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Computational study on thermodynamics of mixing and phase behaviour for CoO/FeO and CoO/MnO solid solutions

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Abstract

In this paper, a modified Monte Carlo technique, referred to as Monte Carlo exchange (MCX), is used to investigate the thermodynamic properties of CoO/FeO and CoO/MnO solid solutions. From MCX simulations the phase behaviour of CoO/FeO and CoO/MnO systems can be studied. The results show that these two systems exhibit a high degree of linear dependence of unit cell volume on composition. The calculated enthalpy of mixing shows very near-ideal behaviour at all compositions for CoO/FeO, but it predicts small positive deviation for CoO/MnO. The CoO/FeO solid solutions are completely miscible and form a single phase at all compositions (300, 1000, and 2000 K). The CoO/MnO solid solutions form two-phase region at 300 K but at high-temperatures (1000 and 2000 K) they are completely miscible and form a single phase at all compositions.

Keywords: Monte Carlo technique; CoO; FeO; MnO; Solid solutions; Thermodynamics

1. Introduction

Understanding of the thermodynamics of solid solutions of oxides, which are often strongly non-ideal, is essential for much of solid-state chemistry and mineralogy, including inorganic geochemistry. The thermodynamics of mixing in these systems is important in determining solid solubility, physical properties, and the distribution of components among coexisting solid phases. It has been revealed about the effect of cation properties (e.g. size, charge, and electron configuration) on the thermodynamics of mixing [1–3]. In order to understand the thermodynamics of solid solutions of oxides for more complex systems, the binary oxide solid solutions with the rocksalt structure, for example, are suitable simple systems to be considered as a first step.

In this work, we are interested in studying the effect of cation sizes in the binary oxide solid solutions, and hence the CoO/FeO and CoO/MnO systems are chosen, for which CoO, FeO, and MnO adopt the rocksalt structure. The thermodynamics of mixing for these two systems are calculated using a modified Monte Carlo technique, i.e. Monte Carlo exchange (MCX) [4–6]. The main purpose of this paper is to investigate the thermodynamic properties and phase behaviour of CoO/FeO and CoO/MnO systems, in which the radii of Co^{2+}, Fe^{2+}, and Mn^{2+} ions are 0.75, 0.78, and 0.83 Å, respectively.

The experimental results for CoO/FeO and CoO/MnO solid solutions had been revealed over the past several years [7,12]. In the work studied by Aukrust and Muan [7], the activities of CoO in the solid solutions CoO/MnO and CoO/FeO had been determined by equilibrating oxide samples with a metal phase in atmospheres of known oxygen activities. Results of their activity measurements showed that the CoO/MnO system is ideal, but a slight positive deviation from ideality exists in the CoO/FeO. On the other hand, in the work studied by Catlow et al. [12], the CoO/MnO system was shown to deviate positively from ideality by using the solid-state electrochemical techniques.

2. Theoretical methods

The modified Monte Carlo method, so-called Monte Carlo exchange (MCX) [4–6], has been used to perform the calculations. In this approach, both the atomic configurations and the atomic coordinates of all the atoms are changed in the course of the simulation. In any step, a random choice is made whether to attempt a random exchange between two atoms, a random displacement of an ion, or a random change in the volume of the simulation box. To determine whether

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Table 1
Potential parameters used for CoO/FeO and CoO/MnO

Interaction	A (eV)	ρ (Å)	
Cation–anion short-range potential parameters			
Co^{2+}–O^{2-}	1491.7	0.2951	
Fe^{2+}–O^{2-}	1207.6	0.3084	
Mn^{2+}–O^{2-}	1007.4	0.3262	
Interaction	A (eV)	ρ (Å)	C (eV Å^{-6})
Anion–anion short-range potential parameters			
O^{2-}–O^{2-}	22764.3	0.1490	20.37

the change is accepted or rejected, the usual Metropolis algorithm [8–10] is applied. The maximum changes in the atomic displacements and the lattice parameters are governed by the variables r_{max} and v_{max}, respectively, and these are adjusted automatically during the equilibration part of the simulation to maintain an acceptance ratio of approximately 0.3 [6].

The main purpose of using the MCX simulations is to study the phase behaviour of the CoO/FeO and CoO/MnO solid solutions by evaluating the variation of the difference in chemical potential of the exchanged cations (Co–Fe or Co–Mn ions) using semigrand-canonical ensemble simulations [13].

Here, we use a cubic shape of box containing 512 ions ($4\times 4\times 4$ primitive cubic unit cells). The MCX calculations are carried out using NPT ensemble, in which the thermodynamic data are collected over 10^7 steps, prior to which a 10^7 equilibration-step is carried out. All calculations in this paper are based on a rigid-ion model using two-body potentials taken from Lewis and Catlow [11] to present short-range forces. The potentials used are Buckingham potentials of the form

$$V_{ij}(r_{ij}) = A_{ij}\exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} \tag{1}$$

and the values of A, ρ, and C, are listed in Table 1.

3. Results and discussion

3.1. Unit cell volume

First of all, we consider the change in unit cell volume with composition calculated at 300, 1000, and 2000 K for CoO/FeO and CoO/MnO solid solutions. The results are shown in Fig. 1. From the results, the calculated values for these two systems exhibit a high degree of linear dependence on composition indicating an ideal behaviour for CoO/FeO and CoO/MnO systems. The linear behaviour shows that both systems obey Vegard's Law. The ideal behaviour for CoO/MnO obtained in this work is consistent with the work studied by Aukrust and Muan [7], but it does not agree with Catlow et al. [12], in that they predict a positive deviation from ideality. For CoO/FeO, it has been revealed a slight positive deviation [7], whereas in this study it shows an ideal behaviour.

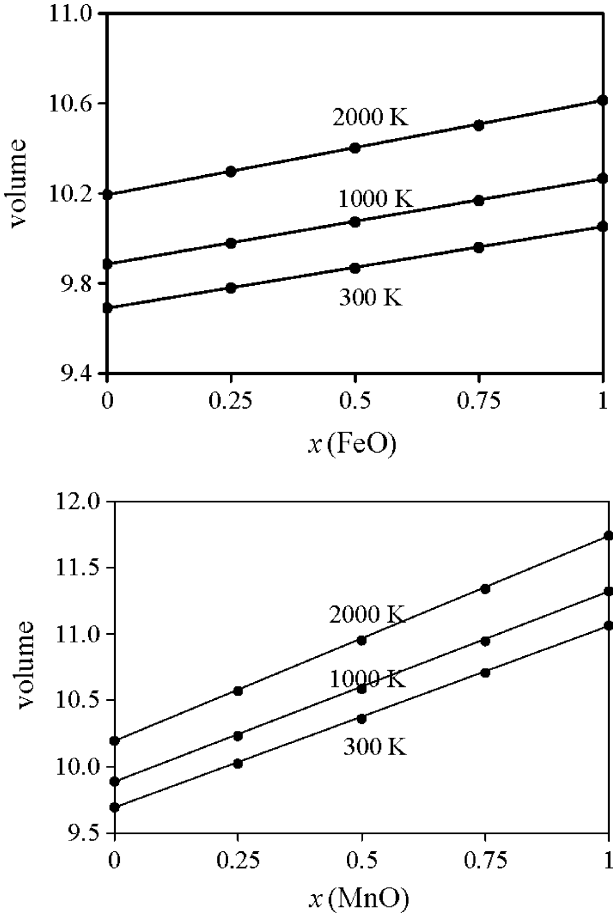

Fig. 1. Unit cell volumes (in Å^3) as a function of composition calculated at 300, 1000 and 2000 K for CoO/FeO and CoO/MnO solid solutions.

3.2. Enthalpies of mixing

In this part the change in enthalpy for the CoO/FeO and CoO/MnO systems will be considered. Here, the enthalpies of mixing, ΔH_{mix}, for these two systems are calculated by using the equations

$$\Delta H_{mix} = H_{Co_{(1-x)}Fe_xO} - (1-x)H_{CoO} - xH_{FeO} \tag{2}$$

(for CoO/FeO system)

$$\Delta H_{mix} = H_{Co_{(1-x)}Mn_xO} - (1-x)H_{CoO} - xH_{MnO} \tag{3}$$

(for CoO/MnO system)

where H_{CoO}, H_{FeO}, H_{MnO}, $H_{Co_{(1-x)}Fe_xO}$, and $H_{Co_{(1-x)}Mn_xO}$ denote the calculated enthalpies obtained from MCX simulations for CoO, FeO, MnO, CoO/FeO and CoO/MnO, respectively. x is the mole fraction of Fe or Mn ions in CoO system.

The calculated enthalpies of mixing for CoO/FeO and CoO/MnO solid solutions (at 300, 1000, and 2000 K) are plotted as a function of composition in Fig. 2. In this figure the experimental results for CoO/MnO (at 973 K) reported by Catlow et al. [12] is also shown. The results show, for CoO/FeO, that the calculated ΔH_{mix} at each temperature is asymmetric and shows very near-ideal behaviour at all