First-principles calculation of the formation energy in MgO-CaO solid solutions

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The electronic structure and total energy were calculated for ordered and disordered MgO-CaO solutions within multiple-scattering theory in real space and the local density approximation. Based on the dependence of the total energy on the unit-cell volume the equilibrium lattice parameter and formation energy were determined for different solution compositions. The formation energy of the solid solutions is found to be positive, which is in agreement with the experimental phase diagram, which shows a miscibility gap.

I. INTRODUCTION

In the last decade significant progress was achieved in application of first-principles methods to calculate properties of materials. The full-potential linearized-augmented-plane-wave (FLAPW) and ultrasoft pseudopotential methods allow one to map phonon potential surfaces and describe the phase transitions, electromechanical properties of ferroelectrics,[1–3] and magnetic properties of materials.[4] However these methods are applicable to ordered systems with translational symmetry, whereas many technologically relevant materials do not meet this requirement. Such important properties as ultrahigh piezoelectric efficiency, colossal magnetoresistance, and high oxygen permeation through fuel cell membranes occur only when corresponding oxides form solid solutions, most of which are disordered.

First-principles methods developed for disordered systems are mostly based on a Green's function formalism such as the Korringa-Kohn-Rostoker (KKR) method,[5,6] which allows one to take into account atomic disorder within the average t-matrix[7,8] (ATA) or coherent potential[9,10] (CPA) approximations. They have been successfully applied to metallic alloys.[11–15] A few calculations were performed for copper oxides[16,17] with mixed covalence-ionic character of chemical bonding. In the present paper, we consider the simplest oxide solid solution, the system MgO-CaO. Magnesiowüstite (Mg,Fe)O is believed to be a major constituent of the Earth's lower mantle, so that it would be an ideal system for study, but the FeO constituent leads to complex Mott insulator behavior. The study of CaO in MgO can be considered as a step in the direction of understanding the solid solution in minerals, as well as important in understanding the behavior of the minor element Ca. Understanding of oxide solid solutions is also important from the perspective of ferroelectric solid solutions and high-temperature superconductors.

Several approaches have been used previously to study the MgO-CaO system. The electronic structure and total energy were calculated for constitutive compounds of the system, MgO and CaO, using the FLAPW method.[18] A potential model[19] was developed to compute the phase diagram of the MgO-CaO solid solution. However, the approach was found to be inadequate to reproduce the properties with the required accuracy. The authors of Ref. 20 applied a tight-binding method to calculate the formation energy of ordered MgO-CaO solutions. Tight-binding parameters were obtained from results of first-principles pseudopotential calculations performed for MgO, CaO, and $MgCaO_2$ compounds and then used for computing the total energy of solutions with different compositions and crystal structures. Comparison with the pseudopotential results suggests that the tight-binding approach is an efficient tool to study ionic oxides. However, those were still ordered systems.

In the present paper, we consider both ordered and fully disordered MgO-CaO solutions using multiple-scattering theory within the local density approximation. We calculated the electron structure, total energy, equilibrium lattice parameters, and formation energy for ordered MgO, CaO, and $MgCaO_2$ compounds as well as for four disordered MgO-CaO solutions with different compositions. The obtained formation energy values were compared to results of Ref. 20.

II. COMPUTATIONAL METHOD

The calculations were performed by means of a computer code based on the local density approximation[21] (LDA) and multiple-scattering theory. The code embodies the local self-consistent multiple-scattering (LSMS) method[22] where a compound is divided into overlapping clusters—local interaction zones (LIZ's) centered around atoms of different sorts. The multiple-scattering problem is solved for each LIZ separately in the *lattice-site–angular-momentum* representation for the *muffin-tin* (MT) potential given the cluster Green's functions, local densities of electron states, and valence charge density for the central atom.

Our approach is self-consistent with respect to local charge densities and potentials. However, it does not treat the disorder self-consistency. We use an actual single-site scattering matrix $t_l^i(E)$ for the central atom of LIZ and average t matrix: $\tilde{t}_l^i = x t_l^a + (1-x) t_l^b$ for surrounding sites, if they belong to a sublattice with a substitutional disorder of the a- and b-sort atoms with concentrations x and $1-x$. According to the Ref. 8, such an approach is more accurate than the regular average t-matrix approximation. In the considered solid solution the Mg and Ca atoms randomly occupy the metal sublattice sites. They have the same number of valence electrons. This also allows us to believe that our approximation is reasonable for the system. One more advantage of the
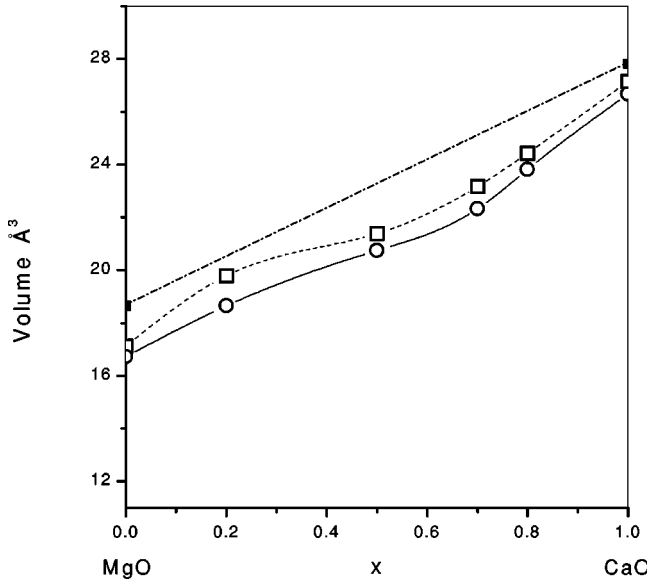
FIG. 1. The composition dependence of the equilibrium volume per oxygen atom calculated with maximum MT radii (squares) and fixed MT radii (circles). The dot-dashed line connects the experimental volume values obtained for stoichiometric MgO and CaO compounds.

FIG. 2. The formation energies calculated in the present work for disordered $Mg_{1-x}Ca_xO$ solid solutions (triangles) and ordered $MgCaO_2$ compound (circle), as well as obtained by means of the pseudopotential method (Ref. 20) for the following ordered phases: $x=0.25$ ($CaMg_3O_4$): higher cross, Ll_2 structure; lower cross, DO_{22} structure. $x=0.33$ ($CaMg_2O_3$): $MoPt_2$ structure. $x=0.5$ ($CaMgO_2$): from higher to lower cross, Ll_0, Ll_1, and A_2B_2 structures, respectively. $x=0.67$ (Ca_2MgO_3): $MoPt_2$ structure. $x=0.75$ (Ca_3MgO_4): higher cross, Ll_2 structure; lower cross, DO_{22} structure. $x=0.8$ (Ca_4MgO_5): Ni_4Mo structure.

approach is it can be explicitly implemented within the ordinary LSMS theory.[22]

Solving the Poisson equation at each iteration, we use the actual charge density for the local contribution to the MT potential and the average charges for the contribution of the substitutionally disordered sublattice to the Madelung potential. The exchange and correlation parts of the potential are determined within the LDA using the technique described in Ref. 23.

The total energy was calculated following procedure described in Ref. 12 and using an expression for a multicomponent compound.[24]

In the present calculations, each LIZ built around Mg, Ca, and O sites contained 123 atoms. This provided good convergence over the LIZ size, since the difference in the total energies obtained for 123- and 93-atom LIZ's was 3 and 5 mRy for MgO and CaO, respectively. To estimate an error induced by MT potentials, the calculations were performed in two approximations: maximum MT radii proportional to the unit-cell volume and fixed MT radii corresponding to a minimum volume considered for a given compound.

III. RESULTS AND DISCUSSION

The density of electron states, charge density, and total energy were calculated versus the unit-cell volume for ordered compounds MgO, CaO, and $MgCaO_2$ and disordered solid solutions $Mg_{1-x}Ca_xO$ with $x=0.2,0.5,0.7,0.8$. For $MgCaO_2$ the structure was chosen where cations were ordered by an alternate stacking of Mg and Ca planes along the [001] direction. Thus the cations form the Ll_0 structure in Strukturbericht notation.[25]

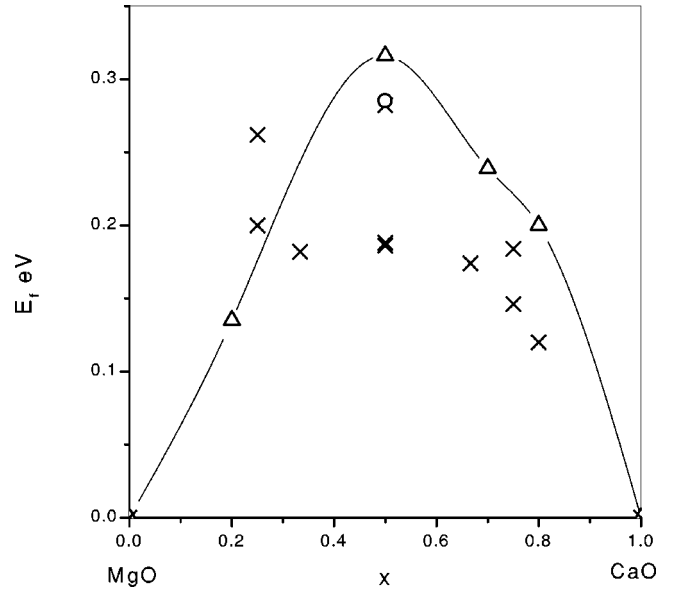Based on the computed volume dependence of the total energy the equilibrium volumes were calculated for each considered compound. The results are shown in Fig. 1. The concentration dependence of the unit-cell volume is found to be close to a linear one, though some wavy behavior is seen. The difference in results obtained by means of maximum and fixed MT radius approaches gives an order of magnitude for the error induced by the *muffin-tin* approximation. For the MgO and CaO compounds the calculated equilibrium volumes are less than the experimental ones, which reflects the well-known feature of the LDA.

Using the calculated values of the total energy we have determined the formation energy of the solutions determined as

$$E_f = E(Mg_{1-x}Ca_xO) - [(1-x)E(MgO) + xE(CaO)],$$

where E is the total energy of the corresponding compound. The E_f values compared to results of pseudopotential calculations[20] are shown in Fig. 2. Our result and the result of Ref. 20 obtained for the ordered Ll_0 phase of $MgCaO_2$ are in a good quantitative agreement (0.285 eV and 0.282 eV, respectively). The difference in formation energy of the ordered and disordered $MgCaO_2$ is less than 10%. Such a small difference takes place since a decay of band states caused by random potentials mostly involves unoccupied states in these ionic compounds and is much lower than in case of materials with covalence bonding.[17] The formation energy is found to be positive for all considered solid solutions, suggesting that

a phase separation is preferable for this system. This is in agreement with the experimental phase diagram,[26] which shows a miscibility gap.

Charge transfer is one of the key mechanisms determining the total energy of complex oxides. Therefore, we have calculated effective charges on atoms in the considered solid solutions by integration of the valence electron density over Wigner-Seitz spheres. It is important at this stage to make a clear reasonable definition of the space belonging to each nonequivalent atom that is determined by the ratio of the Wigner-Seitz radii, r_O^{WS}/r_M^{WS} (subscripts O and M denote oxygen and metal, respectively). We suppose that in the present case it is convenient for interpretation purposes to keep this ratio independent of the metal composition. This ratio should also make some physical sense. Because the considered solutions are definitely ionic, the ratio should be related to the ionic radii. Thus we come to the Wigner-Seitz radii ratio defined as

$$r_O^{WS}/r_M^{WS} = 2R_i^{OII}/[R_i^{MgII} + R_i^{CaII}] = 1.24,$$

where R_i^{OII}, R_i^{MgII}, and R_i^{CaII} are ionic radii of O, Mg, and Ca, respectively. We have also determined the average cation charges in the solutions as $Q_{av} = (1-x)Q_{Mg} + xQ_{Ca}$. The results are shown in Fig. 3. Since the Ca atom has the valence wave functions more extended than Mg, substitution of Mg with Ca leads to a noticeable increase in the electron charge on oxygen atoms (more than $0.2e$, going from MgO to CaO). The concentration dependence of these charges and average cation charges are found to be linear.

In summary, we have calculated the electron structure, total energy, equilibrium lattice constants, and formation energy for ordered and disordered solid solutions $Mg_{1-x}Ca_xO$. A linear composition dependence has been found for lattice parameters and effective charges. The formation energy is positive for all considered materials, which is in agreement
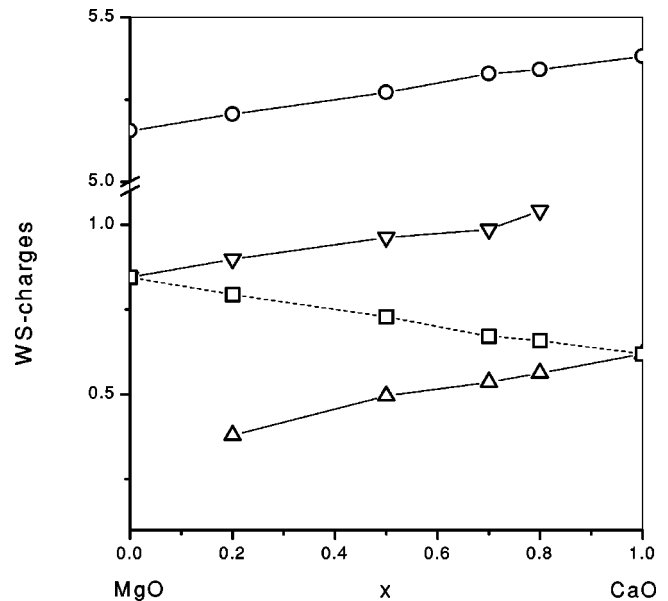

FIG. 3. The composition dependence of Wigner-Seitz charges on Mg (up triangles), Ca (down triangles), O (circles), and average cation charges (squares) in $Mg_{1-x}Ca_xO$.

with the experimental phase diagram. The results suggest that the LSMS method and LDA can be efficient tools to study the properties of disordered ionic solutions.

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