

Comparison of Semi-Empirical and *Ab Initio* Calculations of the Mixing Properties of *MO–M'O* Solid Solutions

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Theoretical predictions of the mixing properties of solid solutions can be made, in principle, via three different approaches: through the use of phenomenological, semi-classical atomistic, and *ab initio* techniques. Comparison of the results, obtained by application of all of the above-mentioned ways, is carried out for an example of the oxide solid solutions with the NaCl-type structure: CaO–MgO, CaO–MnO, MnO–NiO, and MgO–MnO. From this it is inferred that the predicted mixing energies for the whole range of compositions are generally in reasonable agreement with each other and with available experimental measurements for the systems under consideration. However, closer inspection shows marked systematic differences between the values of mixing energy and the structure relaxation parameters predicted with the use of different methods. In particular, this is due to the use of rather small and ordered unit cells for the atomistic and *ab initio* calculations. This allows one to make approximate estimates of disordering energies and propose some ways to improve the theoretical simulation of the solid solutions' mixing properties. © 2000 Academic Press

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INTRODUCTION

Today there are a number of theoretical models for describing and predicting the main mixing properties of oxide solid solutions: mixing energy, mixing volume, vibrational entropy, excess free energy, etc. This allows one to predict in some cases the solid state phase diagram and solubility limits at temperatures below the critical decomposition temperature.

The currently available models can be classified into three main types:

- (1) semi-empirical phenomenological models;
- (2) semi-classical atomistic approaches; and
- (3) first-principles or *ab initio* calculations.

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The aim of this paper is to describe in brief and compare these models using the simple oxide solid solutions with NaCl-type structure as an example. This choice is justified by the facts that these isovalent solid solutions have been subjected to a most extensive theoretical investigation, using all three types of approaches mentioned above, and they are well studied experimentally.

SEMI-EMPIRICAL PHENOMENOLOGICAL MODELS

The first successful attempt to solve the problem of estimation of structure relaxation and mixing energy of ionic solid solutions was reported by Wasastjerna and his colleagues (1,2). The model created by these authors allows for the relaxation of one common ion, i.e., the *C* ion between two next-nearest neighbors *A* and *B* in a solid solution (A_xB_{1-x})*C*. The main proposition about the NaCl-type structure solid solutions is that *A* and *B* ions form a regular close packing so that the distance between *A* and *B* is equal to $2R = 2(x_1R_1 + x_2R_2)$, where R_1 is the *A–C* and R_2 is the *B–C* distances in the end-members, while the common sublattice *C* is distorted in such a way that the linear chain *A–C–B* is divided in the following proportion,

$$\begin{aligned} R_1(x) &= [R_1/(R_1 + R_2)]2R \\ &= R[1 - (\Delta R/2R_1) + (\Delta R/2R_1)^2 + \dots], \\ R_2(x) &= [R_2/(R_1 + R_2)]2R \\ &= R[1 + (\Delta R/2R_2) + (\Delta R/2R_2)^2 + \dots], \quad [1] \end{aligned}$$

where $\Delta R = R_2 - R_1$; $R_2 > R_1$.

This assumption was based on the early X-ray diffraction studies of solid solution structures (3) which detected a decrease in reflection intensities as compared to the case of pure end-member crystals. This observation cannot be explained only by thermal vibrations and implies noticeable static displacements of ions in a nonmixed sublattice around their regular positions. An analysis of such effects showed



that the local displacements are of the order of the difference in interatomic distances of end-members and moreover could be close to half of that value.

For the first-order terms, Eqs. [1] can be rewritten approximately as follows:

$$\begin{aligned} R_1(x) &\approx R - (1/2)\Delta R, \\ R_2(x) &\approx R + (1/2)\Delta R. \end{aligned} \quad [2]$$

From Eq. [2] it is evident that the decrease of $R_1(x)$ amounts to nearly $-\Delta R/2$ and the increase of $R_2(x)$ amounts to nearly $\Delta R/2$. This means that such a model accounts for a structure relaxation and the so-called site compliance parameter c_s equals approximately 0.5, in good agreement with the subsequent determinations of c_s by the use of DLS simulation (4) and EXAFS measurements for the solid solutions with the NaCl-type structure (5).

The energy of a solid solution with relaxed interatomic distances is expanded into a power series up to the second-order terms with respect to small size parameter $\delta = \Delta R/R$. The pair interaction potentials used are assumed to be of the simple central-force type and not specified because only their second derivatives are retained and then determined from the experimental data on isothermal compressibility and molar volume of end-members. The mixing energy in the Wasastjerna-Hovi model takes the following form,

$$\Delta U_{\text{mix}} = x_1 x_2 (\theta/4 + 1/2)(A/R)\delta^2, \quad [3]$$

where A is the Madelung constant, and θ is the empirical parameter related to the coefficients of compressibility and thermal expansion. At 0 K the value of θ is

$$\theta = 18R^4/A\beta = (9V/\beta)(R/A), \quad [4]$$

β being the coefficient of isothermal compressibility. Although this theory takes into account both the local displacement of the common ion and, late in the analysis, even the effect of partial local order, it is not able to describe adequately the available experimental data over the entire composition range.

Hietala's model (6) was based on similar assumptions regarding the structure relaxation of an NaCl-type solid solution. The interatomic distances in the linear chain $\langle A-C-B \rangle = 2R$ was represented as a sum of $\langle A-C \rangle = (R + u)$ and $\langle C-B \rangle = (R - u)$, R being the average interatomic distance ($R = x_1 R_1 + x_2 R_2$) and u the displacement of the C ion from its regular position.

Interatomic potentials were again not specified because the energy expansion into Taylor's series was restricted to the second-order terms and the values of second derivatives were estimated by the use of experimental data on the bulk

modulus K of end-members. The minimization of the mixing energy ΔU_{mix} with respect to R and u yields

$$u \approx \Delta R/2, \quad [5]$$

$$\Delta U_{\text{mix}} = (9/4)x_1 x_2 V_1 K_1 \delta_1^2, \quad [6]$$

where V_1 and K_1 are the molar volume and bulk modulus, $\delta_1 = \Delta R/R_1$, R_1 being the interatomic distance in the end-member 1. If one inserts the third-order terms into the Taylor's series, the effect of asymmetry of ΔU_{mix} as a function of composition can be expressed in the following form,

$$\Delta U_{\text{mix}} = (9/4)x_1 x_2 V_1 K_1 \delta_1^2 [1 + B(x_1 - x_2)], \quad [7]$$

where $B = 0.6 (\text{\AA}^{-1})\Delta R$.

As the product VK for all alkali halide crystals is equal to 630 kJ/mol with an accuracy of a few percent, Eq. [6] can be rewritten in the simple form:

$$\Delta U_{\text{mix}} = 1420 \text{ (kJ/mol)} x_1 x_2 \delta_1^2. \quad [8]$$

Detailed calculations making use of these expressions lead to a very good agreement with all available experimental measurements of the mixing enthalpy for some alkali halide solid solutions. It may be interesting to note that, by substituting [4] into [3], one can easily see a close resemblance between the main expressions of the Wasastjerna-Hovi and Hietala theories, Eqs. [3] and [6], the former being somewhat more complicated and less accurate.

Let us now derive the expression for ΔU_{mix} in a shorter and more generalized way than that used originally by Hietala in order to expand its application to other groups of solid solutions with the NaCl-type crystal structure.

We denote the effective bond potential function by $\varepsilon(R)$. It is implicitly assumed that such a potential includes both long-range and short-range interactions per an ionic pair which are still not specified in detail. The number of bonds $A-C$ in linear chains $A-C-A$ will be proportional to x_1^2 and in chains $A-C-B$ to $x_1 x_2$. In a similar way the number of bonds $B-C$ in chains $B-C-B$ will be proportional to x_2^2 and in chains $B-C-A$ to $x_2 x_1$. Then the energy change at formation of a solid solution $(A_{x_1} B_{x_2})C$ can be represented as follows:

$$\begin{aligned} \Delta U_{\text{mix}} = N\nu \{ &x_1^2 [\varepsilon_1(R) - \varepsilon_1(R_1)] + x_2^2 [\varepsilon_2(R) - \varepsilon_2(R_2)] + \\ &+ x_1 x_2 [\varepsilon_1(\bar{R}_1) - \varepsilon_1(R_1)] + x_1 x_2 [\varepsilon_2(\bar{R}_2) - \varepsilon_2(R_2)] \}. \end{aligned} \quad [9]$$

Here N is Avogadro's number, ν is the coordination number, $\varepsilon_1(R_1)$ and $\varepsilon_2(R_2)$ are the energies of $A-C$ and $B-C$ bonds in the end-members 1 and 2, $\varepsilon_1(R)$ and $\varepsilon_2(R)$ are the energies of these bonds with the average bond distance R in chains $A-C-A$ and $B-C-B$, correspondingly, and $\varepsilon_1(\bar{R}_1)$ and $\varepsilon_2(\bar{R}_2)$ are those in chains $A-C-B$.

The bond lengths \bar{R}_1 and \bar{R}_2 depend on the displacement u of C ions from the centre of the bond chain:

$$\bar{R}_1 = R - u$$

$$\bar{R}_2 = R + u.$$

Now we expand the energy into Taylor's series to the second-order terms, keeping in mind that, due to the lattice equilibrium condition, the first derivative is equal to zero at $T = 0$ K,

$$\varepsilon(R) - \varepsilon(R_i) = (1/2)\varepsilon''(R_i)(R - R_i)^2 = (1/2)k(R - R_i)^2,$$

where $k = \varepsilon''(R_i)$ is the effective force constant of the corresponding bond ($i = 1, 2$).

If one assumes that the bondings in both end-members are closely related to each other, i.e., $k_1 \approx k_2 = k$, then

$$\Delta U_{\text{mix}} = (1/2)Nvk(R)\{x_1^2(R - R_1)^2 + x_2^2(R - R_2)^2 + x_1x_2(R - R_1 - u)^2 + x_1x_2(R - R_2 + u)^2\}. \quad [10]$$

Using the following forms of Vegard's rule,

$$R(x) = R_2 - x_1\Delta R = R_1 + x_2\Delta R,$$

and denoting $Nvk(R)$ by $E''(R)$, the rewrite Eq. [10] as follows:

$$\Delta U_{\text{mix}} = (x_1x_2/2)E''(R)[2x_1x_2(\Delta R)^2 + (x_2\Delta R - u)^2 + (-x_1\Delta R + u)^2].$$

By minimization of ΔU_{mix} with respect to u one has

$$d(\Delta U_{\text{mix}})/du = x_1x_2E''(R)(-x_2\Delta R + u - x_1\Delta R + u) = 0,$$

wherefrom $2u = (x_1 + x_2)\Delta R$. As $x_1 + x_2 = 1$, then

$$u = \Delta R/2. \quad [11]$$

This means that the displacement of C ions amounts to half of the difference in end-member distances in accord with our expectation from the above consideration. Substituting [11] into [10], one has

$$\Delta U_{\text{mix}} = (x_1x_2/4)E''(R)(\Delta R)^2. \quad [12]$$

Using the well-known thermodynamic relation, valid at $T = 0$ K for the NaCl structure type, $E''(R) = 9VK/R^2$, one has

$$\Delta U_{\text{mix}} = (9/4)x_1x_2VK\delta^2. \quad [13]$$

TABLE 1
Structural and Elastic Properties of Pure Oxides

Oxide	R , Å	V , cm ³ /mol	K , GPa	VK , kJ/mol
MgO	2.102	11.25	165	1856
CaO	2.405	16.76	116	1944
SrO	2.570	20.45	98	2003
BaO	2.761	25.35	82	2079
MnO	2.223	13.22	154	2036
NiO	2.088	10.97	190	2084

This expression is very similar to Eq. [6], except that all parameters V , K , and δ are related not to the first end-member but rather to the whole range of compositions of a solid solution and, in principle, are dependent on composition. In addition, it was noted (7, 8) that Eq. [13] has to be valid not only for alkali halide solid solutions but also for all solid solutions with NaCl-type structure: oxides, chalcogenides, nitrides, carbides, and so on. Indeed, the product VK is nearly constant for each group of these substances: 2000 kJ/mol for oxides MO , 1210 for chalcogenides, and 2930 for carbides MX . The experimental data on some structural and physical properties of oxides MO with the NaCl-type structure are given in Table 1. One can see that the product VK is actually nearly constant with an accuracy of a few percent. This means that the composition dependence of ΔU_{mix} is still retained through the slight composition dependence of the size parameter $\delta = \Delta R/(x_1R_1 + x_2R_2)$.

Therefore, with the average value of $VK = 2000(70)$ kJ, Eq. [13] can be used for calculation of the mixing energies ΔU_{mix} for some oxide solid solutions. The results of such calculations are given in Tables 2–5. It can be seen that these are in very satisfactory agreement with available experimental data.

SEMI-CLASSICAL ATOMISTIC APPROACH

Lattice (atomistic) semi-classical calculations of such defects in ionic crystals as vacancies, interstitials, and foreign (substitutional) ions began with the classical work by Mott and Littleton (9). They established the fundamentals of this

TABLE 2
Energies of Mixing (kJ/mol) of the CaO–MnO Solid Solutions

$x_1(\text{CaO})$	Eq. [13]	CRYSTAL	GULP	Exp. (23)	Exp. (24)
0.125	3.2	3.8 (3.6)	5.1	(1.7)	6.2
0.25	5.4		8.5	2.9	9.2
0.5	7.0	5.9 (6.7)	9.2	4.0	10.4
0.75	5.0		9.1	3.2	8.0
0.875	2.9	3.2 (3.2)	5.8	(1.7)	

TABLE 3
Energies of Mixing (kJ/mol) of the MnO–NiO Solid Solutions

$x(\text{NiO})$	Eq. [13]	CRYSTAL	GULP	Exp. (25)	Exp. (26)
0.125	1.8	2.5	3.4	1.3	1.5
0.25	3.2		5.6	2.2	2.5
0.5	4.4	4.1	6.0	2.6	3.5
0.75	3.4		5.8	1.6	2.5
0.875	2.0	2.4	3.6	0.9	1.5

type of calculations, assuming an explicit atomistic model for the crystal in the immediate vicinity of the defect and describing the relaxation of the lattice far from the defect using some continuum approximation. In other words, this model treats an isolated defect as surrounded by an inner region I, which is explicitly relaxed, and an outer region II, where the lattice relaxation is approximated in some continuum fashion. The ionic displacements and dipoles in region II are calculated using simple formulas employing the macroscopic dielectric constants.

According to this methodology (10, 11), the total energy of the system can be found by direct minimization with respect to independent atomic coordinates describing the configuration of region I. Indeed, the defect energy approaches the best estimate as the size of region I is increased and, therefore, the number of variables to be optimized and the computational time are increased, too. It is common that for convergence the number of ions needed in region I is of the order of 10^2 and the total number of variables can be a few times more.

However, direct application of the Mott–Littleton theory allows one to calculate the energy of solution of an isolated defect in the host crystal, so that such a case relates to infinite dilution of a solid solution. In order to perform calculations for concentrated solid solutions the model has to be adopted to represent the bulk materials using periodic boundary conditions.

Such an attempt was recently undertaken (12) for MnO–NiO, MgO–MnO, and CaO–MnO systems. Solid solutions of different compositions were modeled by creating a supercell or a subcell of the host oxide MO and

TABLE 4
Energies of Mixing (kJ/mol) of the MgO–MnO Solid Solutions

$x(\text{MnO})$	Eq. [13]	CRYSTAL	GULP	Exp. (27)	Exp. (28)
0.125	1.6	3.9 (4.4)	2.8	2.2	1.8
0.25	2.7		4.6	3.9	3.0
0.5	3.5	5.2 (6.7)	4.8	5.3	4.0
0.75	2.6		4.4	3.0	3.6
0.875	1.5	3.2 (3.7)	2.7	1.6	2.1

TABLE 5
Energies of Mixing (kJ/mol) of the CaO–MgO Solid Solutions

$x(\text{CaO})$	Eq. [13]	SCPIB (18)	GULP (18)
0.125	9.8	8.0	14.5
0.25	16.4	14.5	26.0
0.50	20.3	15.0	29.0
0.75	14.2	13.9	22.5
0.875	8.1	6.5	13.9

successively replacing the host cation M by another cation M' to give the desired stoichiometry. Thus, 16-ion supercells of the type $MM'_7\text{O}_8$ and $M_7M'\text{O}_8$ were used for the 12.5 and 87.5% solid solutions, while for the 50% solid solutions the 4-ion rhombohedral double subcell $MM'\text{O}_2$ was used. The 25 and 75% solid solutions were represented through the 16-ion supercells of the type $M_2M'_6\text{O}_8$, in which the two metal ions M are placed along the $[110]$ direction. It is necessary to stress that all chosen unit cells allow the relaxation of the oxygen atoms to be taken into account.

The atomistic calculations were performed (12) with the computer code GULP (13), using interatomic short-range Buckingham potentials to represent both the M –O and O–O interactions,

$$V(RT_{ij}) = A_{ij} \exp(-R_{ij}/\rho_{ij}) - C_{ij}/R_{ij}^6, \quad [14]$$

where R_{ij} is the distance between ions i and j , and A_{ij} , ρ_{ij} , and C_{ij} are parameters that depend on the identity of ions i and j . The shell model was used to represent the anionic polarizability in the conventional form $k_{cs}(\Delta r_{cs})^2$, where Δr_{cs} is the distance between the inner core of an oxygen atom with charge q_c and a massless shell with charge q_s , connected by an isotropic, harmonic spring with spring constant k_{cs} . O–O interaction parameters were taken from (14) (employing a core-shell spring constant of $53.9 \text{ eV}/\text{\AA}^2$) and the M –O parameters from (15). All the calculations based on interatomic potentials allowed the simultaneous relaxation of the cell parameters and of all the internal coordinates. The results of these calculations are listed in Tables 2–4.

Somewhat earlier, analogous theoretical investigations of the CaO–MgO solid solutions were performed with the GULP code in (18). The potential set involved the shell–core interactions for oxygen and both cations. For comparison purposes the calculations were made with different potential parameters. Those authors used 21 supercells with different cation arrangements, representing different compositions. The largest supercell for a “single cation” defect in a nearly pure host crystal contained 216 ions ($3 \times 3 \times 3$ supercell of the conventional FCC unit cell). The largest structure for modeling more concentrated solid solutions contained 64 ions in the unit cell, while most of the

mixed atomic configurations were represented by smaller unit cells. The energies of all structures were minimized with respect to cell parameters and ionic positions. Part of the results of these calculations is given in Table 5 for comparison with the results of other approaches.

AB INITIO CALCULATIONS

The above-cited work (12) also used the computational model at the *ab initio* Hartree–Fock (HF) level of approximation, based on periodic boundary conditions as implemented in the CRYSTAL code (16). The open-shell solution of the magnetic oxides MnO and NiO has been represented via an unrestricted Hartree–Fock (UHF) treatment of the spin-independent part of the wave functions.

As is known, the wave function of the solid is described by CRYSTAL in terms of crystalline orbitals, obtained as linear combinations of atomic orbitals (LCAO method), localized on atomic positions. The basis sets have been derived from previous studies on the pure oxides MgO, CaO, MnO, and NiO (the oxygen basis set uses the exponents of 0.500 and 0.191 bohr⁻² for the 3*sp* and 4*sp* electron shells) and correspond to a split-valence, triple- ζ -quality basis set for the *sp* atomic orbitals, while the *d* atomic orbitals of Mn and Ni are described with a double- ζ basis set; a set of single- ζ polarization functions was also included for Ca. The properties (lattice constants and bulk moduli) of pure oxides were correctly reproduced with the above Hamiltonian and basis functions.

Finally, HF results have been corrected to estimate the effect of electron correlation. Once the HF energy and wave function have been calculated, the correlation correction to the energy is evaluated *a posteriori* with a density functional of the Hartree–Fock equilibrium density, according to the generalized gradient approximation (GGA) scheme proposed by Perdew (17). However, no correction has been made for the HF wave function.

An alternative *ab initio* approach, the so-called self-consistent potential-induced breathing (SCPIB) model, was used to compute the formation and free mixing energies for the system MgO–CaO in (18). The SCPIB model (19) is a first-principles energy calculation in which the charge density is localized at each ion. The total energy of the crystal is the sum of the self-energy of each ion and the interatomic interaction energy. The energy is determined using the local density approximation following the approach of Gordon and Kim (20). One-particle wavefunctions are obtained from a Schrödinger equation in which the potential energy term is averaged spherically. The total energy of the crystal is then calculated from the self-consistent charge density. This approach extends that of Gordon and Kim by allowing the interatomic interactions to deform the charge density at each ion. This method has been called the spherical self-consistent deformation (SSCAD) model.

In its present form, its use is restricted to highly ionic crystals, where the nonspherical components of the charge density about each ion are unimportant. The authors of (18) proposed that these conditions have to be satisfied fairly well in the MgO–CaO system. For comparison, some benchmarking calculations were performed with the pseudopotential technique (21) and the linearized augmented plane wave method (LAPW) (22).

It is significant that this investigation applied a cluster expansion of the configurational free energy fitted to the results of quantum mechanical methods. It enables one to consider only a limited number of pair interactions, for instance, sixth nearest cation–cation neighbors, three three-body and two four-body terms. Effective cluster interactions in the cluster expansion can be determined by fitting to the semi-empirical or first-principles energy computations. Only a limited number of terms can be retained in the cluster expansion in order to provide a very good convergence and compute the energy of many other structures that were not included in the fit. As a result, only structures with small unit cells are required to obtain accurate value of energy: none of the structures in the limited fit contained more than 20 ions in the unit cell.

COMPARISON OF THE RESULTING MIXING ENERGIES

Tables 2–5 contain the results of the mixing energy calculations using the above-described different semi-empirical, atomistic, and first-principles techniques in comparison with available experimental data. Not all theoretical data obtained are listed in these tables. For instance, there are no results of calculations with the use of CRYSTAL code (12) for the fixed oxygen coordinates (the so-called virtual crystal approximation), because relaxation of the internal coordinates is absolutely necessary for the correct reproduction of the mixing energy. As is well known, the virtual crystal approximation yields ΔU_{mix} values which are nearly 2 times larger, due to relaxation elimination. The values obtained with CRYSTAL code (12) without regard for electron correlation are given in parentheses in Tables 2 and 4. As is seen, the inclusion of electron correlation usually reduces the calculated values of the mixing energy with respect to the pure HF values. For the MnO–NiO system only the results of CRYSTAL calculations for antiferromagnetic spin state are given in Table 3, because the antiferromagnetic ordering of spins is more stable for both end-member oxides. With regard to the CaO–MgO system, only the lowest values of ΔU_{mix} , obtained both with the classical computations and with the first-principles procedure, are listed in Table 5.

As is seen from Tables 2–5, there is a general satisfactory agreement between the calculated and experimental data, especially if one keeps in mind the large uncertainty of the latter data. For instance, different experimental

measurements of ΔU_{mix} for the CaO–MnO system differ by more than a factor of 2 (Table 2) and in this case all theoretical results fall between the lower and upper experimental limits.

However, closer inspection of all the data in Tables 2–5 shows that there is clear evidence of some systematic discrepancy between the results of different methods. First, one can indicate a good agreement between the semi-empirical and *ab initio* approaches, while the calculations with the semi-classical method give too large values of ΔU_{mix} for all systems under consideration. Second, in the case of the CaO–MgO system the semi-empirical method apparently yields nearly 30% as high values as the SCPIB, especially in the region of middle compositions. The application of the SCPIB lends credence to ΔU_{mix} values, obtained by this method, because, together with the simulation of vibrational free energy, they lead to computation of the CaO–MgO solid state phase diagram in excellent agreement with experimental data. This suggests that the semi-empirical approach suffers from some oversimplification. In particular, as is seen from Table 1, the VK values for these two oxides are the least and, therefore, using the average value of this quantity leads to overestimation of the calculated ΔU_{mix} by about 5%. Besides, it has long been known (29) that the composition dependence of the bulk modulus $K(x)$ of a solid solution undergoes substantial negative deviation from linearity. Therefore, it is likely that Eq. [13] suggests too strong a dependence of ΔU_{mix} on composition than appears to be the case. The same conclusion can be drawn from a close examination of Tables 2, 3, and 4: all calculations with CRYSTAL and GULP codes provide reason to speculate that the composition dependence of ΔU_{mix} is somewhat lower than that presumed by using the phenomenological model. A proper correction of this model is very likely to give ΔU_{mix} values in accordance with more sophisticated calculations and experimental data.

As mentioned above, the semi-classical calculations yield essentially larger values of the mixing energy than the *ab initio* and semi-empirical estimates. Such a difference is quite pronounced for the CaO–MgO system (Table 5) and that is why special attention was drawn to this fact in (18). The authors undertook extensive calculations using the pair potentials [14] with four different parameter sets. Nevertheless, in all cases the calculated values of ΔU_{mix} were nearly 2 times larger than those predicted by the SCPIB method. For instance, for the middle composition (molar fractions of both components are equal to 0.5) the SCPIB results were within the interval ~ 14.5 – ~ 24.0 kJ/mol, while the results of atomistic calculations fall in the range from ~ 29.0 to ~ 53.0 kJ/mol. The best results were obtained only after fitting the pair potential parameters to SCPIB results over a wide range of lattice constants (3.3–5.0 Å).

In order to give a better insight into the nature of such a divergence the authors (18) made some calculations of

formation energies of a few ordered structures: Ca_3MgO_4 (L_2 structure), CaMgO_2 (L_1 structure), and CaMg_3O_4 (L_2 structure). They used the pair potential model with different parameters, pseudopotentials, LAPW, SCPIB, and SCPIB with oxygen wavefunctions fixed at the self-consistent values in pure CaO and pure MgO. The pseudopotential, LAPW, and SCPIB results were in close agreement to each other: for instance, the formation energy of CaMgO_2 was varied through a range from 20.6 to 27.2 kJ/mol ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}$). At the same time, the atomistic calculations for the same structure gave the results within the interval 36.4–49.2 kJ/mol. The pair potentials with partial charges of all ions (+ 1.7 on cations and – 1.7 on oxygen atoms) gave the lowest values of ΔU_{mix} : about 30% lower than the formal-charge parameters, although still 30% higher than the *ab initio* results.

Now consider these data with respect to possible explanations of the above-mentioned disagreement. First, comparison of the results obtained by the *ab initio* methods for disordered and ordered structures of the same composition can give some useful estimates of the disordering energy. Indeed, the difference between ΔU_{mix} values for ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}$) solid solution and the formation energy of the hypothetical compound $(\text{CaMgO}_2)_{1/2}$ is not less than – 4.8–5.8 kJ/mol. Therefore, the solid solution is more stable than the ordered structure because of this considerable energy gain, consistent with the well-established tendency of this system to decompose at very high temperatures (above 2500 K) and not to form any ordered compounds.

For other systems under question both GULP and CRYSTAL calculations were performed for strictly ordered structures of different compositions (Tables 2–4). Hence, this makes it possible to estimate roughly the disordering energy for these systems by subtraction of the mixing energies obtained with the GULP and CRYSTAL techniques from those obtained with the use of the phenomenological approach. It is easy to see that this energy for middle compositions is of the order of – 1 to – 2 kJ/mol, consistent with the much weaker tendency of these solid solutions to decompose than in the previous case.

It is also possible, in principle, to convert approximately the values of formation energies, calculated for the ordered structures, to ΔU_{mix} values for random solid solutions. For instance, it is obvious that a probability of formation of the local order, corresponding to the structure of CaMgO_2 (L_1), is extremely low for the random solution. At the same time, probabilities of formation of the local structures, described by the L_2 -type compounds (Ca_3MgO_4 and CaMg_3O_4), appear to be much larger. From this it is inferred that the mean value of the formation energies of the L_2 -type compounds would be closer to the mixing energy of the random solid solution. Indeed, this mean value comprises 15.6–18.3 kJ/mol ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}$) for different SCPIB approximations, slightly larger than the result of SCPIB

calculations for the mixing energy of the solid solution of the middle composition (Table 5). It is very likely that a better understanding can be gained of such a “randomization” procedure.

However, similar averaging of the results of atomistic calculations (Table 5) for $x(\text{CaO}) = 0.25$ and 0.75 provides a markedly larger value of 24.3 kJ/mol ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O}$). This means, as was already emphasized by the authors (18), that the atomistic calculations strongly overestimate the mixing energy. They explained this fact by the oxygen “breathing” effect, that is by variations of the size of the oxygen ion, depending on the composition of solid solution. The importance of this effect appears in two ways: first, errors as large as 15% were found, when the energy was computed with oxygen wavefunctions that were not allowed to breathe; second, the small difference between the exact SCPIB energies and those computed with the potential parameters fit to the SCPIB results suggested that the oxygen “breathing” cannot be exactly reproduced by the metal–oxygen pair potential because of the multibody nature of this effect.

Nevertheless, in the present author’s opinion, as to the atomistic calculations, the use of different shell-model parameters for both end-members with allowance made for their dependence on composition of a solid solution would bring theory and experiment into better agreement. A check of this assumption is now in the development stage.

Another way to improve the results of theoretical predictions is to calculate structural and energetic properties for a solid solution with a given composition represented by a series of supercells with different degrees of short-range order. This makes it possible to estimate those of a random solid solution by extrapolation of the values of calculated properties as a function of the ordering degree to zero value of the ordering parameter. Such calculations for the systems MgO–CaO , CaO–SrO , and SrO–BaO are now in progress, too.

LOCAL ATOMIC DISPLACEMENTS AND DEVIATIONS FROM VEGARD’S RULE

Both semi-empirical and *ab initio* calculations enable one to determine the displacements of atoms in a common sublattice, for the case studied, oxygen atoms, from their regular positions. According to Eqs. [2] and [11] of the semi-empirical phenomenological model, the displacement u is equal to approximately $\pm \Delta R/2$. Thus, for instance, the oxygen atom displacements have to be 0.067 , 0.060 , and 0.091 \AA for the systems MnO–NiO , MgO–MnO , and CaO–MnO , correspondingly.

Now it is possible to compare all three approaches for the same three systems. The atomistic GULP calculations (12) give the following values of the oxygen ion displacements: $\pm 0.036(2)$, $0.032(1)$, and $0.049(1) \text{ \AA}$, correspondingly, while

the *ab initio* CRYSTAL (with the correction for electron correlation) calculations yield ± 0.03 , 0.04 , and 0.04 \AA , correspondingly. The comparison of these results led to the following conclusions: first, the displacements of the common sublattice atoms are not dependent, to a first approximation, on the composition; second, the semi-empirical phenomenological approach predicts the values of these displacements, which are by a factor of 2 larger than those predicted with GULP and CRYSTAL codes.

In other words, these results suggest that the relaxation parameter or the site compliance factor comprises for the semi-empirical phenomenological model 50%, while for the GULP and CRYSTAL calculations it amounts to about 70–75%. In this connection, it is worth noting that the experimental EXAFS measurements for NaCl-type structure solid solutions yield values of this factor of about 60% (5). It follows that the phenomenological model underestimates the relaxation of solid solution structure, while the GULP and CRYSTAL calculations overestimate it. The former appears to be a consequence of neglect of some second-order effects in interatomic interactions and the latter is likely to be a result of the use of small ordered supercells to model the solid solution structure.

A geometric and statistical analysis of the secondary atomic displacements (the displacements of the next nearest neighbors), which has been performed previously (30), provides a possibility of estimating deviations of the interatomic distances and lattice parameters of solid solutions from linearity, described by the well-known Vegard’s rule. For the NaCl-type crystal structure the deviations $\delta R(x)$ can be calculated by means of the simple equation:

$$\delta R(x) = (3/2)x_1x_2(\Delta R)^2/R. \quad [15]$$

This expression predicts small positive deviations from Vegard’s rule for all systems under investigation. For instance, the calculated deviations do not exceed 0.005 \AA at maximum for equimolar composition ($x = 0.5$) of the CaO–MnO system. For the two other systems (MgO–MnO and MnO–NiO) the estimated deviations are approximately 2 times lower. This means that a high precision of measurements is needed to determine such deviations experimentally. Indeed, the repeated experimental evidence suggests that the lattice constants of the MnO–NiO and CaO–MnO systems obey Vegard’s rule, whereas those of the MgO–MnO system reveal small positive deviations from Vegard’s rule (27,31–33). The calculations with the GULP and CRYSTAL codes for these systems (12) showed that the equilibrium lattice parameters obey Vegard’s law, except for the MgO–MnO system, in which the HF technique found small positive deviations from linearity (maximum value at $x = 0.5$ is of about 0.007 \AA).

CONCLUDING REMARKS

The discussion herein gives promise that accurate theoretical prediction of solid solution mixing properties may be attained, using various approximations, from very simple semi-empirical models to the most sophisticated, although much more time- and labor-consuming, *ab initio* calculations. The recent considerable and independent achievements of several groups of investigators are very encouraging and pave the way for the near future refinement of our understanding of the problem under consideration. It may be worth noting a very recent survey (34) of the developments to which the Mott–Littleton approach (9) has led. Among other new ways to model structure and properties of solid solutions, one can mention molecular dynamics simulations (35). In recent years very fast progress has taken place in quantum-mechanical studies of defective crystals. In this field one should mention a series of works by Pisani and co-workers (36–39), who have developed EMBED code (36), utilizing the “embedded cluster approximation” for Hartree–Fock treatment of isolated point defects. It is the author’s opinion that all these models are useful in order to give a better insight into the nature of disorder of solid solution structure and all of the relevant properties of these materials.

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REFERENCES

1. J. A. Wasastjerna, *Soc. Sci. Fenn., Comm. Phys.-Math.* **15**(3), 1 (1949).
2. V. Hovi, *Soc. Sci. Fenn., Comm. Phys.-Math.* **15**(12), 1 (1950).
3. J. A. Wasastjerna, *Soc. Sci. Fenn., Comm. Phys.-Math.* **13**(50), 1 (1946).
4. W. A. Dollase, *Phys. Chem. Miner.* **6**, 29 (1980).
5. J. B. Boyce and J. C. Mikkelsen, *Phys. Rev. B* **31**, 6903 (1985).
6. J. Hietala, *Ann. Acad. Sci. Fenn., Ser. AVI NN121*, 122 (1963).
7. V. S. Urusov, *Neorg. Mater.* **5**(4), 705 (1969).
8. V. S. Urusov, “Theory of Isomorphous Miscibility.” Nauka, Moscow, 1977 (in Russian).
9. N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).
10. A. B. Lidiard and M. J. Norgett, in “Computational Solid State Physics” (F. Herman, N. W. Dalton, and T. R. Kochler, Eds.), p. 385. Plenum Press, New York, 1972.
11. M. J. Norgett, AERE Report, N AERE-R7605, 1974.
12. M. Königstein, F. Corà, and C. R. A. Catlow, *J. Solid State Chem.* **137**, 261 (1998).
13. J. D. Gale, “GULP User’s Manual.” Royal Institution and Imperial College, London, 1997.
14. C. R. A. Catlow, *Proc. R. Soc. London. Ser. A* **353**, 533 (1977).
15. G. V. Lewis and C. R. A. Catlow, *J. Phys. C* **18**, 1149 (1985).
16. R. Dovesi, V. R. Saunders, C. Roetti, *et al.*, “CRYSTAL95 User’s Manual.” Univ. Torino, Torino, Italy, 1996.
17. J. P. Perdew, in “Electronic Structure of Solids” (P. Ziesche, and H. Eschrig, Eds.). Akad. Verlag, Berlin, 1991.
18. P. D. Tepeesch, A. F. Kohan, G. D. Garbulsky, *et al.*, *J. Am. Ceram. Soc.* **79**(8), 2033 (1996).
19. L. L. Boyer and M. J. Mehl, *Ferroelectrics* **150**(1–2), 13 (1993).
20. R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**(6), 3122 (1972).
21. M. C. Payne, M. P. Teter, D. C. Allan, *et al.*, *Rev. Mod. Phys.* **64**, 1045 (1992).
22. M. J. Mehl, R. E. Cohen, and H. J. Krakauer, *Geophys. Res.* **93**(B7), 8009 (1988).
23. G. Rog, A. Koslowska-Rog, W. Pycior, and K. Zakula, *J. Solid State Chem.* **100**, 115 (1992).
24. S. Radhavan, G. N. K. Iyengar, and K. P. Abraham. *Trans. Indian. Inst. Met.* **33**, 51 (1980).
25. C. R. A. Catlow, B. E. F. Fender, and P. J. Hampson. *J. Chem. Soc., Faraday Trans. 2* **73**, 911 (1977).
26. D. J. Cameron and A. E. Unger. *Metal. Trans.* **1**, 2615 (1970).
27. H. Gripenberg, S. Seetharaman, and L.-I. Staffanson, *Chem. Scr.* **13**, 162 (1978–1979).
28. S. Raghavan, Ph.D. Thesis, Ind. Inst. of Science, Bangalore, India, 1977.
29. D. L. Fancher and G. R. Barsch, *J. Phys. Chem. Solids* **30**, 2517 (1969).
30. V. S. Urusov. *J. Solid State Chem.* **98**, 223 (1992).
31. E. Woermann and A. Muan, *Mater. Res. Bull.* **5**, 779 (1970).
32. H. Schenk, M. G. Frohberg, and R. Nunninghoff. *Arch. Eisenhüttenwes.* **35**, 269 (1964).
33. W. C. Hahn and A. Muan, *Mater. Res. Bull.* **5**, 955 (1970).
34. C. R. A. Catlow, *Theor. Chem. Acc.* **103**, 205 (2000).
35. T. Akamatsu, M. Fukuhama, H. Nukui, and K. Kawamura, *Mol. Simul.* **12**(3–6), 431 (1994).
36. C. Pisani, F. Corà, R. Nada, and R. Orlando, *Comp. Phys. Commun.* **82**(2–3), 139 (1994).
37. F. Corà and C. Pisani, *Model. Simul. Mater. Sci. Eng.* **2**(5), 965 (1994).
38. V. B. Sulimov, C. Pisani, F. Corà, and V. O. Sokolov, *Solid State Commun.* **90**(8), 511 (1994).
39. R. Nada, C. R. A. Catlow, C. Pisani, and R. Orlando, *Model. Simul. Mater. Sci. Eng.* **1**(2), 165 (1993).