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Thermodynamics of Solid Solution Formation in NiO–MgO and NiO–ZnO

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High-temperature calorimetric measurements of the enthalpies of solution in molten $2PbO \cdot B_2O_3$ of $(Ni_xMg_{1-x})O$ and $(Ni_xZn_{1-x})O$ permit the calculation of the enthalpy of the zincite to rocksalt transformation in ZnO, and the enthalpies of mixing, relative to rocksalt standard states, in the two solid solution series. The enthalpy of the zincite to rocksalt transformation is 24,488 ± 3,592 J mole^{-1} with a corresponding positive entropy change of 0.48 ± 3.3 J K^{-1} mole^{-1}. The small positive entropy change for the transformation necessitates a very flat and perhaps negative dP/dT slope for the phase boundary. Both solid solutions, when referred to rocksalt standard states, show negative enthalpies of mixing. For $(Ni_xMg_{1-x})O$ the negative enthalpies of mixing are fitted by a subregular model, where $\Delta H_{\text{mix}} = X_AX_B(BX_A + AX_B)$, with $A = -21{,}971 \pm 4{,}953$ J mole^{-1} and $B = -5103 \pm 1151$ J mole^{-1}. The associated negative excess entropies of mixing, calculated from the heats of mixing and previously measured activity–composition relations, are similarly modeled with $A = -10.7$ J K^{-1} mole^{-1} and $B = +1.1$ J K^{-1} mole^{-1}. Negative enthalpies of mixing in $(Ni_xZn_{1-x})O$ conform to a regular solution model with $W = -13520 \pm 5581$ J mole^{-1}. The negative enthalpies of mixing are interpreted in terms of a tendency toward ordering in the solid solutions, the proposed ordering scheme finding support in spectroscopic, structural, and magnetic data. These tendencies toward order are used to explain observed phase relations and thermodynamic properties in some other systems containing a transition metal cation and another ion of similar size, namely carbonates, hydrated sulfates and the systems CuO–MO (M = Mg, Co, Ni).

Introduction

The thermodynamics of mixing in oxide solid solutions is important in determining solid solubility, physical properties, diffusion coefficients, and the distribution of components among coexisting solid and liquid phases. Oxide solid solutions having the rocksalt structure offer a relatively simple structural environment in which to assess the effect of cation properties (size, charge, electron configuration) on the thermodynamics of mixing. It has generally been assumed that cation size is the most important factor in determining solid solubility, with a strain energy term leading to positive deviations from ideal mixing. This strain energy term is related to the mismatch in molar volumes and several expressions for its exact form have been proposed (*1–4*).

Experimental studies of the thermodynamics of binary metal oxide systems include the measurement of the Gibbs free energies of mixing by gas equilibration or solid-state galvanic-cell techniques. Enthalpies and entropies of mixing can be calculated from the variation of the activities with temperature. However, both the small temperature range over which equilibrium

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measurements often can be made and errors inherent in defining the temperature dependence of these data frequently make such derived ΔH and ΔS values quite uncertain. Direct calorimetric measurements of heats of solution can given more reliable values of heats of mixing in solid solutions (*5*).

There have been a number of previous investigations of the thermodynamic properties of binary oxide solid solutions having the rocksalt structure and a review of some of these was given by Driessens (*6*). A regular solution parameter, W, may be calculated for each solid solution from the activity data by fitting the expression:

$$RT \ln a_{MO} = (1 - X_{MO})^2 W + RT \ln X_{MO}. \quad (1)$$

The W parameter gives an indication of the direction and extent of deviations from ideality. When the data warrant, more complex equations, such as the subregular (Margules) model, can be used to fit the activities.

With the exception of NiO–MgO, all the systems investigated deviated positively from Raoult's law. FeO–MgO, studied by Hahn and Muan (*7*) showed considerable positive deviations, probably complicated by the effects of nonstoichiometry. CoO–MgO was originally found to be ideal (*8*, *9*) but a later study (*10*) showed evidence of positive deviations. MnO–MgO activity relations were first derived from measurements on the NiO–MnO–MgO system (*11*). Between 1373 and 1573 K strong positive deviations were found; direct measurements on the binary by Woermann and Muan (*12*) confirmed these. Recent calorimetric work by Gripenberg *et al.* (*13*) has revealed sizeable positive enthalpies of mixing in this system.

The system MnO–CoO was first found to be ideal at 1473 K (*8*). However, a recent redetermination using emf techniques (*14*) has shown it to deviate positively. The NiO–MnO system has been the subject of several studies (*14–18*). One of the more recent investigations (*14*) showed the system to deviate from a regular solution model, with asymmetric positive enthalpies of mixing. The latest work on this system (*18*) gave slightly different results for the activities but confirmed the positive deviation. CoO solid solutions with FeO (*8*) showed slight positive deviations, and emf measurements on NiO–CoO (*19*) indicated a small positive deviation at 1000 K with almost ideal behavior at 1300 K.

There have been two previous studies of the NiO–MgO system. The first, by Hahn and Muan in 1961 (*15*), found ideal behavior between 1373 and 1573 K. Later work (*20*) has revealed a small negative deviation at 1673 K.

In all the above solid solutions, both the end-member oxides possess the rocksalt structure and form continuous binary solid solutions. The NiO–ZnO system, in which the end-members are not isostructural, can show only partial solid solubility (*21–23*). The ZnO end-member crystallizes with a hexagonal wurtzite-type structure (zincite), in which zinc is four-coordinated by oxygen. At atmospheric pressure solid solution formation near 1273 K does not occur for $X_{\mathrm{NiO}} < 0.60$ apart from a very small range, $X_{\mathrm{NiO}} < {\sim}0.03$, where the resultant solution has the wurtzite structure (*23*). Solubility in the rocksalt phase is expected to increase with pressure and we have synthesized single-phase rocksalt solid solution with $X_{\mathrm{NiO}} = 0.55$ at 2500 GPa, see below.

The solid solution occuring for the Ni-rich compositions has the cubic rocksalt structure and in its formation Zn undergoes a coordination change from four to six. Navrotsky and Muan (*23*) showed that the lattice constants for the solid solution extrapolated to a value for pure rocksalt ZnO close to that reported for the high-pressure rocksalt phase of ZnO (*24*). They also calculated a value of 23849 J $mole^{-1}$ for the free energy of the transformation of zincite to the rocksalt modification from activity–composition relations in the CoO–ZnO and ZnO–NiO systems.

In the present study, we have concentrated on the thermodynamic properties of solid solutions containing NiO and two oxides having cations of similar size to Ni^{2+}, namely, ZnO and MgO. The molar volumes, ionic radii, electron configurations, and electronegativities relevant to these systems are summarized in Table I. Because of the similarity in lattice parameter, the energetics of mixing may be expected to show ideal behavior if no factors other than size are important and, conversely, any deviations from ideal behavior will reflect effects of electron configuration, covalency, and other factors. In this study we have measured the enthalpy of solution in molten $2PbO \cdot B_2O_3$ at 986 K of $(Ni_xMg_{1-x})O$ throughout the solid solution series, and of $(Ni_xZn_{1-x})O$ in the range $0.55 \leq X_{NiO} \leq 1$. These data are used to obtain the enthalpy of the zincite to rocksalt transformation in ZnO, and the enthalpies of mixing in the solid solutions with rocksalt structure. Combined with the available activity–composition data, measurement of the enthalpies of mixing of the various solid solution compositions should give important insight into the entropies of mixing and the nature of interactions in oxide solid solutions in these and similar systems.

TABLE I

SOME PROPERTIES OF OXIDES WITH ROCKSALT STRUCTURE

	Molar volume (cm^3 $mole^{-1}$)	Cation radius (Å)	Electronegativity of cation
MgO	11.249[a]	0.72[b]	1.2[c]
NiO	10.974[a]	0.69	1.8
ZnO	11.805[d]	0.74	1.6

[a] Ref. (*25*).
[b] Ref. (*26*).
[c] Ref. (*27*).
[d] Ref. (*24*).

Experimental

Sample Preparation and Characterization

Samples corresponding to compositions ranging from $(Ni_{0.65}Zn_{0.35})O$ to pure NiO were prepared by heating stoichiometric mixtures of the pure oxides at 1323 K. Starting materials were reagent-grade oxides which were dried at 973 K for 24 hours before use. Approximately 3 g of the appropriate mixture was weighed out and ground under acetone; after being dried, samples were pelletized and heated for 24 hours in a muffle furnace. They were reground and reheated three or four times over a period of 5 to 6 days to ensure homogeneity.

The solubility limit in the nickel–zinc oxide system could be extended to X_{NiO} = 0.55, by synthesis at 2500 GPa and 1373 K. This was accomplished in a non-end-loaded piston–cylinder apparatus (*28*). Using a 0.508-cm-diameter platinum capsule, it was possible to synthesize approximately 100 mg of the solid solution at a time and hence three runs were necessary to obtain sufficient sample for characterization and calorimetry. To check composition and homogeneity, the run products were analyzed using a Cameca MS-46 electron microprobe with a 16-kV accelerating potential and 40-nA specimen current. The $(Ni_xZn_{1-x})O$ solutions were further analyzed by standard X-ray fluorescence techniques. In all cases, compositions were within 1 mole% of nominal.

Samples throughout the entire NiO–MgO solid solution series were prepared in an analogous manner. Starting materials were the reagent-grade oxides, and the temperature of synthesis was 1373 K. Generally five cycles of heating and regrinding were required to produce homogeneous solid solutions.

After heating, all samples were examined under an optical microscope and their powder patterns obtained on a Norelco diffractometer using Cu$K\alpha$ radiation and a scanning speed of 0.5° (2θ) per minute. Dry sodium chloride was used as an internal standard. Lattice parameters were calculated from the d spacings of the (2 0 0) reflections. These lattice parameters, which confirmed Vegard's Law is obeyed in both solutions, are in agreement with those reported by Navrotsky and Muan (*23*), Cimino *et al.* (*29*), and Hahn and Muan (*15*).

Calorimetry

The high-temperature twin Calvet solution calorimeter, and the technique used have been described previously (*30*). Although 30 g of lead–borate flux was used for dissolution with no more than two runs being made in each batch, problems with incomplete dissolution were initially encountered in both systems. These were overcome by using sample containers with platinum foil bottoms through which several holes were punctured, as described recently by Navrotsky *et al.* (*31*). The holes were all less than 250 μm in diameter, the grain size of the sample being 250–325 μm. Several "dummy" runs were performed to ensure that no loss of sample occurred before dissolution. This procedure, with several rapid stirrings at the beginning of each run, improved the dissolution process by preventing the accumulation of saturated melt near the undissolved sample grains. Subsequent stirrings, which then introduced fresh solvent to the sample grains, resulted in rapid and complete dissolution. In the NiO–MgO system, the most Mg-rich compositions tended to dissolve by a two-step process, a fast exothermic reaction followed by a slow and somewhat unreproducible endothermic step. This effect, which has been seen both in this study and in previous work (*32*) for pure MgO, may be related to the formation of a magnesium borate complex or metastable precipitate as an intermediate in the solution, although such a product could never be isolated or characterized. This problem was avoided by mixing the sample with 33 wt% SiO_2 (quartz) (*32*). This led to quicker dissolution and consistent heat of solution data. The small and well-known heat of solution of quartz (−5146 J mole^{-1} (*32*)) was subtracted from the experimental data to obtain the heat of solution of the solid solution. It was only necessary to use this technique with $(Ni_{0.1}Mg_{0.9})O$ and MgO. In separate "dummy" runs, X-ray diffraction of samples left in the calorimeter overnight confirmed no reaction between MgO and SiO_2.

The time of preequilibration of samples in the calorimeter was held to a minimum, in the case of the high-pressure $(Ni_{0.55}Zn_{0.45})O$ samples less than 2.5 hours. "Dummy" runs were performed on each composition to ensure no unmixing of the solid solutions occurred during preequilibration, this was checked both by X-ray measurements and examination under the optical microscope of samples which had been equilibrated in the calorimeter but not dissolved. After each run all sample containers were checked under a microscope for any traces of undissolved solid. The results in the tables are of runs deemed successful by the following criteria: rapid dissolution and return to an unshifted apparatus baseline, no evidence of incomplete dissolution, and consistent heat effects.

Results

NiO–MgO

Calorimetric results for this system are given in Table II. The enthalpy of solution of pure NiO is in agreement with that reported by Navrotsky and Coons (*33*).

TABLE II

Enthalpies of Solution of $(Ni_xMg_{1-x})O$ and $(Ni_xZn_{1-x})O$ in $2PbO \cdot B_2O_3$ at 986 K

X_{NiO}	X_{MgO}	X_{ZnO}	Sample (mg)	ΔH_{sol} individual	J mole^{-1} average
1.00	0	0	30.31	35,978	36,752 ± 728 (6)[a]
			30.71	37,037	
			30.16	37,158	
			29.41	37,840	
			30.80	36,020	
			26.66	36,476	
0.80	0.20	0	31.58	31,200	32,054 ± 958 (6)
			33.16	31,840	
			30.89	31,317	
			28.73	31,418	
			33.64	33,439	
			30.38	33,108	
0.60	0.40	0	29.91	26,824	26,746 ± 310 (6)
			23.95	26,778	
			30.89	26,832	
			30.05	26,987	
			37.91	26,924	
0.50	0.50	0	33.19	23,927	23,806 ± 531 (5)
			22.51	23,945	
			21.94	23,627	
			24.04	24,489	
			29.25	23,033	
0.40	0.60	0	22.64	20,066	20,947 ± 795 (6)
			24.11	20,548	
			23.98	21,748	
			28.55	20,225	
			32.48	21,953	
			27.52	21,142	
0.20	0.80	0	36.30	13,832	13,981 ± 255 (5)
			29.37	13,933	
			30.04	13,983	
			29.43	14,406	
			31.56	13,749	
0.10	0.90	0	23.69	9,410	10,149 ± 556 (5)
			25.79	10,527	
			30.51	10,740	
			21.08	10,322	
			24.69	9,745	
0	1	0			4,875 ± 619[b]
0.95	0	0.05	35.81	34,664	
			25.90	34,112	34,458 ± 707 (7)
			33.85	33,652	
			26.86	35,263	
			24.70	33,606	
			21.52	35,346	
			34.00	34,564	

TABLE II—*Continued*

X_{NiO}	X_{MgO}	X_{ZnO}	Sample (mg)	ΔH_{sol} individual	J mole^{-1} average
0.90	0	0.10	24.38	33,041	32,962 ± 653 (4)
			25.80	33,614	
			31.43	32,058	
			23.64	33,133	
0.85	0	0.15	19.71	32,141	32,113 ± 247 (4)
			23.33	31,769	
			24.45	32,347	
			26.28	32,196	
0.80	0	0.20	24.45	30,255	30,465 ± 381 (4)
			26.86	30,685	
			21.55	30,874	
			25.92	30,045	
0.75	0	0.25	32.40	28,673	28,316 ± 423 (4)
			27.76	28,380	
			33.80	27,711	
			24.26	28,501	
0.70	0	0.30	19.74	27,581	26,924 ± 674 (5)
			21.09	27,736	
			22.11	26,510	
			31.09	26,447	
			39.10	26,347	
0.675	0	0.325	21.20	25,171	25,296 ± 155 (4)
			25.05	25,171	
			27.92	25,351	
			25.00	25,493	
0.65	0	0.35	24.55	23,970	24,108 ± 799 (5)
			18.98	22,937	
			33.30	24,259	
			18.81	24,204	
			25.46	25,171	
0.55	0	0.45	30.93	21,410	Av. = 20,816 ± 506 (4)
			22.22	20,238	
			19.90	20,610	
			22.40	21,008	
0	0	1.00	25.18	19,435[c]	18,450 ± 1042 (6)
			25.47	18,439	
			25.87	19,246	
			25.42	19,125	
			24.53	16,782	
			26.05	17,673	

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[a] Error is standard deviation, number in parentheses is number of experiments performed.

[b] Average of two sets of determinations, which gave 4937 ± 335 and 4812 ± 586 J mole^{-1} (Ref. (*32*) and (*33*), respectively).

[c] This sample is ZnO (zincite).

The enthalpy of solution of pure MgO was taken to be 4875 ± 619 J $mole^{-1}$, this being the average of the two previous determinations (*32*, *33*). The enthalpies of solution are plotted as a function of composition in Fig. 1. It is immediately apparent that the system shows moderate negative enthalpies of mixing, as shown also in Table III.

TABLE III

THERMODYNAMIC MIXING PROPERTIES OF $(Ni_xMg_{1-x})O$ AND $(Ni_xZn_{1-x})O$ REFFERED TO ROCKSALT STANDARD STATES

X_{NiO}	X_{MgO}	X_{ZnO}	ΔG_{mix}[a]	ΔH_{mix}	ΔS^{excess}_{mix}
0.80	0.20	0	−8,137	−1677	−0.30
0.60	0.40	0	−10,535	−2745	−0.94
0.50	0.50	0	−10,953	−2992	−1.00
0.40	0.60	0	−10,521	−3321	−1.29
0.20	0.80	0	−7,603	−2731	−1.25
0.10	0.90	0	−5,012	−2086	−0.95
0.95	0	0.05	−2,020	−642	−0.61
0.90	0	0.10	−3,563	−1217	−0.93
0.85	0	0.15	−5,142	−1724	−0.93
0.80	0	0.20	−6,225	−2163	−1.09
0.75	0	0.25	−7,362	−2535	−1.03
0.70	0	0.30	−8,453	−2839	−0.84
0.65	0	0.35	−9,632	−3076	−0.43

[a] ΔG_{mix} and ΔH_{mix} in J $mole^{-1}$, ΔS_{mix} in J K^{-1} $mole^{-1}$, see text for discussion of errors.

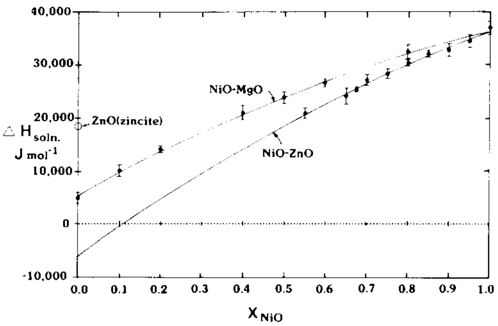

FIG. 1. Enthalpies of solution of $(Ni_xMg_{1-x})O$ and $(Ni_xZn_{1-x})O$ in $2PbO \cdot B_2O_3$ at 986 K (in J $mole^{-1}$). Filled symbols are experimental data on phases with rocksalt structure, open symbol is ZnO with zincite structure. Error bars are one standard deviation of the mean.

Excess free energies of mixing were calculated from the activity data of Evans and Muan (*20*), the activity of the MgO component being calculated by a graphical integration of the Gibbs–Duhem relation (*34*). The activity data of Evans and Muan are at 1673 K, our calorimetric data at 986 K, for samples synthesized at 1373 K. Any possible temperature dependence in the heat of mixing may be related to excess heat capacities and an ordering process discussed below. We believe the measured heats of mixing best characterize the equilibrium state at the synthesis temperature and that the enthalpies and free energies of mixing may be combined to calculate entropies of mixing for solid solutions at high temperature. In addition, an electrochemical study (*35*) at 1073–1273 K has provided activity–composition data. The higher-temperature data gives excess free energies in agreement with those calculated from the data of Evans and Muan. At the lower temperatures, the emf data suggest such tremendous negative deviations from ideality as to imply physically unreasonable heats of mixing, and lack of equilibrium in the solid cell is suspected. The free energies and resultant excess entropies of mixing are given in Table III and Fig. 2. Figure 2 shows that both the enthalpies and excess entropies of mixing deviate from the regular solution approximation. The asymmetric enthalpies may be fitted by a subregular model where,

$$\Delta H_{mix} = X_{NiO}X_{MgO}(BX_{NiO} + AX_{MgO}). \quad (2)$$

For this system $A = -21{,}971 \pm 4{,}953$ J $mole^{-1}$ and $B = -5103 \pm 1151$ J $mole^{-1}$. Similarly for the excess entropies,

$$\Delta S^{excess}_{mix} = X_{NiO}X_{MgO}(BX_{NiO} + AX_{MgO}) \quad (3)$$

with $A = -10.7$ J K^{-1} $mole^{-1}$ and $B = +1.1$ J K^{-1} $mole^{-1}$. It appears, from the asymmetry, that the solid solution is stabilized to a greater degree by substitution of Ni^{2+} in MgO than Mg^{2+} in NiO.

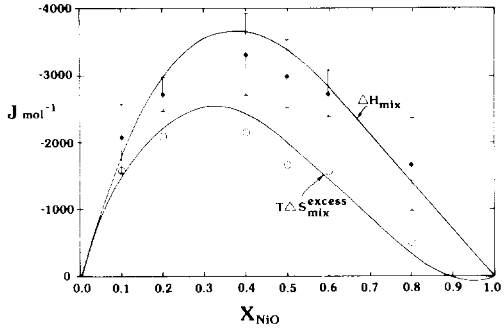

FIG. 2. Enthalpies of mixing, ΔH_{mix}, and the product of temperature and the excess entropy of mixing, $T\Delta S^{\mathrm{excess}}_{\mathrm{mix}}$, in the system $(\mathrm{Ni}_x\mathrm{Mg}_{1-x})\mathrm{O}$ at 1673 K, referred to rocksalt standard states (in J mole^{-1}). The filled circles are difference of experimental heats of solution, error bars are one standard deviation. Open circles are excess entropies of mixing calculated directly from experimental enthalpies and activities at the given composition. The curves are calculated from Eqs. (2) and (3).

Errors in the enthalpy parameters, given by the least-squares program used, reflect the scatter in the heats of solution. Errors in the entropies of mixing are harder to estimate since they depend on errors in both heat and free energy terms. A reasonable estimate, based on simple propagation of error, is ±50%.

NiO–ZnO

Calorimetric results are shown in Table II. The enthalpies of solution are plotted as a function of composition in Fig. 1. They could be fitted by a linear or by a quadratic equation. The linear fit to the heat of solution, ΔH_{sol}, gives

$$\Delta H_{\mathrm{sol}} = 2{,}178 + 34{,}519X_{\mathrm{NiO}} \quad \mathrm{J\ mole^{-1}}, \quad r^2 = 0.980, \qquad (4)$$

with r the correlation coefficient. The quadratic fit gives

$$\Delta H_{\mathrm{sol}} = -6{,}038 + 55{,}941X_{\mathrm{NiO}} - 13{,}520X^2_{\mathrm{NiO}} \quad \mathrm{J\ mole^{-1}}, \quad r^2 = 0.982. \qquad (5)$$

In each case the equation was fitted using all the data points separately rather than the averages at each composition, to assign proper weights to the number of runs of each composition. We believe the curvature, shown in Fig. 1, and Eq. (5) is real. Physically it represents regular solution behavior relative to the rocksalt end-members, with a small negative enthalpy of mixing, analogous to that seen in NiO–MgO, with

$$\Delta H_{\mathrm{mix}} = (-13520 \pm 5581)X_{\mathrm{NiO}}X_{\mathrm{ZnO}} \quad \mathrm{J\ mole^{-1}} \quad \text{(rocksalt standard states)}. \qquad (6)$$

Extrapolation to pure ZnO gives a value for the enthalpy of solution of ZnO having the rocksalt structure of −6038 ± 3438 J mole^{-1}. From Table II the enthalpy of solution of ZnO having the zincite structure is 18,450 ± 1,042 J mole^{-1}. Therefore the enthalpy of transformation of zincite to its rocksalt modifications is 24,488 ± 3,592 J mole^{-1}. This is in close agreement with the value estimated by Jacob (*36*) from measurements of the Gibbs free energies of formation of $\mathrm{ZnAl_2O_4}$ and $\mathrm{ZnCr_2O_4}$. The free energy change for this transformation at 1323 K is 23,849 ± 2,500 J mole^{-1} (*23*). Assuming the enthalpy of transformation is constant over this temperature range, the corresponding entropy change is calculated to be +0.48 ± 3.3 J K^{-1} mole^{-1} with the error as the square root of the sum of the squares of the uncertainties in $\Delta H°$ and $\Delta S°$, divided by T.

Since the zincite to rocksalt transformation in ZnO has an accompanying negative volume change of 2.698 cm^3 mole^{-1}, the Clausius–Clapeyron relation necessitates a very flat and perhaps slightly negative dP/dT slope for the phase boundary between ZnO(rocksalt) and ZnO(zincite). A negative slope has been reported by Inoue (*37*) based on *in situ* X-ray diffraction measurements at high pressure. That a transition with a volume contraction of almost

20% has a positive entropy change is surprising at first sight. This point has been discussed recently by Navrotsky (*38*), who assembled numerous examples of cases in which denser phases have higher entropies. The major factor responsible for the entropy of ZnO (rocksalt) being higher than that of ZnO (zincite) is probably conversion of a tetrahedral framework which is tightly bonded, directional, and covalent to a much more ionic structure with weaker bonds, a presumably higher Debye temperature, and a higher vibrational entropy. Table II shows the free energies of mixing for the NiO–ZnO system with NiO(rocksalt) and ZnO(rocksalt) as standard states. The free energies were calculated from the available activity–composition relations (*23*). Knowing the free energy of the incite to rocksalt transformation one can calculate the free energy of mixing in the system with rocksalt standard states, where,

$$\Delta G_{\text{mix}}\ (\text{zincite–rocksalt}) = \Delta G_{\text{mix}}(\text{rocksalt–rocksalt}) + X_{\text{ZnO}}\Delta G_{\text{trans}} \quad (7)$$

From these free energies of mixing the excess entropies of mixing referred to rocksalt standard states can be calculated using the enthalpies of mixing given by Eq. (1). The excess entropies are negative and conform, approximately, to the equation

$$\Delta S_{\text{mix}}^{\text{excess}} = (-6.95 \pm 3.71)X_{\text{NiO}}X_{\text{ZnO}} \quad \text{J K}^{-1}\ \text{mole}^{-1} \quad (\text{rocksalt standard states}). \quad (8)$$

Discussion

The occurrence of negative heats of mixing, coupled with negative excess entropies of mixing in a solid solution series, can generally be taken as evidence for a tendency toward ordering, with potential compound formation, as opposed to clustering of like atoms, with potential immiscibility. The origin of such stabilization of intermediate compositions, for solid solutions with end-members having similar molar volumes, must arise from the electronic nature of the specific ions being mixed. Ni^{2+}, a d^8 ion, in an octahedral site has its fully occupied d_{xy}, d_{yz}, and d_{xz} orbitals oriented between the surrounding oxygen anions. Its electronic configuration, $t_{2g}^6e_g^2$, is such that it may well allow a closer approach of the anions in one direction, labeled z. This may be thought of in two ways, either as analogous to a Jahn–Teller distortion, in which both anions are drawn closer to the cation to leave it in a "compressed octahedral" coordination, or as a highly directional form of covalency.

Shannon (*39*) was able to correlate the covalency of several transition metal compounds with a volume contraction parameter, R_v, which was defined as the ratio of the unit cell volume of a transition metal compound M_mX_n relative to the unit cell volume of Mg_mX_n. Approximately linear relationships were found to exist between R_v and experimentally determined spin-transfer coefficients for Ni^{2+}, Co^{2+}, Mn^{2+}, and Fe^{2+}. Both high spin Co^{2+} and Ni^{2+} ions show approximately equal covalency, but the major difference between these is that for Ni^{2+} covalent bonding can only involve two orbitals, the singly occupied d_{z^2} and $d_{x^2-y^2}$, both of which have electron density maxima along the metal-ligand directions. In Co^{2+} there are three unpaired electrons in the d_{z^2}, $d_{z^2-y^2}$ and either the d_{yz}, d_{xz}, or d_{xy} orbitals. One would expect, therefore, covalency effects in Ni^{2+} to be somewhat more directional than in Co^{2+}.

Both Mg^{2+} and Zn^{2+} may be regarded as being spherically symmetrical ions, not subject to directional distortions. Now, if Ni^{2+} allows a closer approach of the oxygen anions in the z direction, it is more favorable for it to have either Mg^{2+} or Zn^{2+} as a next nearest neighbor. The energetically unfavorable alternative would have two Ni^{2+} ions competing for the closer approach of the same intermediate oxygen anion. Thus some ordering of Ni^{2+} and Zn^{2+} or Mg^{2+} may occur to permit the closer approach of oxygen to nickel and the slight distortion of the NiO_6 octahedron. In a sense, the result would be that Ni^{2+} would exhibit a slightly smaller than "normal" ionic radius and Zn^{2+} or Mg^{2+} a slightly larger one. These effects would be too small to be reflected in variations in lattice parameters, however.

The mechanism suggested above is consistent with the observed asymmetry of the enthalpies and excess entropies in the NiO–MgO series. Stabilization of the solid solution is a maximum for Mg-rich compositions, suggesting that ordering of Mg^{2+} around Ni^{2+} is the primary source of the negative deviations.

Magnetic susceptibility measurements by Evrard in the NiO–MgO solid solution series (*40*) enabled a determination of the variation of the Néel temperature, T_N, with composition. In pure antiferromagnetic NiO and its magnetically concentrated solid solutions, the Néel temperature depends solely on the strong antiferromagnetic second-nearest-neighbor interactions and the variation of the magnetic ordering temperature can be directly related to the number of magnetic next nearest neighbors (*41*). The number of neighbors is given by T_N/Cn_2 where C is the Curie constant, which varies little with dilution (*41, 42*) and n_2 is the antiferromagnetic field constant. Extrapolation to a 50 : 50 composition showed that each Ni cation has approximately 2 magnetic next nearest neighbors in the solid solution. In a 50 : 50 composition with random distribution each Ni ion would, on average, be expected to have 3 Ni second neighbors. Thus the data of Evrard is consistent with a degree of ordering of Mg ions as next nearest neighbors to nickel.

Both pure NiO and its solid solutions with MgO have been studied by ultraviolet and visible reflectance spectroscopy at low temperatures (*43, 44*). In NiO the authors were able to assign the observed peaks to the expected transitions to ${}^3_aT_{2g}$, ${}^1_aE_g$, ${}^3_aT_{1g}$, ${}^1_aT_{2g}$, ${}^3_bT_{1g}$, and ${}^1T_{1g}$ states, respectively. Similar assignments were also made for the observed peaks in the $(Ni_xMg_{1-x})O$ solid solutions. However, one feature of the solid solution spectra, not commented upon by the authors, is the clear splitting of the ${}^3_aT_{2g}$ peak for lower Ni^{2+} concentrations. For $x = 0.2$ the peak is quite clearly split, as x increases the splitting decreases, for $x = 0.5$ it appears as a shoulder and for $x = 1.0$ there is no evidence of any splitting.

There may be an explanation for the split peak that is consistent with the above evidence for a tendency toward ordering in the solid solution. A closer approach to nickel of the oxygen anions along the z direction would cause a splitting of the e_g orbitals of the Ni^{2+} cation. The d_{z^2} orbital would be destabilized the $d_{x^2-y^2}$ being relatively stabilized. A large decrease in the anion distance in this direction would also lead to a removal of the degeneracy of the t_{2g} orbitals. However any distortions occurring in the NiO–MgO solid solution will necessarily be small, and one would expect to see only the removal of the degeneracy of the e_g orbitals. This we believe to be the origin of the split ${}^3_aT_{2g}$ peak in the spectra of the solid solutions.

Occurrence of a compressed octahedral coordination of Ni^{2+} occurs in other systems. Crystal structure determinations in several compounds where Ni^{2+} is six-coordinated by H_2O ligands, in which the strength of the crystal field is comparable to that in the oxide (*45*), have shown nickel is not always coordinated by an ideal octahedron.

In $NiSO_4 \cdot 6D_2O$ (*46*) the axial Ni–O bonds are approximately 0.05 Å shorter than the equatorial bonds. Similarly in $NiNO_3 \cdot 6H_2O$ (*47*) the coordination around

Ni is deformed to an orthorhombic bipyramid with the two axial bonds being 0.04 Å shorter than the equatorial ones, whereas in $MgNO_3 \cdot 6H_2O$ there is no deformation of the ideal octahedral coordination of magnesium (*48*). In the compounds $MSiF_6 \cdot 6H_2O$ it has been reported (*49*) that the $[M(H_2O)_6]^{2+}$ octahedron is regular in the Zn salt, elongated in the Co salt and compressed in the Ni salt.

Similarly in Tutton's salts, $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, the $[Ni(H_2O)_6]^{2+}$ ion was found to have axial bonds 0.04 Å shorter than those of the equatorially coordinated water molecules (*50*). In the corresponding magnesium salt, however, the axial bonds were only 0.025 Å shorter than the equatorial bonds (*51*). Analogous distortions are also reported to occur in $(NH_4)_2Ni(CrO_4)_2 \cdot 6H_2O$ (*52*) and $(NH_4)_2Ni(BeF_4)_2 \cdot 6H_2O$ (*53*).

This compressed octahedral coordination of Ni has also been reported in $NiCO_3$ and is thought to account for the instability of nickel dolomites (*54*). We feel it may also account for the very limited mutual solubility of $NiCO_3$ and $MgCO_3$ (*55*), which is otherwise surprising since the two cations are of such similar size.

A similar type of thermodynamic effect appears to occur in solid solutions of the sulfate heptahydrates, $MSO_4 \cdot 7H_2O$. Crystallographically it has been shown that the cations are in ideal octahedral coordination in the Mg, Zn, and Ni sulfate compounds (*56*). Determination of the activity–composition relations have shown the $(Ni_xZn_{1-x})SO_4 \cdot 7H_2O$ solid solution series deviates negatively from ideality (*57*). Similar deviations, though not as large, were also found in the corresponding Ni–Mg series (*58*). However, in the Mg–Zn system slight positive deviations occur (*59*) and even larger positive deviations are found in the Co–Fe (*60*), Co–Mg (*59*), and Fe–Mg (*61*) systems. This appears to be further evidence that in solid solution, where Ni is initially in ideal octahedral coordination but on mixing is able to distort its coordination to the more stable compressed octahedron, negative deviations from ideality resulting from partial ordering will occur. It must be stressed, however, that this effect can only be seen in systems where the other cation is of similar size to Ni^{2+}, i.e., Mg and Zn. Otherwise the more important size difference effect will conceal the energetically less important ligand field effect.

Cu^{2+} and Ni^{2+} have comparable octahedral ionic radii (*26*). Pure CuO crystallizes with the tenorite structure in which Cu^{2+} ions are in square planar coordination. Partial solubility of CuO in MgO (*62*), CoO (*63*), and NiO (*64*) does occur, and intermediate ordered $(Cu_xM_y)O_{x+y}$ compounds exist in all three systems (*62–64*).

If one assumes that Ni^{2+} would prefer to adopt a compressed octahedral coordination, drawing the anions away from the Cu^{2+} ions, Cu^{2+} can approach square-planar coordination. Such a distortion therefore would simultaneously stabilize both the Cu^{2+} and Ni^{2+} ions.

Calorimetric study of the system NiO–CuO is being started in this laboratory and will be the subject of a future communication.

We have recently studied several annealed samples of $(Ni_{0.4}Mg_{0.6})O$ by high-resolution transmission electron microscopy. Although most of each sample has no long range order, this study revealed the presence of domains of the order of 50 Å in diameter containing an ordered superstructure (*65*). This investigation will be the subject of a future publication.

Conclusions

The calorimetrically determined heats of solution, coupled with previously determined activity–composition relations, of the $(Ni_xZn_{1-x})O$ and $(Ni_xMg_{1-x})O$ solid solutions have shown both the enthalpies and excess entropies of mixing, relative to rocksalt standard states, are negative. These values together with the observed asymmetry of the enthalpies of mixing in the (Ni_xMg_{1-x})O series have been interpreted in terms of bonding interactions and a tendency towards ordering in the solid solutions. The suggested ordering scheme, supported by spectroscopic, structural, and magnetic data, has been used to interpret observed phase relations and thermodynamic properties in some hydrated sulfates and the systems CuO–MO (M = Mg, Co, Ni). The investigation also finds a very flat and perhaps slightly negative dP/dT slope for the phase boundary between ZnO (rocksalt) and ZnO (zincite).

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References

1. D. L. Fancher and G. R. Barsch, *J. Phys. Chem. Solids* **30**, 3503 (1969).
2. V. S. Urusov, *Geokhimiya* **9**, 1033 (1968).
3. A. Navrotsky, *in* "MTP International Review of Science: Inorganic Chemistry" (D. W. A. Sharp, Ed.), Ser. 2, Vol. 5, p. 29, Univ. Park Press, Baltimore (1974).
4. P. K. Davies, Ph.D. Thesis, Arizona State University, in preparation.
5. R. C. Newton, T. V. Charlu, P. A. M. Anderson, and O. J. Kleppa, *Geochim. Cosmochim. Acta* **43**, 55 (1979).
6. F. C. M. Driessens, *Ber. Bunsenges Phys. Chem.* **72**, 764 (1968).
7. W. C. Hahn, Jr. and A. Muan, *Trans. AIME* **224**, 416 (1962).
8. E. Aukrust, and A. Muan, *Trans. AIME* **227**, 1378 (1963).
9. B. Brezny and A. Muan, *Thermochim. Acta* **2**, 107 (1971).
10. M. Rigaud, G. Giovannetti, and M. Hone, *J. Chem. Thermodyn.* **6**, 993 (1974).
11. W. C. Hahn, Jr., and A. Muan, *Mater. Res. Bull.* **5**, 955 (1970).
12. E. Woermann, and A. Muan, *Mater. Res. Bull.* **5**, 779 (1970).
13. H. Gripenberg, S. Seetharaman, and L. L. Steffansson, *Chem. Scr.* **13**, 162 (1979).
14. C. R. Catlow, B. E. Fender, and P. J. Hampson, *J. Chem. Soc. Faraday Trans. II* **73**, 911 (1977).
15. W. C. Hahn, Jr., and A. Muan, *J. Phys. Chem. Solids* **19**(3/4), 338 (1961).
16. D. J. Cameron and A. E. Unger, *Met. Trans.* **1**, 2615 (1970).
17. L. G. Evans and A. Muan, *Thermoch. Acta* **2**, 277 (1971).
18. H. Paulsson and E. Rosen, *Chem. Scripta* **11**, 204 (1977).
19. K. Torkar and R. Scheneider, *J. Solid State Chem.* **18**, 89 (1976).
20. L. G. Evans and A. Muan, *Thermoch. Acta* **2**, 121 (1971).
21. H. Kedesdy and A. Drukasky, *J. Amer. Chem. Soc.* **76**, 5941 (1954).
22. J. S. Kachauaha, M. P. Garu, and V. B. Tare, *Scr. Met.* **7**, 311 (1973).
23. A. Navrotsky and A. Muan, *J. Inorg. Nucl. Chem.* **33**, 35 (1971).
24. C. H. Bates, W. B. White, and R. Roy, *Science* **137**, 993 (1962).
25. R. A. Robie, P. M. Bethke, and K. M. Beardsley, *U.S. Geol. Survey Bull.*, 1248 (1967).
26. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
27. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., p. 93, Cornell Univ. Press, Ithaca, N.Y. (1960).
28. E. S. Patera, Jr., and J. R. Holloway, *EOS Trans. Amer. Geophys. Union* **59**(12), 1217 (1978).
29. A. Cimino, M. Jacono, P. Porta, and M. Valigi, *Z. Phys. Chem. N. F.* **55**, 14 (1967).
30. A. Navrotsky, *Earth Planet. Sci. Lett.* **19** 471 (1973).
31. A. Navrotsky, R. Hon, D. F. Weill, and D. J. Henry, *Geochim. Cosmochim. Acta* **44**, 1409 (1980).
32. T. V. Charlu, R. C., Newton, and O. J. Kleppa, *Geochim. Cosmochim. Acta* **39**, 1487 (1975).
33. A. Navrotsky, and W. E. Coons, *Geochim. Cosmochim. Acta* **40**, 1281 (1976).
34. F. D. Richardson, "Physical Chemistry of Melts in Metallurgy," Vol. I, p. 123, Academic Press, London/New York (1974).
35. Y. Shirane, *Kumamoto Diagaku Kogakubu Kenkyu Hokoku* **28**(3), 133 (1979).
36. K. T. Jacob, *Thermochim. Acta* **15**, 79 (1976).
37. K. Inoue, Ph.D. Thesis, University of Tokyo (1975).

38. A. Navrotsky, *Geophys. Res. Lett.* **7**(9), 709 (1980).
39. R. D. Shannon and H. Vincent, *Struct. Bonding (Berlin)* **19**, 1, (1974).
40. O. Evrard, F. Jeannot, and J. M. Lecuire, *Rev. Chim. Min.* **9**, 463 (1972).
41. O. Evrard, *Rev. Chim. Min.* **8**, 63 (1971).
42. N. Elliott, *J. Chem. Phys.* **22**, 1924 (1954).
43. V. Propach and D. Reinen, *Z. Naturforsch.* **336**, 619 (1978).
44. J. Von Grefer and D. Reinen, *Z. Anorg. Allg. Chem.* **404**, 167 (1974).
45. M. Lo Jacono, A. Sgamellotti, and A. Cimino, *Z. Phys. Chem. N. F.* **70**, 179 (1970).
46. B. H. O'Connor and D. H. Dale, *Acta Crystallogr.* **21**, 705 (1966).
47. F. Bigoli, A. Braibanti, A. Tiripicchio, and M. Camellini, *Acta Crystallogr. Sect. B* **27**, 1427 (1971).
48. A. Braibanti, A. Tiripicchio, A. M. Mannotti Larfredi, and F. Bigoli, *Acta Crystallogr.* **25**, 354 (1969).
49. S. Ray, A. Zalkin, D. H. Templeton, *Acta Crystallogr. Sect. B* **29**, 2741 (1973).
50. H. Montgomery and E. C. Lingafetter, *Acta Crystallogr.* **17**, 1478 (1964).
51. H. Montgomery and E. C. Lingafetter, *Acta Crystallogr.* **17**, 1295 (1964).
52. H. Montgomery, *Acta Crystallogr. Sect. B* **35**, 155 (1979).
53. H. Montgomery, *Acta Crystallogr. Sect. B* **36**, 2121 (1980).
54. P. E. Rosenberg and F. F. Foit, Jr., *Geochim Cosmochim. Acta* **43**, 951 (1979).
55. A. M. Gaines, and J. R. Goldsmith, *Z. Kristallogr.* **133**, 432 (1971).
56. Kh. Balarev, B. Karaivanoca, and S. Aslarian, *Kristallogr. Technik.* **8**, 115 (1973).
57. T. Oykova, L. L. Makarov, Kh. Balarev, and M. Miloschova, *Z. Phys. Chem. (Leipzig)* **255**, 453 (1974).
58. V. T. Oykova, Kh. Balarev, and L. Makarow, *Z. Phys. Chem. (Leipzig)* **256**, 890 (1975).
59. V. T. Oykova, Kh. Balarev, and L. L. Makarov, *Zh. Fiz. Khim.* **50**, 347 (1976).
60. V. T. Oykova, and L. L. Makorov, *C.R. Acad. Sci. Bulg.* **31**(4), 425 (1978).
61. V. T. Oykova and Khr. Balarev, *C.R. Acad. Sci. Bulg.* **27**(9), 1211 (1974).
62. A. Navrotsky, *J. Solid State Chem.* **11**, 10 (1974).
63. C. Landolt and A. Muan, *J. Inorg. Nucl. Chem.* **31**, 1319 (1969).
64. M. G. Rog, J. Deren, P. Grange, and H. Charcosset, *Bull. Soc. Chim. Fr.* **3**(4), 471 (1975).
65. P. K. Davies, I. D. R. Mackinnon, and A. Navrotsky, *EOS Trans. Amer. Geophys. Union* **61**, 1148 (1980).