JOURNAL OF SOLID STATE CHEMISTRY 37, 144–150 (1981)

Thermopower Composition Dependence in Ferrospinels

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Received May 12, 1980; in revised form August 15, 1980

The composition dependence of thermoelectric power (Seebeck coefficient) in ferrospinels with fixed valence foreign cations has been calculated via combined small polaron and cation distribution models. Satisfactory agreement with experimental data is achieved assuming cation distribution thermodynamic constants to be independent of foreign cation concentration. Data are analyzed for a trivalent foreign cation (Al^{3+}) at elevated temperature and for divalent foreign cations (Ni^{2+}, Mg^{2+}, Zn^{2+}) at lower temperatures.

Introduction

The physical behavior of transition metal oxide spinels is intimately related to the distribution of cations between tetrahedral and octahedral sublattices. Electrical and magnetic properties are dependent on the quantities and distributions of transition metal valence states. These, in turn, are fixed by overall cation composition and temperature in the case of equilibrium structures or by the remanent degree of inversion in the case of quenched structures. To a lesser degree the distribution of valence states is also a function of oxidation state. In the present work spinels with significant concentrations of two valence states of the transition metal cation will be considered and oxidation effects will be neglected.

It is widely accepted that thermal redistribution of cations A and B between tetrahedral (A) and octahedral sublattices (B) can be treated via simple mass action equilibrium,

$$\overset{(1-x)}{A_A} + \overset{(2-x)}{B_B} \rightleftarrows \overset{x}{A_B} + \overset{x}{B_A};$$

$$K_{CD} = \frac{[A_B][B_A]}{[A_A][B_B]} = \frac{x^2}{(1-x)(2-x)} = \exp\left(\frac{-\Delta G^\circ_{CD}}{RT}\right) \quad (1)$$

for which K_{CD} is the cation distribution equilibrium constant and ΔG°_{CD} is the free energy of the reaction. By plotting $\ln K_{CD}$ versus $1/T$ from the few existing high temperature equilibrium studies, Navrotsky and Kleppa (*1*) concluded that ΔH°_{CD} was not temperature dependent and that nonconfigurational entropy terms were effectively zero. Callen *et al.* (*2*) have argued on the basis of their work in magnesium–manganese ferrite (*3*) that ΔH°_{CD} is, instead, a function of the degree of inversion (x in Eq. 1). Other models suggesting a temperature dependence of ΔH°_{CD} (*4*) or nonzero, nonconfigurational entropy terms (*5*) resemble the Callen *et al.* argument in that

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0022-4596/81/050144-07$02.00/0

the redistribution thermodynamics are supposed to change with the octahedral and tetrahedral cation environments, which change with the degree of inversion and hence with temperature.

An excellent test of site occupation dependence of redistribution thermodynamics is to study the distribution equilibrium of a given set of cations in mixed spinel systems. In particular, the opportunity exists to preferentially dilute one or both sublattices with a foreign cation of fixed valence while studying the effect on overall cation distribution. It has already been reported that thermodynamic values back-calculated from spinel structural studies show a strong composition dependence (*6*). This analysis, however, suffers in that it draws largely from data for quenched spinels. It is dubious that high-temperature cation distributions can be quenched with sufficient speed to retain the equilibrium structure. In fact, the only *in situ* high-temperature study quoted in Ref. (*6*) showed composition independence of the cation distribution thermodynamics (*7*). This concurs with Pelton *et al.* who have found in modeling studies of mixed spinels that no composition dependence of K_{CD} need be assumed in computer fitting of experimental high-temperature phase boundary data (*8, 9*). The *in situ* structural studies necessary to corroborate such a claim are at best extremely difficult at the temperatures in question, 1200–1600°C. The purpose of this work is to analyze a promising technique for investigation of equilibrium cation distributions in transition metal oxide spinels over a wide temperature range using thermoelectric power measurements. Literature data for several iron-containing mixed spinel systems exist against which to test the structural and thermoelectric models.

Theory

Small polaron localized "hopping" of charge carriers between equivalent transition metal sites has been confirmed in at least two ferrospinel systems (*10, 11*). It has been established that such conduction involves octahedral (*B*) cations only. In such cases the thermoelectric power of Seebeck coefficient is given (*12, 13*) as

$$Q = \frac{-k}{e}\left[\ln 2\left(\frac{1-c}{c}\right) + \frac{S_T^*}{k}\right] \qquad (2)$$

where $c = [\mathrm{Fe}_B^{2+}]/([\mathrm{Fe}_B^{2+}] + [\mathrm{Fe}_B^{3+}])$. The second term has been shown from theoretical considerations (*14*) and experiment (*11, 13*) to contribute less than 10 μV/°K to the thermopower in the case of small polaron conduction. Neglecting this term Eq. (2) reduces to Eq. (3),

$$Q \cong \frac{-k}{e}\ln 2\,\frac{[\mathrm{Fe}_B^{3+}]}{[\mathrm{Fe}_B^{2+}]}. \qquad (3)$$

Using Eq. (3), values of the thermopower can be calculated based on any given cation distribution model and compared with existing thermopower data. To test the composition independence of ΔG°_{CD} in mixed transition metal spinels, we will assume K_{CD}^{Fe} to be composition independent and calculated thermopower values will be compared with the existing experimental results. The basic assumptions for the structural model are that the spinels in question are essentially oxygen stoichiometric, that the cations behave as ideal solute on both cation sublattices and that both iron and foreign cation distribution constants are independent of overall cation composition. The first of these assumptions amounts to ignoring changes in oxidation state with variations in oxygen chemical potential. Valence changes with oxidation proved to be secondary in systems with nearly equivalent di- and trivalent transition metal concentrations (*11*). The effect of neglecting such valence changes will show up most markedly when either valence state becomes very small (*15*). The assumption of ideal solute behavior, though not well understood, is well supported by previous studies of spinel cation distribution (*16*), phase equilibrium (*8, 9*), point defect thermodynamics (*17*), mass transport (*18, 19*), and nonstoichiometry (*20*). The final assumption of composition-independent cation distribution thermodynamics is the assumption to be tested in the present analysis.

Denoting the octahedral (*B*) sublattice species in brackets, the structural formula for iron-containing mixed spinels may be written as

$$\mathrm{Fe}_a^{2+}\mathrm{Fe}_b^{3+}\mathrm{Me}_c^{n+}(\mathrm{Fe}_d^{2+}\mathrm{Fe}_e^{3+}\mathrm{Me}_f^{n+})\mathrm{O}_4 \quad (4)$$

where subscripts *a*–*f* stand for cation concentrations per lattice molecule. Here the foreign cation is assumed to have a fixed valence ($n = 2, 3$, or 4). To solve for the six unknowns *a*–*f*, it is necessary to write four site, charge and mass balance equations and two of the three dependent cation distribution equilibrium expressions. The site balance equations are

$$\text{tetrahedral: } a + b + c = 1 \quad (5)$$

$$\text{octahedral: } d + e + f = 2 \quad (6)$$

the charge balance is:

$$2(a + d) + 3(b + e) + n(c + f) = 8. \quad (7)$$

And the mass balance, written in terms of the cation mole fraction $\xi_{\mathrm{Me}} = n_{\mathrm{Me}}/(n_{\mathrm{Me}} + n_{\mathrm{Fe}})$ is:

$$c + f = 3\xi_{\mathrm{Me}}. \quad (8)$$

For the two cation distribution reactions we have chosen:

$$\mathrm{Fe}_{\mathrm{A}}^{2+} + \mathrm{Fe}_{\mathrm{B}}^{3+} \rightleftarrows \mathrm{Fe}_{\mathrm{B}}^{2+} + \mathrm{Fe}_{\mathrm{A}}^{3+};$$

$$K_{\mathrm{CD}}^{\mathrm{Fe}} = \frac{d \cdot b}{a \cdot e} = \exp\left(\frac{-\Delta G_{\mathrm{CD}}^{\mathrm{o(Fe)}}}{RT}\right) \quad (9)$$

$$\mathrm{Me}_{\mathrm{A}}^{n+} + \mathrm{Fe}_{\mathrm{B}}^{3+} \rightleftarrows \mathrm{Me}_{\mathrm{B}}^{n+} + \mathrm{Fe}_{\mathrm{A}}^{3+};$$

$$K_{\mathrm{CD}}^{\mathrm{Me}} = \frac{f \cdot b}{c \cdot e} = \exp\left(\frac{-\Delta G_{\mathrm{CD}}^{\mathrm{o(Me)}}}{RT}\right). \quad (10)$$

The choice of Eq. (10) is dictated in that the trivalent iron concentrations on both sublattices are finite for $1 \leq K_{\mathrm{CD}}^{\mathrm{Fe}} \leq \infty$ while the divalent concentrations are not as $K_{\mathrm{CD}}^{\mathrm{Fe}} \rightarrow \infty$. To solve for the ratio $[\mathrm{Fe}_{\mathrm{B}}^{3+}]/[\mathrm{Fe}_{\mathrm{B}}^{2+}]$ it is necessary only to isolate *d* and *e* in Eq. (9). This is done via Eqs. (5–8) and results in the following expression:

$$K_{\mathrm{CD}}^{\mathrm{Fe}} = \frac{d \cdot b}{a \cdot e} = \frac{d[2 - e - (n - 2)3\xi_{\mathrm{Me}}]}{[1 - d - (3 - n)3\xi_{\mathrm{Me}}]e} \quad (11)$$

from which the theoretical cation composition or ξ_{Me}-dependence of the thermopower can be calculated.

Data Analysis

The simplest thermopower behavior as a function of cation composition (ξ_{Me}) occurs when $K_{\mathrm{CD}}^{\mathrm{Fe}}$ goes to unity. In this case the iron cations are randomly distributed between tetrahedral and octahedral sublat-

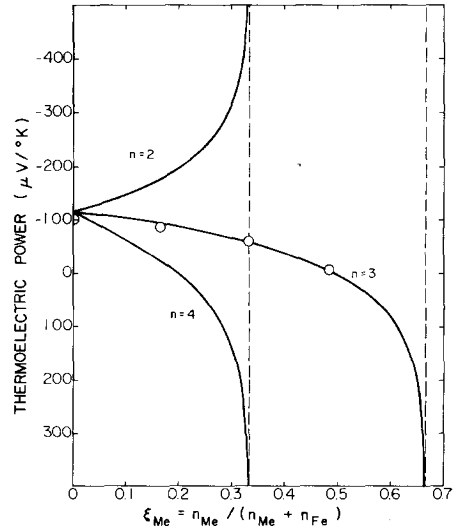

FIG. 1. Calculated ferrospinel thermopower composition dependences for divalent, trivalent, and tetravalent foreign cations at elevated temperature assuming random iron distribution, $K_{\mathrm{CD}}^{\mathrm{Fe}} = 1$. (See text for explanation.) Data is for Al^{3+} from Ref. (*11*).

tices. This has been proposed for Fe_3O_4 at elevated temperatures based on defect and mass transport studies (*17, 18*) and for the Fe_3O_4–$FeAl_2O_4$ system based on structural and electrical studies (*11, 16, 20*). Setting $K_{CD}^{Fe} = 1$ in Eq. (11), solving for the quantity e/d and substituting for $[Fe_B^{3+}]/[Fe_B^{2+}]$ in Eq. (3) we obtain:

$$Q \cong \frac{-k}{e} \ln \left[\frac{4 - (n - 2)6\xi_{Me}}{1 - (3 - n)3\xi_{Me}}\right]. \quad (12)$$

This equation is plotted versus ξ_{Me} in Fig. 1 for $n = 2$, 3, and 4. As might be expected, the dominant factor in the composition dependence is the valence of the foreign cation, i.e., whether divalent or trivalent iron is being replaced in the process. Divalent cations reduce $[Fe_B^{2+}]$ and make the thermopower more negative while cations of higher valence reduce $[Fe_B^{3+}]$ thus making the thermopower more positive according to Eq. (3). Also, as anticipated, the asymptotes correspond to ξ_{Me} values of the end members, i.e., $Me^{2+}Fe_2O_4$, $FeMe_2^{3+}O_4$ and $Fe_2Me^{4+}O_4$. The unexpected result is that for $K_{CD}^{Fe} = 1$ the thermopower composition dependence is independent of K_{CD}^{Me}. High-temperature thermopower in ferrites should therefore be independent of the choice of foreign cation in each valence category.

Unfortunately, very little high-temperature ($T >$ 1000°C) thermoelectric power data exist for oxide spinels. The only study displayed on Fig. 1 was carried out on oxygen-stoichiometric, polycrystalline iron aluminates at 1427°C under controlled oxygen activities (*11*). Within the limits of experimental certainty these results are in agreement with the predicted curve for a trivalent foreign cation.

The opposite limiting case for iron cation distribution is to allow K_{CD}^{Fe} to become very large. This translates into an inverse iron distribution which has long been accepted as the structure of Fe_3O_4 at low temperatures. For large values of K_{CD}^{Fe} the predicted thermopower expression will depend somewhat on the nature of the foreign cation or K_{CD}^{Me}. Equations (9) and (10) are soluble for the thermopower ratio e/d under the assumptions that the foreign cation strongly prefers (a) the tetrahedral sublattice ($K_{CD}^{Me} \rightarrow 0$) or (b) the octahedral sublattice ($K_{CD}^{Me} \geq K_{CD}^{Fe}$). In case *a* (tetrahedral foreign cations) the predicted thermopower dependence on composition becomes:

$$Q \cong \frac{-k}{e} \ln \left[\frac{2 + (3 - n)6\xi_{Me}}{1 - (3 - n)3\xi_{Me}}\right]. \quad (13)$$

And for the case *b* (octahedral foreign cations) the predicted dependence is:

$$Q \cong \frac{-k}{e} \ln \left[\frac{2 + (2 - n)6\xi_{Me}}{1 - (3 - n)3\xi_{Me}}\right]. \quad (14)$$

Once again very few experimental observations have been made as a function of composition in mixed spinel systems so remarks will be restricted to the case of divalent foreign cations (n = 2). Figure 2 displays theoretical thermopower curves

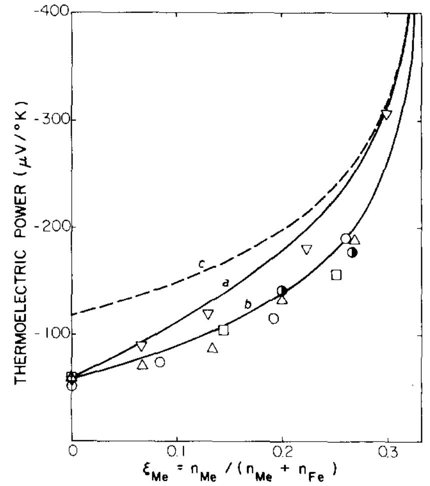

FIG. 2. Calculated ferrospinel thermopower composition dependences for divalent foreign cations. Case *c* is for random iron distribution (K_{CD}^{Fe} = 1); cases *a* (tetrahedral foreign cation) and *b* (octahedral foreign cation) are calculated assuming low-temperature, inverse iron distribution ($K_{Fe} \gg 1$). (See text for explanation.) Data shown are for nickel ferrites, ○ (*10*), △ (*22*), and ◑ (*24*); magnesium ferrites, □ (*23*); and for zinc ferrites, ▽ (*22*).

for the limiting cases *a* and *b* ($K_{\mathrm{CD}}^{\mathrm{Fe}} \gg 1$). The curve of Eq. (12) ($K_{\mathrm{CD}}^{\mathrm{Fe}} = 1$) is also shown for comparison and is labeled case *c*. The value of *n* obviously determines the direction and asymptote of the expected thermopower behavior. The value of $K_{\mathrm{CD}}^{\mathrm{Fe}}$ plays the next most important role in the value of the thermopower and the value $K_{\mathrm{CD}}^{\mathrm{Me}}$ plays a secondary role in the precise value of Q. Literature data for Me = Ni, Mg, and Zn are superimposed on the figure for comparison. The nickel and magnesium ferrite behavior are in agreement with that expected for octahedral preferring cations while that of zinc ferrite more closely resembles tetrahedral preference behavior. This is in agreement with existing site preference energy schemes for cations in oxide spinels (*21*); $ZnFe_2O_4$ is a normal spinel at low temperatures while $Fe(Fe, Ni)O_4$ and $Fe(Fe, Mg)O_4$ are both inverse spinels at low temperature. It should be pointed out that the octahedral preference of Mg^{2+} need only be larger than that of Fe^{3+} but may be on the same order as that of Fe^{2+} ($K_{\mathrm{CD}}^{\mathrm{Me}} \geq K_{\mathrm{CD}}^{\mathrm{Fe}}$). Intermediate values of $0 < K_{\mathrm{CD}}^{\mathrm{Me}} < K_{\mathrm{CD}}^{\mathrm{Fe}}$ will have thermopower curves falling between those given in Fig. 2 for the limiting cases *a* (tetrahedral preference) and *b* (octahedral preference).

Certain reservations must be emphasized concerning the low-temperature data analyzed. Sample preparation was not detailed in the case of the zinc ferrite and the nickel ferrite measurements simultaneously reported (*22*). All of the reported data were for polycrystalline specimens and the role of grain boundaries in thermoelectric power, although expected to be minor, is not well understood. Some of the experimental data were taken below the Curie temperatures for the given spinels and the influence of magnetic ordering on the Seebeck coefficient in transition metal oxides is not clearly established. Finally, the localized hopping conduction behavior must persist to these lower temperatures in order for our analysis to be valid. It apparently does in the systems dealt with in the present study.

Discussion

The major observation of this study is that reasonable agreement exists between experimental and theoretical thermopower values in several ferrospinel systems. This agreement implies that the thermoelectric effect may be useful in the study of cation distribution thermodynamics in transition metal spinels at elevated temperatures where other experimental techniques are not as practicable. An additional implication is that the issue of spinel cation distribution thermodynamics may need to be readdressed as new data are generated.

In transition metal spinels where small polaron conduction is operative due to substantial concentrations of two valence states, thermoelectric measurements may prove useful in establishing the temperature and composition dependences of cation distribution thermodynamics. The observations of the present study were in every case consistent with a composition-independent iron distribution constant ($K_{\mathrm{CD}}^{\mathrm{Fe}}$). At low temperatures it can only be concluded that $K_{\mathrm{CD}}^{\mathrm{Fe}}$ must be consistently very large, however, the absolute value and the value of $\Delta G^\circ_{\mathrm{CD}}(\mathrm{Fe})$ remain in question. At elevated temperatures, however, where $K_{\mathrm{CD}}^{\mathrm{Fe}} \approx 1$ and thermopower should be independent of $K_{\mathrm{CD}}^{\mathrm{Me}}$, results should be particularly sensitive to composition-dependence of $K_{\mathrm{CD}}^{\mathrm{Fe}}$. The fact that no such dependence is observed is consistent with other results in the iron-aluminate system (*16*, *20*) and with Pelton and Schmalzried who have successfully modeled spinel phase boundaries in the systems Fe_3O_4–Mn_3O_4, Fe_3O_4–Co_3O_4 (*8*), Fe_3O_4–$NiFe_2O_4$ and Fe_3O_4–$FeCr_2O_4$ (*9*) assuming $K_{\mathrm{CD}}^{\mathrm{Fe}} = 1$, independent of composition. It is obvious that high-temperature thermopower studies in ferrospinels with divalent or tetravalent foreign cations are of particular interest and are in progress at the present time. At the same time the potential exists to extend the thermopower technique to cobalt and manganese spinel systems.

The randomization of iron cations as temperature increases ($K_{\mathrm{Fe}} \rightarrow 1$; $\Delta G^{\circ}_{\mathrm{CD}}(\mathrm{Fe}) \rightarrow 0$) has profound implications for existing thermodynamic models. In particular the model of Narrotsky and Kleppa (*1*) assumes $\Delta S^{\circ}_{\mathrm{CD}}$ (nonconfigurational entropy) to be zero and $\Delta H^{\circ}_{\mathrm{CD}}$ to be temperature independent. The present results showing ΔG° tending to zero require $\Delta H^{\circ}_{\mathrm{CD}}$ to be temperature dependent or $\Delta S^{\circ}_{\mathrm{CD}}$ to be nonzero. A suitable model must explain both why Fe_3O_4 is inverse ($\Delta G^{\circ}_{\mathrm{CD}} \ll 0$) at low temperature and yet random ($\Delta G^{\circ}_{\mathrm{CD}} \sim 0$) at high temperature. Measurements in pure stoichiometric Fe_3O_4 as a function of temperature will contribute to our understanding of iron cation distribution as a function of temperature and will be reported in a later communication.

Conclusion

Thermoelectric and cation distribution models have been combined to predict thermopower composition dependences in iron-containing mixed spinels. The thermoelectric model assumed small polaron conduction to be operative and the cation distribution model assumed distribution constants to be independent of overall cation concentration. Predicted thermopower behavior at elevated temperatures for a trivalent foreign cation (Al^{3+}) and at lower temperatures for divalent foreign cations (Ni^{2+}, Mg^{2+}, Zn^{2+}) was in agreement with the existing experimental data. Implications for the study of cation distribution in transition metal spinels and for the theory of distribution thermodynamics were discussed.

Acknowledgments

This work was initiated under seed funding by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant No. DMR76-80847) and was subsequently supported by the National Science Foundation under Grant No. DMR79-08054. The authors are grateful to Professor H. Schmalzried for helpful discussion.

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