3})_2(O^{-2})_4$. A solution between two simple spinels with a common divalent cation, $A_1E_2O_4$ and $A_1F_2O_4$, will be described with the formula $(A^{+2}, E^{+3}, F^{+3})_1(A^{+2}, E^{+3}, F^{+3})_2(O^{-2})_4$. In order to illustrate such systems, one may use the diagrams presented in Fig. 9 and 10. They have a neutral plane extending between two points representing normal spinels and two points representing inverse spinels. The horizontal axis in that plane represents the composition, and the other axis represents the site distribution or "the degree of inverseness." For each composition, the site distribution must be found by minimizing the Gibbs energy. All states of equilibrium may thus be represented by a curve between the two vertical sides of the neutral plane. This is illustrated in Fig. 11 for the Fe_3O_4-$FeAl_2O_4$ system according to an assessment by Gisby.[12] A series of curves are given for a series of temperatures. Below a critical temperature, 1133 K, there is a miscibility gap. In Fig. 12, it is shown better and is compared with experimental data.[13]

Before combining the descriptions of the two simple spinels with a common trivalent cation, E^{+3}, it is essential to express them with the same reference for charged compounds. The most convenient choice is $^{o}G_{EE}$ because E is the common cation. Expressions for $A_1E_2O_4$ are already given by Eq 20 to 22, and for $B_1E_2O_4$ we get in the same way

$$^{o}G_{BE} = G_{nBE} \qquad \text{(Eq 25)}$$
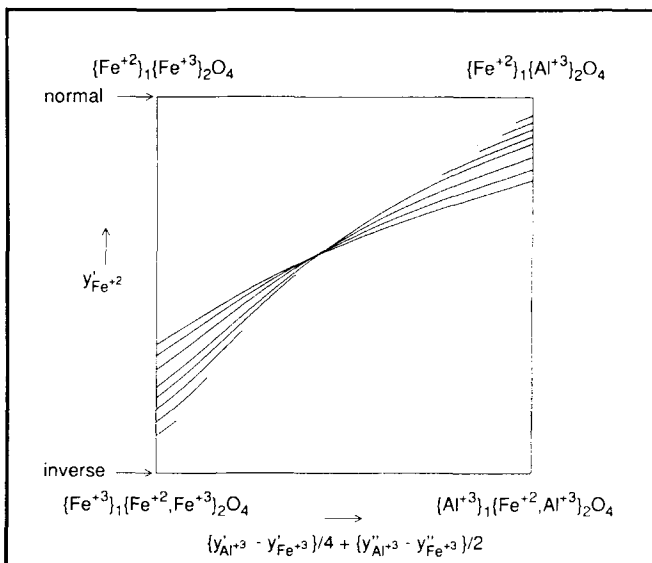
Fig. 11 The neutral plane in the FeO · Fe_2O_3–FeO · Al_2O_3 system showing curves representing equilibria at 773, 873, 973, 1073, 1173, 1373, 1573, and 1773 K.
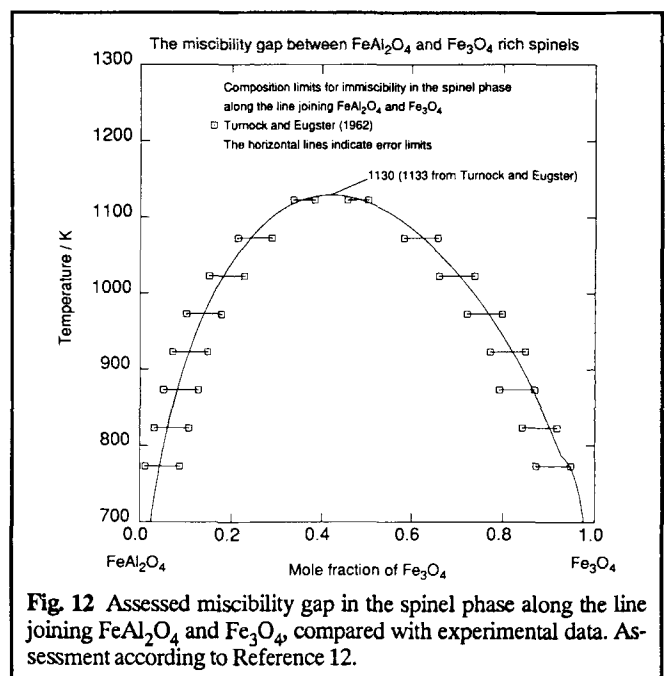
Fig. 12 Assessed miscibility gap in the spinel phase along the line joining $FeAl_2O_4$ and Fe_3O_4, compared with experimental data. Assessment according to Reference 12.

$$^{o}G_{EB} + {^{o}G_{EE}} = 2{^{o}G_{iBE}} + 4RT \ln 2 \qquad \text{(Eq 26)}$$

$$^{o}G_{BB} + 2{^{o}G_{EE}} = G_{nBE} + 2G_{iBE} + 4RT \ln 2 \qquad \text{(Eq 27)}$$

Formally there is a third simple spinel in the system, $(A^{+2}, B^{+2},)_1(A^{+2}, B^{+2})_2(O^{-2})_4$, and it contains two new component compounds, AB and BA. However, this spinel cannot be studied directly because it is never neutral. As a consequence, $^{o}G_{AB}$ and $^{o}G_{BA}$ may not be of much practical importance, and it may be suggested that their values are calculated simply by assuming that $\Delta^{o}G$ for the following two reciprocal reactions are zero,

$$AB + BE = AE + BB \qquad \text{(Eq 28)}$$

$$BA + AE = BE + AA \qquad \text{(Eq 29)}$$

Thus we get, by introducing the chosen reference for charged compounds, $^{o}G_{EE}$,

$$^{o}G_{AB} + 2{^{o}G_{EE}} = ({^{o}G_{BB}} + 2{^{o}G_{EE}}) + {^{o}G_{AE}} - {^{o}G_{BE}} \qquad \text{(Eq 30)}$$

$$^{o}G_{BA} + 2{^{o}G_{EE}} = ({^{o}G_{AA}} + 2{^{o}G_{EE}}) + {^{o}G_{BE}} - {^{o}G_{AE}} \qquad \text{(Eq 31)}$$

We now have a complete set of the nine $^{o}G_{ij}$ parameters and could combine them to calculate the properties of the solution $(A^{+2}, B^{+2}, E^{+3})_1(A^{+2}, B^{+2}, E^{+3})_2(O^{-2})_4$. However, then we encounter new interaction energies. Suppose the whole solution phase is close to being a normal spinel. Then the formula would simply be $(A^{+2}, B^{+2})_1(E^{+3})_2(O^{-2})_4$, and one may consider the interaction $L_{AB:E}$. If the solution phase instead is close to being inverse, the formula would be $(E^{+3})_1(A^{+2}, B^{+2}, E^{+3})_2(O^{-2})_4$, and there are three binary interaction energies on the second sublattice. However, we have already decided to put $L_{E:AE}$ to zero and also $L_{E:BE}$ to zero although it was not stated explicitly. The third parameter, $L_{E:AB}$, may be introduced, and it may be important for the description of the solution behavior.
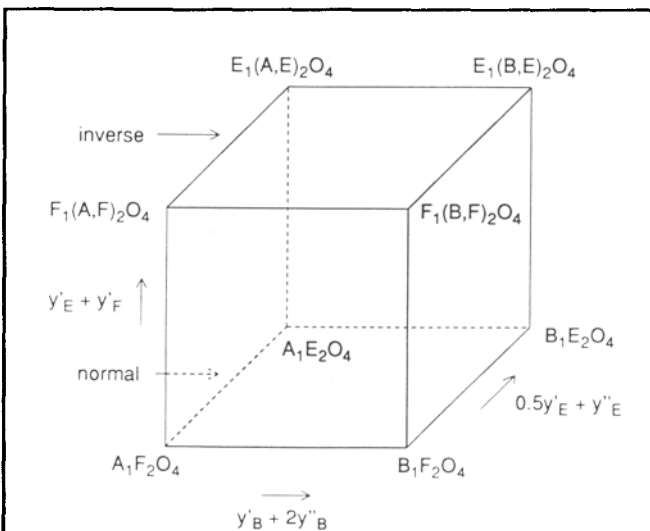
If the actual situation falls between the normal and inverse cases, then both parameters $L_{AB:E}$ and $L_{E:AB}$ will play an important role. If it is not possible to evaluate them both, then it may be reasonable to assume that $L_{E:AB} = 2L_{AB:E}$ where the factor 2 is justified by an argument given in section 8. We thus have a complete description of the properties of a solution

$(A^{+2}, B^{+2}, E^{+3})_1(A^{+2}, B^{+2}, E^{+3})_2(O^{-2})_4$ based upon the properties of two simple spinels and one or two new parameters to be evaluated from the properties of the solution.

It may be objected that one should not introduce interaction energies as new parameters while related $\Delta^{o}G$ quantities are arbitrarily put to zero. An alternative to the new L parameters discussed here would be to relax the condition $\Delta^{o}G = 0$ for the reciprocal reactions defined by Eq 28 and 29. In fact, the spinel solution in the Fe_3O_4–$FeAl_2O_4$ system was assessed[12] with three adjustable parameters, $\Delta^{o}G_{Fe^{+3},Al^{+3}:Fe^{+3},Al^{+3}}$, $L_{Fe^{+2}:Al^{+3},Fe^{+3}}$, and $L_{Fe^{+3}:Al^{+3},Fe^{+3}}$.

A solution between two spinels with a common divalent cation, $A_1E_2O_4$ and $A_1F_2O_4$, can be treated in the same way, and the most
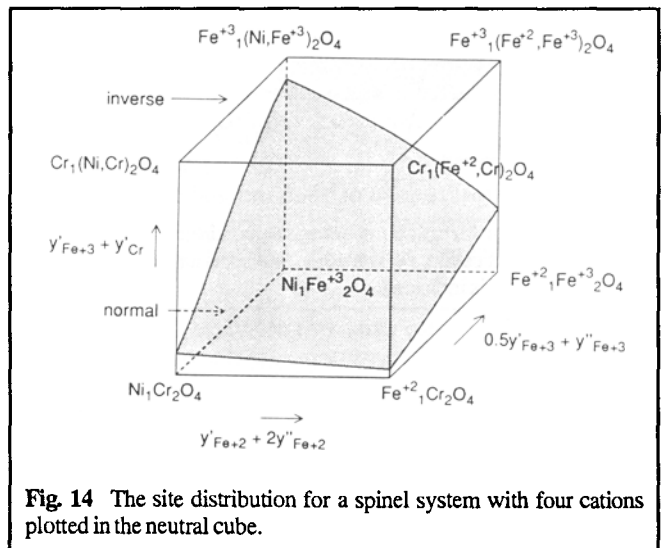

Fig. 14 The site distribution for a spinel system with four cations plotted in the neutral cube.

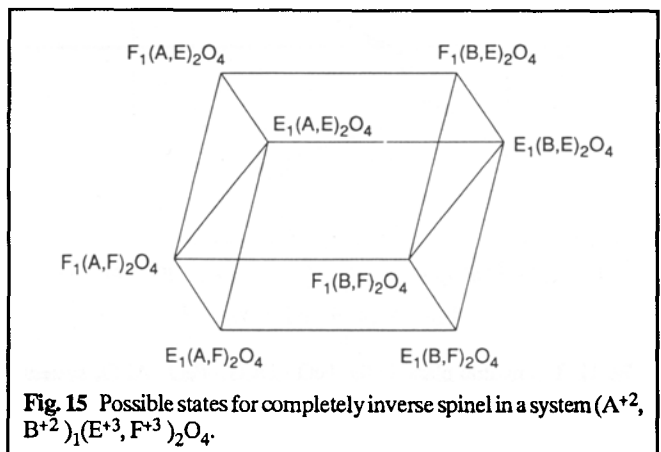Fig. 13 Neutral cube for a spinel system with four cations, two divalent and two trivalent.

Fig. 15 Possible states for completely inverse spinel in a system $(A^{+2}, B^{+2})_1(E^{+3}, F^{+3})_2O_4$.

convenient choice of reference for charged compounds would now be $^{o}G_{AA}$ because A is the common ion. However, in order to combine with the previous set of $^{o}G_{ij}$ parameters and obtain a description of a higher order system, it is necessary to accept a common choice of reference. The relation between the two references is available from Eq 22, and it is easy to change from one reference to the other. The new interaction energies, encountered in the solution between two spinels with a common divalent cation, would be four: $L_{EF:A}, L_{A:EF}, L_{E:AF},$ and $L_{F:AE}$. They can be used to model a miscibility gap like the one shown in Fig. 12. One adjustable parameter may be eliminated by assuming that $L_{A:EF} = 2L_{EF:A}$.

10. Spinel Solutions With Four Cations

Let us now consider a spinel solution with two divalent and two trivalent cations, $(A^{+2}, B^{+2}, E^{+3}, F^{+3})_1 (A^{+2}, B^{+2}, E^{+3}, F^{+3})_2 (O^{-2})_4$. This solution contains four simple spinels, $A_1E_2O_4$, $A_1F_2O_4$, $B_1E_2O_4$, and $B_1F_2O_4$. If these were all normal spinels, the system could be regarded as an ordinary reciprocal system $(A^{+2}, B^{+2})_1 (E^{+3}, F^{+3})_2 (O^{-2})_4$ and all compositions on the composition square would be neutral and could be studied experimentally. The solution behavior could be predicted from the properties of the four component compounds, $G_{nAE}, G_{nAF}, G_{nBE},$ and G_{nBF}, and from the binary interaction energies, $L_{AB:E}, L_{AB:F}, L_{A:EF},$ and $L_{B:EF}$.

If all four spinels were inverse, one would have a more complicated situation. But the basic parameters would be $G_{iAE}, G_{iAF}, G_{iBE},$ and G_{iBF}; and $L_{E:AB}, L_{F:AB}, L_{EF:A},$ and $L_{EF:B}$.

As already mentioned, for a case between the normal and inverse cases it may be logical to use both sets of interaction energies, but we may reduce the number of adjustable parameters by assuming

Fig. 16 Schematic representation of a spinel system with four cations, illustrating the relations between the four simple spinels.

$$L_{E:AB} = 2L_{AB:E} \tag{Eq 32}$$

$$L_{F:AB} = 2L_{AB:F} \tag{Eq 33}$$

$$L_{A:EF} = 2L_{EF:A} \tag{Eq 34}$$

$$L_{B:EF} = 2L_{EF:B} \tag{Eq 35}$$

It is not possible to construct a diagram showing all sixteen component compounds in this higher order system. However, there will be a neutral cube, which can be shown. See Fig. 13. The bottom square represents the limiting case of completely normal spinel, and it can be used to represent the composition. The top square represents the limiting case of completely inverse spinel. The vertical axis represents the degree of inverseness, represented by the sum of trivalent ions on the tetrahedral sublattice.

In the present solution phase, there are eight site fractions with two stoichiometric conditions, $\Sigma_{y_i'} = 1$ and $\Sigma_{y_i''} = 1$, and one condition of electroneutrality. Furthermore, by fixing the composition, one may introduce two more conditions. Thus there are three degrees of freedom, which are utilized in order to minimize the Gibbs energy of the system. One of them can be used to express how inverse the spinel solution is, i.e. the vertical axis in Fig. 13. As an example, the minimization of the Gibbs energy in a recent assessment of the $NiFe_2O_4–Fe_3O_4–FeCr_2O_4–NiCr_2O_4$ system performed by Taylor[14] gave the result presented schematically in Fig. 14. The shaded surface illustrates how the inverseness, expressed as $y_{Fe^{+3}}' + y_{Cr^{+3}}'$, varies with composition.

The other two degrees of freedom cannot be represented in this kind of diagram, but one of them can be illustrated for the limiting case of perfect inverse spinel, i.e. for the top square of Fig. 13. A point on that square can represent a situation falling anywhere on the corresponding vertical line in Fig. 15. The upper half of that parallelepiped represents cases where F^{+3} has a stronger tendency than E^{+3} to occupy the first (tetrahedral) sublattice. The lower part represents cases where E^{+3} has the stronger tendency. For a case between the normal and inverse cases, the situation is more complicated because there is a similar competition between A^{+2} and B^{+2} to occupy the first sublattice. These two degrees of freedom may be represented by ordinary distribution coefficients, $y_E' y_F'' / y_F' y_E''$ and $y_A' y_B'' / y_B' y_A''$ as functions of the composition. One of these degrees of freedom also exists in a solution between two spinels—$y_E' y_F'' / y_F' y_E''$ if there is a common divalent cation, and $y_A' y_B'' / y_B' y_A''$ if there is a common trivalent cation.

In principle, the properties of the complete system with four cations can be described by combining all the parameters discussed. Of course, many reciprocal parameters could also be added, but it is highly unlikely that they can ever be evaluated. In practice, the information may be too limited to allow evaluation of even the sixteen $^{o}G_{ij}$ parameters. For such situations, it has been proposed[9] that one could assume $\Delta^{o}G = 0$ for as many of the reciprocal reactions as are necessary.
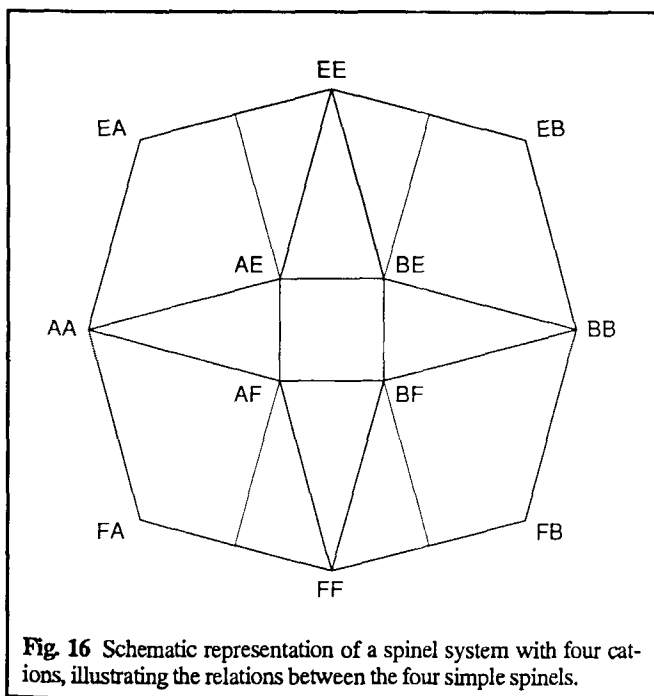
11. A Problem of Consistency

Before leaving the present discussion, it should be emphasized that there is a relation between the parameters discussed. In order to explain this fact, it may be useful to refer to the simple diagram in Fig. 16, showing schematically the relations between the four simple spinels. In order to show their connections, it was necessary to distort the composition squares of the four simple spinels. The neutral lines have been included, and it should be recognized that the central square is neutral over its whole area. It does not represent a simple spinel but a reciprocal solution of four normal spinels. Actually, it is identical to the bottom square of the neutral cube in Fig. 13. The four neutral lines in Fig. 16 are identical to the four vertical edges in Fig. 13, but the sides of the cube and the top square in Fig. 13 are not shown in Fig. 16.

Suppose that the upper two spinels in Fig. 16 are assessed first, using $^oG_{EE}$ as the reference for charged compounds, and then the lower two spinels, using $^oG_{FF}$ as the reference. When combining these for a complete description, one must evaluate the relation between the two references. This can be done by using the connecting point AA. We have already derived the relation between $^oG_{EE}$ and $^oG_{AA}$; see Eq 22. In the same way, we may derive the relation between $^oG_{FF}$ and $^oG_{AA}$

$$^oG_{AA} + 2^oG_{FF} = G_{nAF} + 2G_{iAF} + 4RT\ln 2 \qquad (Eq\ 36)$$

We thus obtain by taking the difference between Eq 22 and 36,

$$2(^oG_{EE} - ^oG_{FF}) = G_{nAE} + 2G_{iAE} - G_{nAF} - 2G_{iAF} \qquad (Eq\ 37)$$

However, the picture shows that there is another connecting point, BB. By equating similar expressions for $^oG_{BB}$, we get

$$2(^oG_{EE} - ^oG_{FF}) = G_{nBE} + 2G_{iBE} - G_{nBF} - 2G_{iBF} \qquad (Eq\ 38)$$

Of course, these results must be the same, and we thus have the following relation:

$$G_{nBE} + 2G_{iBE} + G_{nAF} + 2G_{iAF} - G_{nBF} - 2G_{iBF} - G_{nAE}$$
$$- 2G_{iAE} = 0 \qquad (Eq\ 39)$$

In view of this relation, one should not regard the assessment of a simple spinel as finished until the results have been checked through at least one group of four spinels. Any discrepancy that arises may be corrected by making changes to one or more assessments. Ideally, one should apply Eq 39 and assess all four simple spinels simultaneously. That would give a better chance to satisfy Eq 39 and still get a reasonable fit of the experimental data. If this is not possible, then one may introduce a nonzero value for Δ^oG of one of the simple spinels and reassess that system alone. On the other hand, it should be noticed that the condition defined by Eq 39 may be relaxed, and the inconsistency between the four assessments of the simple spinels may be resolved by the following procedure, which does not require any reassessment.

In the assessment of a simple spinel described in section 8, two simplifications were introduced by putting two combinations of parameters equal to zero. Evidently, the assessment will not be affected if the individual parameters are changed, as long as the two combinations are equal to zero. In section 8 this requirement was

satisfied by simply putting Δ^oG and all Ls equal to zero. If it now turns out that Eq 39 is not satisfied and one decides to give Δ^oG for a simple spinel a nonzero value, then one may compensate for this change by giving some L parameters for the same spinel such nonzero values that the two combinations are still equal to zero. We shall now explore this possibility by retaining Δ^oG and all the L parameters for the AE spinel in the derivation and put the two combinations of parameters equal to zero later on.

First we must subtract $0.5L_{E:AE}$ from the right-hand side of Eq 21 in view of Eq 18. We can thus make the following derivation:

$$\Delta^oG_{AE:AE} + \Delta^oG_{BF:BF} - \Delta^oG_{AF:AF} - \Delta^oG_{BE:BE} = {}^oG_{AE}$$
$$+ {}^oG_{EA} - {}^oG_{EE} - {}^oG_{AA} + {}^oG_{BF} + {}^oG_{FB} - {}^oG_{FF}$$
$$- {}^oG_{BB} - {}^oG_{AF} - {}^oG_{FA} + {}^oG_{FF} + {}^oG_{AA} - {}^oG_{BE}$$
$$- {}^oG_{EB} + {}^oG_{EE} + {}^oG_{BB} = G_{nAE} + 2G_{iAE}$$
$$+ 4RT\ln 2 - 0.5L_{E:AE} + G_{nBF} + 2G_{iBF} + 4RT\ln 2$$
$$- G_{nAF} - 2G_{iAF} - 4RT\ln 2 - G_{nBE} - 2G_{iBE}$$
$$- 4RT\ln 2 = G_{nAE+} 2G_{iAE} + G_{nBF} + 2G_{iBF} - G_{nAF}$$
$$- 2G_{iAF} - G_{nBE} - 2G_{iBE} - 0.5L_{E:AE} \qquad (Eq\ 40)$$

On the other hand, the values of the left-hand side may be derived directly by inserting a value of $\Delta^oG_{AE:AE} = -0.5L_{E:AE} + 2L_{AE:E} + L_{A:AE}$ in order to keep one of the combinations of parameters for the AE spinel equal to zero. As the descriptions of the other three simple spinels remain unchanged, then $\Delta^oG_{BF:BF} = \Delta^oG_{AF:AF} = \Delta^oG_{BE:BE} = 0$. The left-hand side will thus be equal to $-0.5L_{E:AE} + 2L_{AE:E} + L_{A:AE}$. Instead of Eq 39, we obtain

$$G_{nBE} + 2G_{iBE} + G_{nAF} + 2G_{iAF} - G_{nBF} - 2G_{iBF} - G_{nAE}$$
$$- 2G_{iAE} = -2L_{AE:E} - L_{A:AE} \qquad (Eq\ 41)$$

We can thus use either one of $L_{AE:E}$ or $L_{A:AE}$ to eliminate a discrepancy, as long as we can give $\Delta^oG_{AE:AE}$ the value $2L_{AE:E} + L_{A:AE} - 0.5L_{E:AE}$. On the other hand, $L_{E:AE}$ is not useful and may still be put to zero.

The other combination of parameters, which is defined as $(2L_{AE:E} - 2L_{AE:A} - L_{E:AE} + L_{A:AE})$, must not be affected by introducing a nonzero value of $2L_{AE:E} + L_{A:AE}$. In view of the choice $L_{E:AE} = 0$, it is necessary to put

$$2L_{AE:A} = 2L_{AE:E} + L_{A:AE} \qquad (Eq\ 42)$$

For the $NiFe_2O_4-Fe_3O_4-FeCr_2O_4-NiCr_2O_4$ system, Taylor[14] chose

$$\Delta^oG_{Fe^{+2},Fe^{+3}:Fe^{+2},Fe^{+3}} = 0 \qquad (Eq\ 43)$$

$$\Delta^oG_{Ni, F^{+3}:Ni, F^{+3}} = 0 \qquad (Eq\ 44)$$

$$\Delta^oG_{Fe^{+2},Cr:Fe^{+2},Cr} = 0 \qquad (Eq\ 45)$$

$$\Delta^oG_{Ni, Cr:Ni,} \neq 0 \qquad (Eq\ 46)$$

$$L_{Cr:Ni, C} = L_{Ni:Ni, C} = 0 \qquad (Eq\ 47)$$

$$L_{Ni, Cr:C} = L_{Ni, Cr:N} = 0.5\Delta^{\circ}G_{Ni, Cr:Ni,} \qquad (Eq\ 48)$$

The calculated properties of the NiCr2O4 system, which was primarily assessed assuming $\Delta^{\circ}G = L = 0$, are unaffected by this change in parameter values.

12. Introduction of Vacancies

Often the composition of oxides, e.g. simple spinels, can vary on both sides of the stoichiometric composition. An oxygen excess may be modelled by introducing neutral vacancies on a cation sublattice. For spinels, it is not certain whether the vacancies prefer to go into the tetrahedral or octahedral sublattice. Experimental evidence from electron diffraction,[15] X-ray photoelectron spectroscopy,[16] and nuclear magnetic resonance[17] is contradictory. For the present discussion, it will be assumed that they go into the octahedral one. As an example, we can thus model the metastable γ modification of Al_2O_3, which has a spinel related structure, by the formula $(Al^{+3})_1(Al^{+3}, Va)_2(O^{-2})_4$ with $y_{Va} = 1/6$. Three formula units of this compound will correspond to four formula units of γ–Al_2O_3. The component compounds in this model would be $(Al^{+3})_1(Al^{+3})_2(O^{-2})_4$ and $(Al^{+3})_1(Va)_2(O^{-2})_4$, in the short-hand notation AlAl and AlVa. They are both charged and will appear only in the neutral combination 5AlAl + AlVa. Assuming random mixing on the second sublattice, the Gibbs energy of 8 moles of γ-Al_2O_3 will be written as

$$8G_{\gamma Al_2O_3} = 6G_m = 5^{\circ}G_{AlAl} + {}^{\circ}G_{AlVa} + 12RT[(5/6)\ln(5/6)$$

$$+ (1/6)\ln(1/6)] + {}^{E}G_m \qquad (Eq\ 49)$$

and by neglecting the interaction between Al^{+3} and Va on the octahedral sublattice and rearranging the ideal entropy expression,

$$8G_{\gamma Al_2O_3} = 5^{\circ}G_{AlAl} + {}^{\circ}G_{AlVa} - 2RT[6\ln6 - 5\ln5] \qquad (Eq\ 50)$$

An example of the simplest case of a spinel with off-stoichiometric compositions is found in the $AlN\cdot Al_2O_3$ spinel, which has the ideal structure $(Al^{+3})_1(Al^{+3})_2(O^{-2}, N^{-3})_4$ with $y_N = 1/4$. Off-stoichiometric compositions can be described with the formula $(Al^{+3})_1(Al^{+3}, Va)_2(O^{-2}, N^{-3})_4$, and by extending the short-hand notation we can represent its component compounds with AlAlO, AlVaO, AlAlN, and AlVaN. The model gives

$$G_m = y_{Al}y_O{}^{\circ}G_{AlAlO} + y_{Va}y_O{}^{\circ}G_{AlVaO} + y_{Al}y_N{}^{\circ}G_{AlAlN}$$

$$+ y_{Va}y_N{}^{\circ}G_{AlVaN} - TS_c + {}^{E}G_m \qquad (Eq\ 51)$$

The component compounds are all charged, and the condition of electroneutrality is

$$3 + 6(1-y_{Va}) = 8(1-y_N) + 12y_N \qquad (Eq\ 52)$$

$$6y_{Va} + 4y_N = 1 \qquad (Eq\ 53)$$

The neutral line thus goes from the point representing the stoichiometric spinel, AlN·Al2O3, to the point representing γAl2O3. See Fig. 17.

For the stoichiometric spinel, we obtain by inserting $y_N = 1/4$ and $y_{Va} = 0$ and neglecting the excess Gibbs energy

$$G_{Al_3NO_3} = (3/4)^{\circ}G_{AlAlO} + (1/4)^{\circ}G_{AlAlN}$$

$$+ 4RT[(3/4)\ln(3/4) + (1/4)\ln(1/4)]$$

$$= (1/4)[3^{\circ}G_{AlAlO} + {}^{\circ}G_{AlAlN} - 4RT(4\ln4 - 3\ln3)]$$

$$(Eq\ 54)$$

By further introducing $\Delta^{\circ}G$ for the reciprocal reaction

$$\Delta^{\circ}G = {}^{\circ}G_{AlAlO} + {}^{\circ}G_{AlVaN} - {}^{\circ}G_{AlVaO} - {}^{\circ}G_{AlAlN} \qquad (Eq\ 55)$$

we can express three of the $^{\circ}G$ quantities relative to the fourth one

$${}^{\circ}G_{AlVaO} + 5^{\circ}G_{AlAlO} = 8G_{\gamma Al_2O_3} + 2RT(6\ln6 - 5\ln5) \quad (Eq\ 56)$$

$${}^{\circ}G_{AlAlN} + 3^{\circ}G_{AlAlO} = 4G_{Al_3NO_3} + 4RT(4\ln4 - 3\ln3) \qquad (Eq\ 57)$$

$${}^{\circ}G_{AlVaN} + 9^{\circ}G_{AlAlO} = \Delta^{\circ}G + 8G_{\gamma Al_2O_3} + 4G_{Al_3NO_3}$$

$$+ RT(12\ln6 - 10\ln5 + 16\ln4 - 12\ln3) \qquad (Eq\ 58)$$

We can introduce the mole fraction x of Al2O3 in the AlN-Al_2O_3 system and obtain on the neutral line

$$y_{Va} = \frac{2x-1}{2(2x+1)} \qquad (Eq\ 59)$$

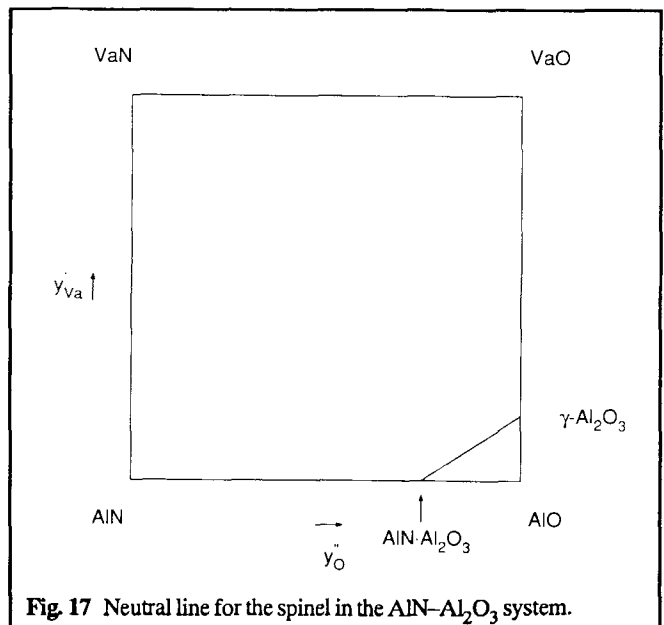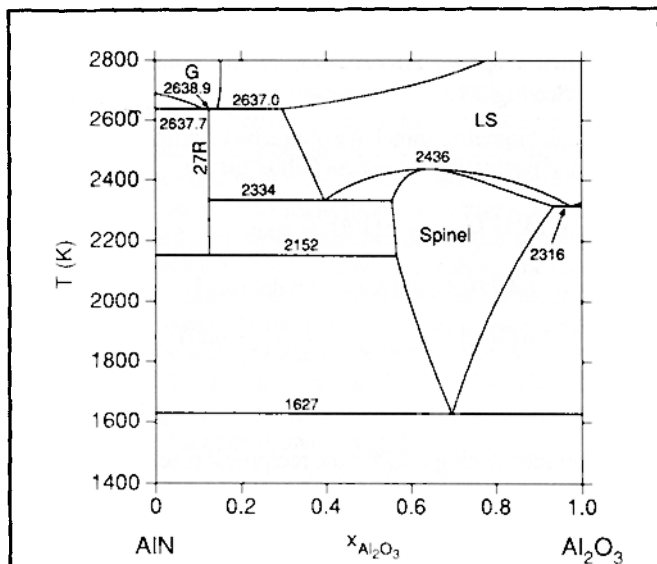Fig. 17 Neutral line for the spinel in the AlN–Al_2O_3 system.

Fig. 18 An assessment of the main features of the AlN-Al$_2$O$_3$ phase diagram using the compound energy model. Assessment according to Reference 18.
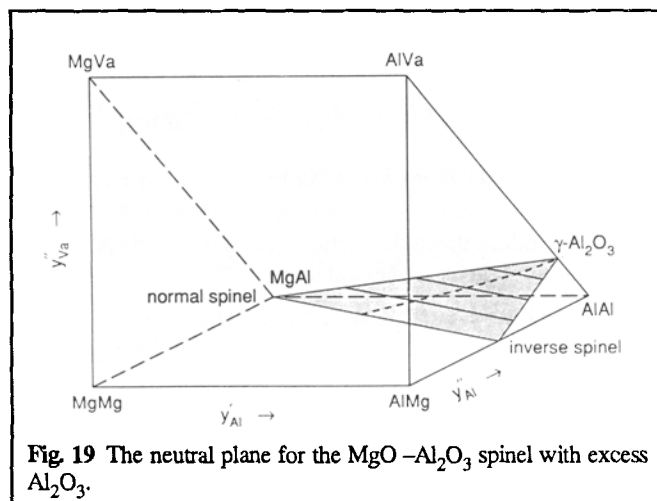

Fig. 19 The neutral plane for the MgO –Al$_2$O$_3$ spinel with excess Al$_2$O$_3$.

$$y_N = \frac{1-x}{2x+1} \qquad (Eq\ 60)$$

$$G_m = \frac{4(1-x)}{2x+1}[G_{Al_3NO_3} + RT(4ln4 - 3ln3)] + \frac{2x-1}{2x+1}[4G_{\gamma Al_2O_3}$$

$$+ RT(6ln6 - 5ln5)] + \frac{(1-x)(2x-1)}{2(2x+1)^2}\Delta^\circ G - TS_c \qquad (Eq\ 61)$$

With the above model, Hillert and Jonsson[18] described the main features of the AlN-Al$_2$O$_3$ phase diagram, Fig. 18. No excess Gibbs energy was introduced, and the spinel was predicted to have a wide range of composition at high temperatures,

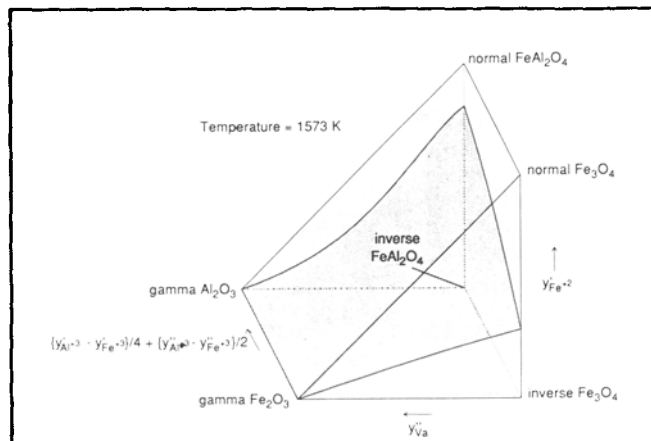**Fig. 20** The site distribution for the spinel phase in the FeO-Fe$_2$O$_3$-Al$_2$O$_3$ system, plotted in the neutral volume.

falling between the two limits, which are $x = 0.5$ for Al$_3$NO$_3$ and $x = 1$ for Al$_2$O$_3$.
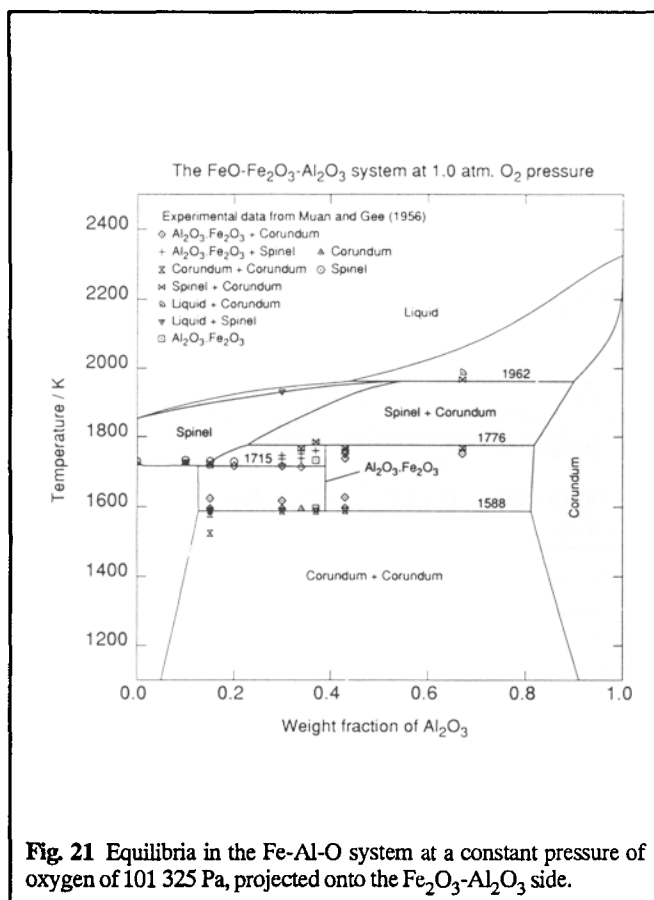
An example of a spinel with two cations and off-stoichiometric compositions is found in the MgO-Al$_2$O$_3$ system. For excess oxygen, it can be represented by the formula (Mg^{+2}, Al^{+3})$_1$(Mg^{+2}, Al^{+3}, Va)$_2$(O^{-2})$_4$, which has six component compounds, MgMg, MgAl, MgVa, AlMg, AlAl, and AlVa, and they form a prism. See Fig. 19. The condition of electroneutrality gives

$$2(1-y'_{Al}) + 3y'_{Al} + 4(1-y''_{Al} - y''_{Va}) + 6y''_{Al} = 8 \qquad (Eq\ 62)$$

$$y'_{Al} + 2y''_{Al} - 4y''_{Va} = 2 \qquad (Eq\ 63)$$

There will thus be a neutral plane and it goes through the three points representing normal spinel, inverse spinel, and γ–Al$_2$O$_3$. The line between the normal and inverse spinel represents all possible situations for the stoichiometric composition. Compositions with higher Al contents are represented by a series of parallel lines. For each line, one must minimize the Gibbs energy in order to find the state of equilibrium. The last line degenerates to a point falling on the Al$_2$O$_3$ composition. The dashed curve shows schematically the states of equilibrium at some temperatures.

Gisby[12] recently assessed the FeO-Fe$_2$O$_3$-Al$_2$O$_3$ system using the formula (Fe^{+2}, Fe^{+3}, Al^{+3})$_1$ (Fe^{+2}, Fe^{+3}, Al^{+3}, Va)$_2$ (O^{-2})$_4$ for the spinel. Such a large system cannot be illustrated in a three-dimensional diagram, but it has a neutral volume, which can be shown. It extends between six points representing normal and inverse spinels of FeO·Fe$_2$O$_3$ and FeO·Al$_2$O$_3$ and also γ–Fe$_2$O$_3$ and γ–Al$_2$O$_3$. See Fig. 20, where the surface representing the states of equilibrium has been added. The phase diagram is three-dimensional and difficult to illustrate. As an example of a two-dimensional section, Fig. 21 presents a projection onto the Fe$_2$O$_3$-Al$_2$O$_3$ plane of equilibria in the system Fe-Al-O at a constant pressure of oxygen of 101 325 Pa. This may be compared with a diagram derived from experimental studies by Muan and Gee.[19] This system also provides an example of the use of the model to represent nonideal mixing in the spinel phase along the line joining FeAl$_2$O$_4$ and Fe$_3$O$_4$ as already shown in Fig. 12.

Fig. 21 Equilibria in the Fe-Al-O system at a constant pressure of oxygen of 101 325 Pa, projected onto the Fe_2O_3-Al_2O_3 side.

Fig. 22 Model of the arrangement of ions in one quarter of the unit cell of spinel. To facilitate comparison with periclase, MgO, the oxygen rather than metal ions have been allocated to cube corners and face centers. The oxygen ions are thus in ideal positions and not displaced by an amount dependent on the cation sizes as is more generally the case.
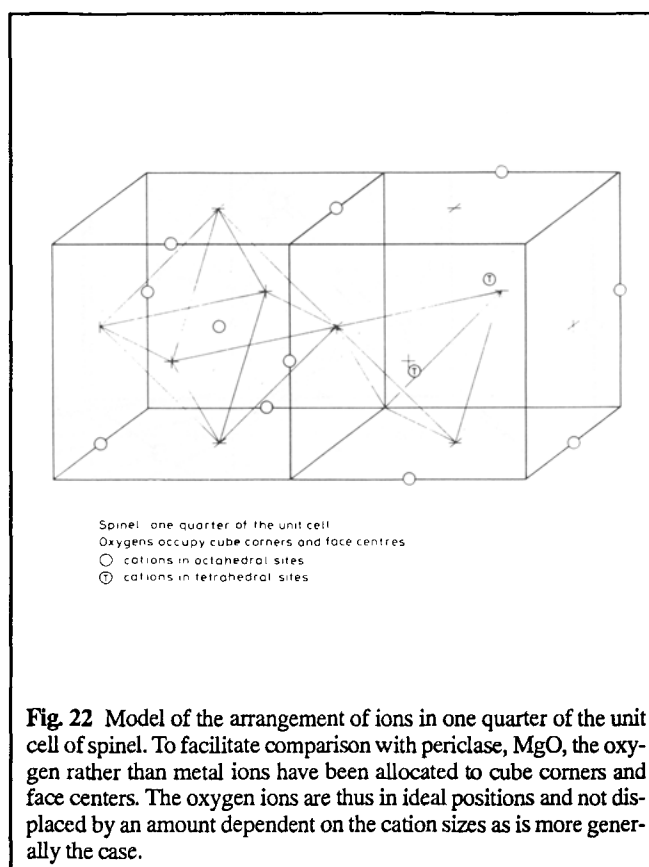
In general, the oxygen potential increases with y''_{Va}, and the surface in Fig. 20 represents various oxygen potentials. The states in the spinel phase field in Fig. 21, being calculated for an oxygen pressure of 101 325 Pa, thus fall on some line in the surface illustrated in Fig. 20. In the same way, the states of spinel representing equilibrium with corundum fall on another line in the surface, and the intersection of the two lines gives the phase boundary spinel/spinel+corundum in Fig. 21.

13. Introduction of Interstitial Cations

An oxygen deficit is obtained in a 2-3 spinel if there is an excess of divalent atoms. This excess is usually small and could probably be modelled reasonably well with any dilute solution model. One may also use the compound energy model and the simplest assumption for the excess divalent atoms, which is that they dissolve interstitially. The following formula was thus proposed by Sundman[20] when considering magnetite, $(M^{+2}, N^{+3})_1(M^{+2}, N^{+3}, Va)_2(Va, M^{+2})_2(O^{-2})_4$.

The choice of 2 interstitial sites per formula unit was based on a consideration of the atomic arrangement. If the displacements of the oxygen atoms in spinel are ignored, then they have the same fcc arrangement as in periclase, MgO, for instance. In periclase there is one octahedral site for metal atoms per oxygen atom. Only half of them are filled in spinel, but in addition, there are metal at-

oms in tetrahedral sites. The Sundman model was simply based upon the assumption that the excluded octahedral sites are available for the excess metal atoms.

The unit cell of the spinel structure is composed of 8 cubic subcells, and 2 of them are shown in Fig. 22, which can be used to illustrate a formula unit of $M_2M_4O_8$ of stoichiometric 2-3 spinel. In this idealized arrangement, the oxygen atoms are not shown but occupy all the cube corners and the centers of all the cube faces. The octahedral sites for metal atoms fall in the middle of the cubes and in the middle of the cube edges, and they are all occupied in periclase. Figure 22 shows that only half of them are occupied in spinel. The arrangement of the excluded sites is explained by the occupancy of some tetrahedral sites. One of the tetrahedral sites is illustrated to the right in Fig. 23. In fact, the whole volume of the spinel structure can be filled by stacking octahedral and tetrahedral cells. In each cubic subcell, there is an octahedral cell in the center, and it is surrounded by 8 tetrahedral cells, each sharing a face with the octahedral cell. In addition, the subcell contains small parts of 12 other octahedra.

Only 1/8 of the tetrahedral sites are occupied, and they are arranged in such a way that a tetrahedron and an octahedron are never occupied at the same time if they share a face. This is the simple exclusion principle explaining the structure shown in Fig. 22. It is further illustrated in Fig. 23 where the right-hand subcell of Fig. 22 is shown with the excluded octahedral sites marked. The distance between two neighboring octahedral sites is $1/\sqrt{2} = 0.707$ of the side of the cubic subcell, but the distance be-
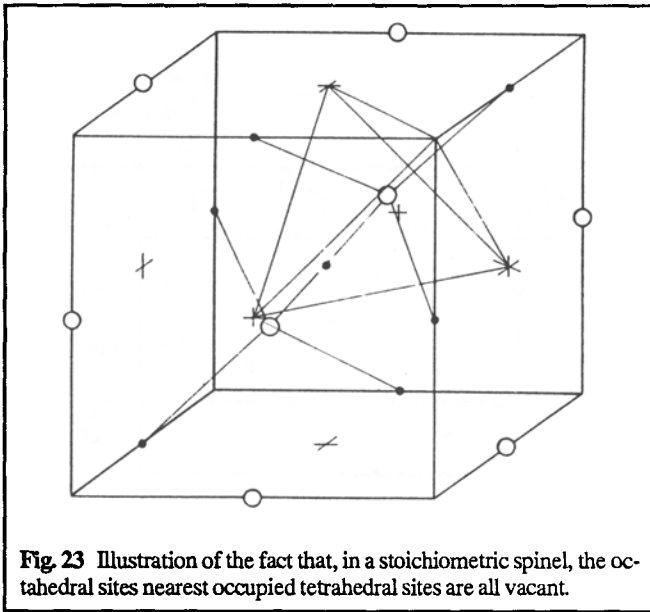
Fig. 23 Illustration of the fact that, in a stoichiometric spinel, the octahedral sites nearest occupied tetrahedral sites are all vacant.

Fig. 24 The neutral plane for the MgO-Al_2O_3 spinel with excess MgO.

tween neighboring octahedral and tetrahedral sites is only $\sqrt{3}/4 = 0.433$. No such pair of neighbors exists in the ideal spinel structure, but they would form if an extra metal atom were simply introduced into one of the excluded octahedral sites. It thus seems more likely that the tetrahedral sites will gradually be excluded as additional octahedral sites become occupied. One would thus move gradually from the spinel structure to the periclase structure. On the average, each excluded tetrahedral site will make two octahedral sites available, suggesting a model based upon the formula,

$$(M^{+2}, N^{+3}, Va)_1(M^{+2}, N^{+3})_2(Va, M^{+2})_2(O^{-2})_4$$
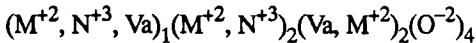
where $y'_{Va} = 1 - y'''_{Va}$. However, it would be very difficult to derive a mathematical expression for this model because the first excluded tetrahedral site will make not 2 but all 4 of the neighboring octahedral sites more preferable than the others. Furthermore, it seems likely that the continuous series of structures between periclase and spinel would show several changes in ordering. The stable equilibrium between periclase with a few vacant octahedral sites and spinel with a small excess of metal atoms may be regarded as the result of an ordering transition of the first order. No attempt has yet been made to model the continuous series of structures, and it seems reasonable to use the Sundman model for the small stable range of composition of spinel. The model could be made slightly more general by allowing both N^{+3} and M^{+2} to occupy the new octahedral sites. However, there is not enough information for evaluating the distribution, and from a thermodynamic point of view, this modification is not significant for small deviations from the stoichiometric composition. The original Sundman model was thus used in the present work.

In a recent assessment of the $MgAl_2O_4$ spinel, Hallstedt[21] thus used the formula $(Mg^{+2}, Al^{+3})_1 (Mg^{+2}, Al^{+3})_2 (Va, Mg^{+2})_2(O^{-2})_4$. The system has eight component compounds, and they may be denoted by MgMgVa, MgAlVa, AlMgVa, AlAlVa,

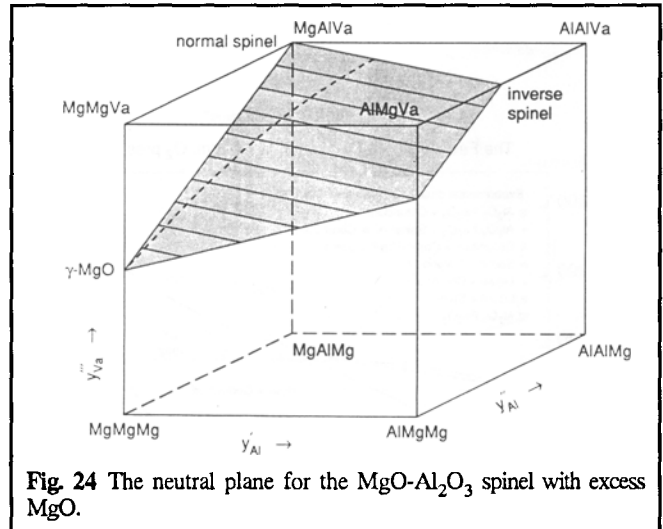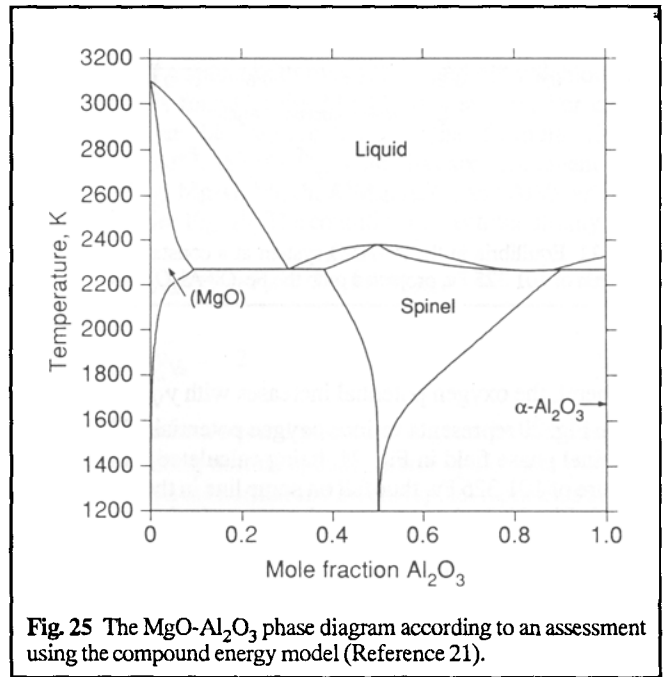**Fig. 25** The MgO-Al_2O_3 phase diagram according to an assessment using the compound energy model (Reference 21).

MgMgMg, MgAlMg, AlMgMg, and AlAlMg. The system may be illustrated with a cube, and the condition of electroneutrality gives the neutral plane. See Fig. 24.

$$2(1 - y'_{Al}) + 3y'_{Al} + 4(1 - y''_{Al}) + 6y''_{Al} + 4y'''_{Mg} = 8 \qquad \text{(Eq 64)}$$

$$y'_{Al} + 2y''_{Al} + 4y'''_{Mg} = 2 \qquad \text{(Eq 65)}$$

The neutral plane goes between four points. Two of them represent the normal and inverse spinels of the stoichiometric composition. The line between them represents all possible situations for that composition. Compositions with higher Mg contents are represented by a series of parallel lines. For each line one must mini-
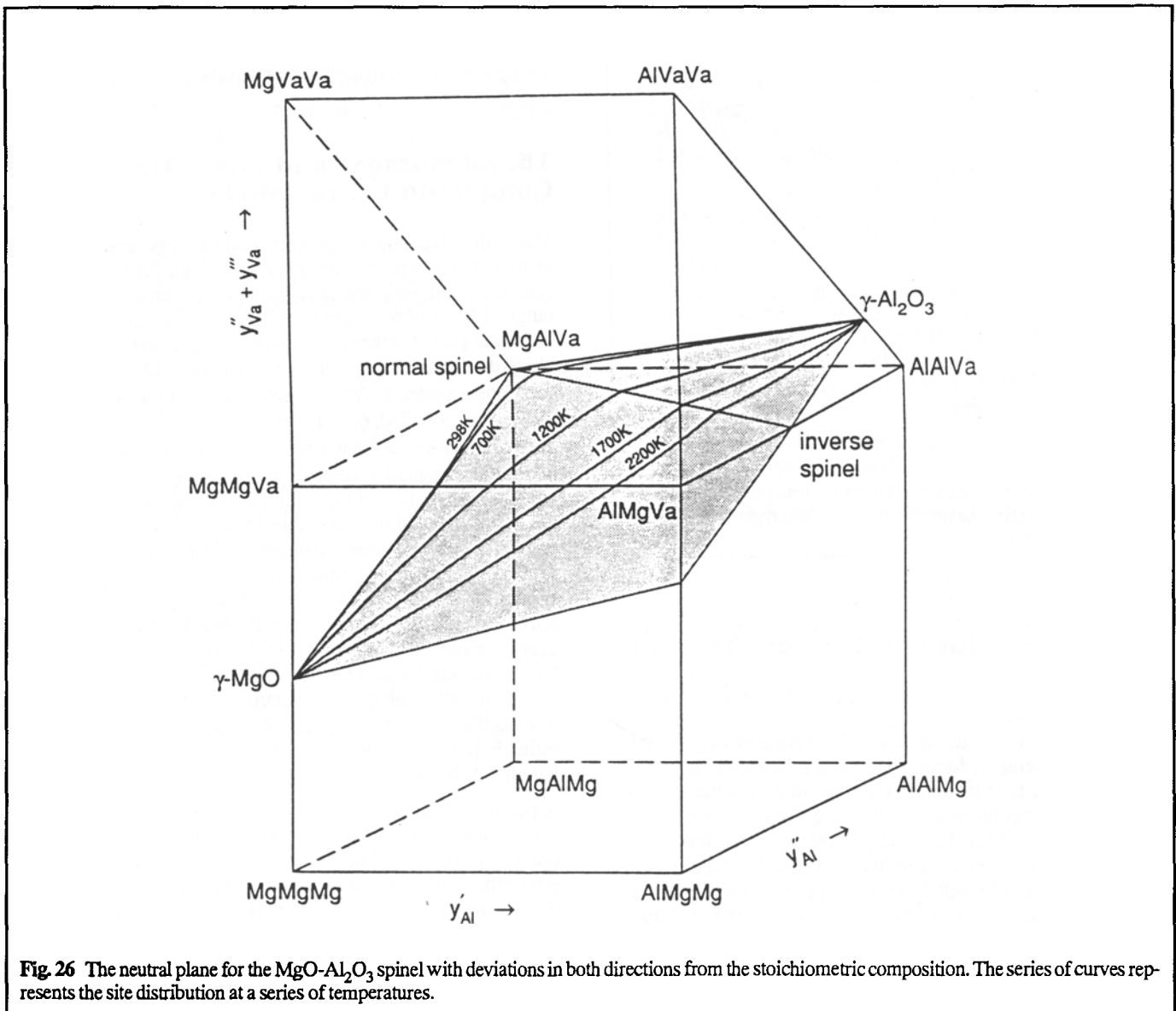
Fig. 26 The neutral plane for the $MgO-Al_2O_3$ spinel with deviations in both directions from the stoichiometric composition. The series of curves represents the site distribution at a series of temperatures.

mize the Gibbs energy in order to find the state of equilibrium. The dashed curve in Fig. 24 shows the states of stable and metastable equilibria at 1200 K, calculated with the periclase phase excluded. The last straight line degenerates to a point denoted by γ–MgO. It can be represented by the formula $(Mg^{+2})_1(Mg^{+2})_2(Va, Mg^{+2})_2(O^{-2})_4$ with $y'''_{Mg} = 0.5$, and it may be regarded as a hypothetical modification of MgO, less stable than periclase.

Hallstedt[21] recently assessed the whole $MgO-Al_2O_3$ phase diagram by allowing for both oxygen deficiency and excess. The formula will thus be $(Mg^{+2}, Al^{+3})_1(Mg^{+2}, Al^{+3}, Va)_2(Va, Mg^{+2})_2 (O^{-2})_4$. The assessed phase diagram is reproduced in Fig. 25. From the assessment, one may calculate the site distributions in the spinel at various compositions and temperatures. The results are illustrated in Fig. 26, which may be regarded as a combination of Fig. 19 and 24. The vertical axis is now $y''_{Va} + y'''_{Va}$

and goes from 0 to 2. The stoichiometric composition occurs at the value 1, and the curves change their slope rather abruptly there. The change would have been discontinuous if $y''_{Va} = 1$ and $y'''_{Va} = 0$ at the stoichiometric composition as required by the two individual descriptions of the part systems. However, this condition is relaxed when they are combined, and an accurate calculation shows that y''_{Va} is slightly less than 1 and y'''_{Va} is slightly larger than 0.

Sundman[20] used the same model for magnetite, $(Fe^{+2}, Fe^{+3})_1(Fe^{+2}, Fe^{+3}, Va)_2(Va, Fe^{+2})_2(O^{-2})_4$, and a diagram like Fig. 26 could be used to illustrate his results as well. Here we shall just show a projection of the neutral plane, Fig. 27, but it should be emphasized that the oxygen pressure here varies along each curve and only one point holds at an oxygen pressure of 1 bar, for instance. In Fig. 26 the MgO/Al_2O_3 ratio varies along each curve and the oxygen potential is indeterminate.
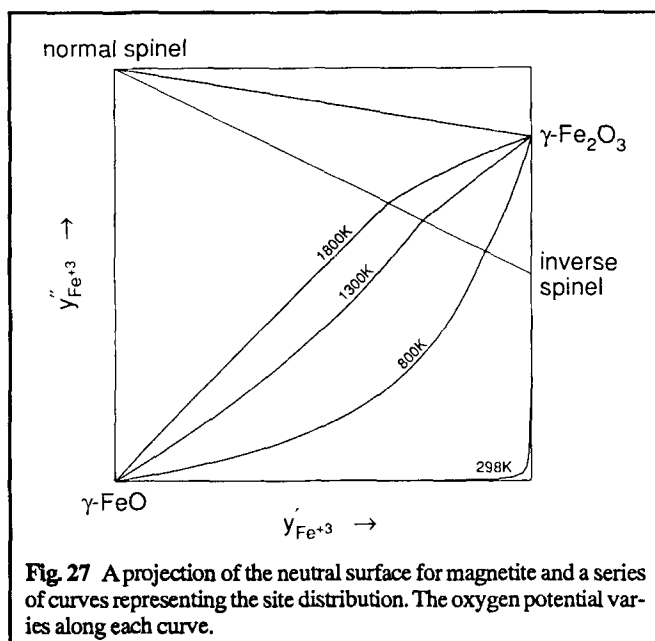
Fig. 27 A projection of the neutral surface for magnetite and a series of curves representing the site distribution. The oxygen potential varies along each curve.

14. The Need for a Reference State for Charge

Gibbs energies have no absolute value and are always given relative to some reference, for example with reference to formation from the elements at the current temperature or some standard temperature. The contribution from charged species in any phase also requires a reference. For gases, the reference for charge is the gaseous electron; for aqueous solutions, it is the hydrogen ion. An inconsistency would result from putting together data based on different reference states for charged species in the same phase. As indicated in sections 9 and 11, it is possible to combine data for spinel systems that have been assessed independently by adjusting for differences in the original reference states for charge. In cooperation between Royal Institute of Technology and National Physical Laboratory, we have chosen a reference for spinels by making the Gibbs energy of $Fe^{+3}Fe^{+2}_2O^{-2}_4$, which has a net charge of -1, equal to that of the normal spinel $Fe^{+2}Fe^{+3}_2O^{-2}_4$, which is neutral. The transfer of this reference state to linked systems is straightforward.

When constructing a data set for a certain phase, it is of course necessary to define what phase it concerns but also to define what reference is used for charged compounds. Thus, two separate data sets for a particular phase can be combined only after they have been put on the same reference basis, and that is possible only if there is experimental information on some link between them. As an example, FeO and MgO have the same structure as NaCl and may thus be regarded as belonging to the halite phase. However, FeO and MgO are chemically very different from NaCl, and it is most unlikely that experimental information will ever be available for a linking system. The data set for FeO and MgO and related oxides must be stored under its own phase name, because bad mistakes may occur if data based on different reference states are combined. For the same reason, as data sets are being built up

for oxides of the halite structure, it is possible that there are several subsets that have not yet been linked. Until that happens, it is necessary to regard them as different phases.

15. Advantages and Limitations of the Compound Energy Model

The main advantage of the compound energy model is that, as demonstrated here, it provides a formalism for describing in a self-consistent way the thermodynamic properties of a wide range of types of solid solution. This is particularly important in the development of thermodynamic databases to be used for compiling data and making calculations of phase equilibria in multicomponent systems. Any inconsistencies in the way individual phases are modelled, or in the reference data used in the assessment of data for subsystems, will prevent meaningful calculations on multicomponent systems. This advantage results from individual consideration of the mixing on the sublattices, which has the effect of making it possible to generalize the methods by which the data are stored, manipulated, and applied in equations for Gibbs energy. The counterpart to this advantage lies in the necessity for assigning data to charged "compounds," which cannot exist in practice and for which the data have to be established using a reference state, which is currently arbitrary but needs perhaps to be established by convention, as is the reference data for the elements and the gaseous electron and aqueous hydrogen ion. The need to maintain consistency in applying experimental and estimated data when undertaking assessments of related systems has already been referred to in relation to Fig. 16.

A potential limitation is that, at least in its simple form as described here, the model does not provide explicitly for short-range order on an individual sublattice, which may occur due to interactions either within the sublattice or with ions on another sublattice. In many silicate phases, particularly silicates containing magnesium ions such as pyroxenes and melilites, two aluminum ions can substitute for a pair of magnesium and silicon ions on different sublattices. It is generally considered that the aluminum ions on the silicon sublattice are ordered with respect to the positions of the aluminum ions on the magnesium sublattice.

16. Comparison With Other Models

For simple cases, the compound energy model is formally identical to the bond energy model in its zeroth approximation[5] i.e., when short-range order is not considered. For such cases, the compound energy model may provide a convenient formalism for extending the bond energy model to multicomponent systems. On the other hand, there are many important phases where different species can exchange position between sublattices with different numbers of neighbors. For such cases, the compound energy model can be applied directly, but the bond energy model needs a major modification.

It is important to note that both models may work with interaction energies between species on the same sublattice. On the other hand, interactions between species on different sublattices are

treated through bond energies in one model and through compound energies in the other model.

When considering spinels, it may also be interesting to compare with the model by O'Neill and Navrotsky.[22, 23] Their configurational entropy is the same, and their enthalpy term of disordering for a simple spinel is

$$\Delta H_D = \alpha x + \beta x^2 \qquad \text{(Eq 66)}$$

where x is the site fraction of the trivalent ion on the tetrahedral sublattice. As shown in the section on simple spinels, the same expression is obtained from the compound energy model, and comparison gives

$$2\alpha = {}^0G_{AA} + 2{}^0G_{EE} - 3{}^0G_{AE} \qquad \text{(Eq 67)}$$

$$2\beta = {}^0G_{AE} + {}^0G_{EA} - {}^0G_{AA} - {}^0G_{EE} = \Delta{}^0G_{AE:AE} \qquad \text{(Eq 68)}$$

For a higher order system, $AE_2O_4 - BE_2O_4$, the compound energy model yields an expression that depends upon the relative amounts of A and B, whereas O'Neill and Navrotsky have chosen an expression that does not.

Acknowledgments

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