Defect Energetics in Oxide Materials from First Principles

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We have made fully *ab initio* calculations on the energetics of defects in the oxide materials MgO and Li_2O using a parallel computing methodology. The calculations, based on density functional and pseudopotential theory, yield results for the formation and migration energies of Schottky defects in MgO and Frenkel defects in Li_2O which are in excellent accord with experiment. The work gives new insight into the defect-induced redistribution of valence electrons.

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We describe in this Letter calculations on the energetics of defects in oxide materials performed entirely from first principles, i.e., without adjustable parameters or empirical interaction potentials. Specifically, we have studied the Schottky energy and the cation and anion vacancy migration energies in MgO, and the Frenkel energy and the cation vacancy and interstitial migration energies in Li_2O. Our work builds on recent advances in the study of the energetics of SiO_2 [1,2]. As well as making a significant step forward in the ability of theory to treat oxide materials, we believe our results provide a timely illustration of the rapid progress in the first-principles study of solids now being stimulated by parallel computational techniques.

Metal oxides have a wide-ranging importance in many areas of physics, geophysics, chemistry, and technology. Semiconducting oxides play a key role in devices such as photovoltaic cells and gas sensors. Some of the most important minerals are oxides; MgO, for example, constitutes around 10% of the Earth's lower mantle. In industrial chemistry, a large proportion of the important catalysts are oxides. Finally, we mention the important application of oxides as high-temperature ceramics. In all these areas, a key role is played by point defects, surfaces, or interfaces. Point defects, the subject of this Letter, govern the stoichiometry and hence the electronic properties of semiconducting oxides; defect diffusion determines the electrical conductivity and influences the response to stress in minerals and ceramics such as MgO. The importance of being able to calculate the energetics of defective oxides reliably is therefore considerable.

Past work on defect energetics in ionic materials has generally been based on empirical interaction models, which usually assume pair potentials between the ions, with the electronic polarizability of the ions represented by an empirical scheme such as the shell model. Although this approach has had many successes, there is increasing recognition of the need for support for the models from fundamental quantum-mechanical theory.

First-principles calculations on defective oxides are at present very demanding, because one needs to treat systems containing at least tens of atoms. The present work is performed within the framework of density functional theory (DFT) using pseudopotentials [3]. To avoid surface effects, periodic boundary conditions are employed, so that the system treated consists of a periodically repeated supercell of ions and valence electrons. The valence electron orbitals are represented by a plane-wave expansion, including all plane waves whose kinetic energy is less than a chosen cutoff energy. For some materials, particularly the much studied group-IV elements and III-V compounds, point defects and surfaces have already been successfully treated within the present approach [4]. Large repeating systems containing oxygen present substantial problems, due to the localized nature of the oxygen valence p electrons which requires a very large number of plane waves in the expansion of the orbitals. The use of plane waves (rather than, for example, a localized basis set) is nevertheless highly desirable, because it avoids bias, and because it allows the calculations to be systematically taken to essentially complete convergence with respect to the size of the basis set. The work on SiO_2 mentioned above [1,2] has demonstrated the power of the pseudopotential-plane-wave approach for oxide materials, and has shown that with suitably constructed pseudopotentials large enough systems for the study of defect energetics can be treated [5]. The use of the Kleinman-Bylander separable form of pseudopotential [6] plays a key role in making such calculations feasible [1].

Our calculational approach resembles that pioneered by Car and Parrinello [7]: The attainment of the electronically self-consistent ground state is treated as a global minimization problem, in which the total-energy functional is minimized with respect to the plane-wave coefficients of the occupied orthonormal orbitals. We perform the minimization by the very efficient conjugate-gradient technique developed by Teter, Payne, and Allan [8]. An important feature of our calculations is that they have been performed on a parallel supercomputer (a 64-node Meiko Computing Surface), using a new parallelized code CETEP specifically designed for this type of machine. The Car-Parrinello scheme is ideally suited to parallel implementation. The basic reason for this is that the total-energy functional is a sum of parts which are local either in reciprocal space or in real space. The calculations can therefore be distributed over almost independently working processors, with each processor assigned to a particular region of either reciprocal space or real space. Only transformation between the two spaces, accomplished by fast Fourier methods, requires substantial redistribution of data between processors; this is performed by specially written communication routines. The code will be fully described elsewhere [9].

We turn now to our calculations on MgO and Li_2O, two simple and representative oxides (having the rocksalt and antifluorite structures, respectively), which exhibit two of the main kinds of defect disorder. In MgO, the dominant defects are of Schottky type (cation and anion vacancies), while in Li_2O they are of cation-Frenkel type (vacancies and interstitials on the Li sublattice). Technical details of the *ab initio* calculations are as follows. We use *ab initio* norm-conserving nonlocal pseudopotentials [10] for Mg, Li, and O. The O pseudopotential needs to be very carefully constructed if the number of plane waves is to be kept manageable. This is achieved by the recent optimization technique of Rappe *et al.* [11]. The Mg and Li pseudopotentials do not require optimization, and are constructed by the standard Kerker method [12]. All the pseudopotentials are applied in the Kleinman-Bylander form [6], with the *s*-wave components local for Li and Mg, and the *d*-wave component local for O. The Monkhorst-Pack scheme [13] is used for Brillouin-zone sampling. The exchange-correlation energy is evaluated assuming the local density approximation (LDA) with the Perdew-Zunger [14] functional form.

Tests on the perfect crystals show that total energies (and energy differences) are well converged with respect to the size of basis set at energy cutoffs of 1000 eV (and 600 eV), respectively. All our calculations use a cutoff of at least 600 eV (corresponding to a basis set of roughly 15000 plane waves for a system of 32 atoms of MgO). For repeated cells of eight ions or more, four sampling points are enough to give well-converged results. We summarize in Table I a comparison of calculated and experimental values for the equilibrium lattice parameter, bulk modulus, and selected phonon frequencies of a MgO perfect crystal. The very good agreement is typical of that normally expected in modern pseudopotential calculations.

TABLE I. Calculated and experimental values of lattice parameter a_0, bulk modulus B, and five phonon frequencies of MgO. Phonon modes are the transverse optic mode at the Γ point and the transverse and longitudinal acoustic and optic modes at the X point of the Brillouin zone.

	Calculated	Experimental
a_0 (Å)	4.17	4.22[a]
B (Mbar)	1.54	1.55[a]–1.62[a]
TO(Γ) (THz)	12.39	12.23[a]
TA(X) (THz)	8.65	8.96[b]
LA(X) (THz)	12.57	12.65[b]
TO(X) (THz)	13.24	13.15[b]
LO(X) (THz)	16.36	16.61[b]

[a] Cited by Chang and Cohen [5].
[b] Reference [18].

In MgO, cation vacancies are formed by the removal of an Mg core, and anion vacancies by the removal of an O core together with eight electrons, so that the defects normally observed carry charges of $-2e$ and $2e$, respectively. (Other more complex defects having different charge states such as F centers and trapped-hole centers are also experimentally observable [15], but are not treated here.) The Schottky formation energy in MgO is the energy required to form a well separated vacancy pair minus the energy regained in replacing the removed ions and electrons to form a new unit cell. The Frenkel formation energy in Li_2O is the energy needed to remove an Li^+ ion and replace it on a distant interstitial site. The migration energy of each defect is the (fully relaxed) energy barrier that must be surmounted as the defect jumps from one stable site to the next. For the vacancies, there is little doubt that the relevant saddle point has the migrating ion midway between the initial and final sites, and our calculations are based on this assumption. For the Li^+ interstitial, the situation is more complex. Empirical modeling on many fluorite and antifluorite materials [16] indicates that the interstitial migrates by the interstitialcy mechanism, in which the interstitial moves onto a regular site, simultaneously displacing its previous occupant onto a new interstitial site; we have assumed this mechanism. In calculating both the formation and the migration energies, relaxation of the ionic positions is extremely important, and we stress that this is fully included in our calculations; details of the relaxation procedure and migration

TABLE II. *Ab initio* and experimental results for the Schottky energy E_S and the cation and anion vacancy migration energies ΔE_m of MgO, and the Frenkel energy E_F and the cation vacancy and interestitial migration energies ΔE_m of Li_2O (all energies in eV). All calculated results are for the 32-ion system of MgO and 48-ion system of Li_2O.

		Ab initio	Experiment
MgO	E_S	6.88	⋯
	ΔE_m (cation vacancy)	2.39	2.2[a], 2.28[a]
	ΔE_m (anion vacancy)	2.48	2.42[a], 2.61[a]
Li_2O	E_F	2.20	1.58[b], 2.53[b]
	ΔE_m (cation vacancy)	0.34	0.40[b], 0.49[b]
	ΔE_m (cation interstitial)	0.58	⋯

[a] Reference [19]. [b] Reference [20].

geometries will be given in a later paper.

Our defect energies are obtained from calculated ground-state energies of systems having a *single* defect in a large supercell. The issues involved in treating supercells for which the total charge of ion cores plus electrons is nonzero have been investigated in earlier work [17], based on empirical model potentials. It is well established that the method yields defect energies which converge rapidly with respect to the size of the repeated cell provided (i) the net charge of the cell is compensated by a uniform neutralizing background, and (ii) a correction ΔE is applied to compensate for the residual Coulomb interaction between defect images. The correction takes the form $\Delta E = -aq^2/2\varepsilon_0 R$, where q is the net defect charge, R is the lattice constant of the supercell, a is the Madelung constant of the superlattice, and ε_0 is the static dielectric constant of the bulk crystal. To support the present work, we have made extensive tests on the calculation of defect energies in MgO and Li_2O using empirical interaction models, which show that with the repeated cells of 32 ions (MgO) and 48 ions (Li_2O) used here, the periodic boundary conditions will introduce only small errors. Details of these tests will be published elsewhere.

Our *ab initio* values for the defect formation and migration energies in MgO and Li_2O are compared with experiment in Table II. At present, reliable experimental values for the Schottky energy in MgO and the interstitial migration energy in Li_2O are not available. However, for all the other energies the agreement with experimental values is striking. This strongly suggests that the calculated Schottky energy in MgO is reliable, and indeed that *ab initio* methods based on pseudopotentials and LDA can be used to provide values for defect energies in other oxides where experimental evidence is lacking.

Because the defects carry net charges, we expect them to induce a strong polarization of the surrounding lattice, and to distort the electron clouds on neighboring ions. An understanding of such polarization effects is important in assessing the validity of empirical models for the energetics, such as the shell model. In order to display these effects, we plot the defect-induced electron density difference: the valence electron density in the defective system minus the density in the perfect crystal. We separate the electronic polarization effects from those due to ionic relaxation by studying this difference with the ions fixed on their regular sites. Figure 1 shows the density difference for the Mg and O vacancies in MgO. In both plots, the prominent features represent the distortion of charge density on the neighboring oxygen ions, which is considerably more complex than the simple dipolar polarization that would be predicted by the shell model. For the Mg vacancy, the valence electrons of neighboring oxygens are repelled by the effective negative charge of the vacancy. The figure shows that the charge redistribution is due mainly to the distortion of the oxygen p orbitals pointing towards the vacancy. The double peak-trough structure arises from the shift of charge within the lobes of these orbitals. Around the O vacancy, an important aspect of the electronic redistribution is the transfer of electrons from the nearest oxygens to a spherical shell region covering the Mg neighbors of the vacancy. The transfer is mainly from the p orbitals pointing towards the vacancy, and this leaves a prominent quadrupole moment on the oxygen neighbors.

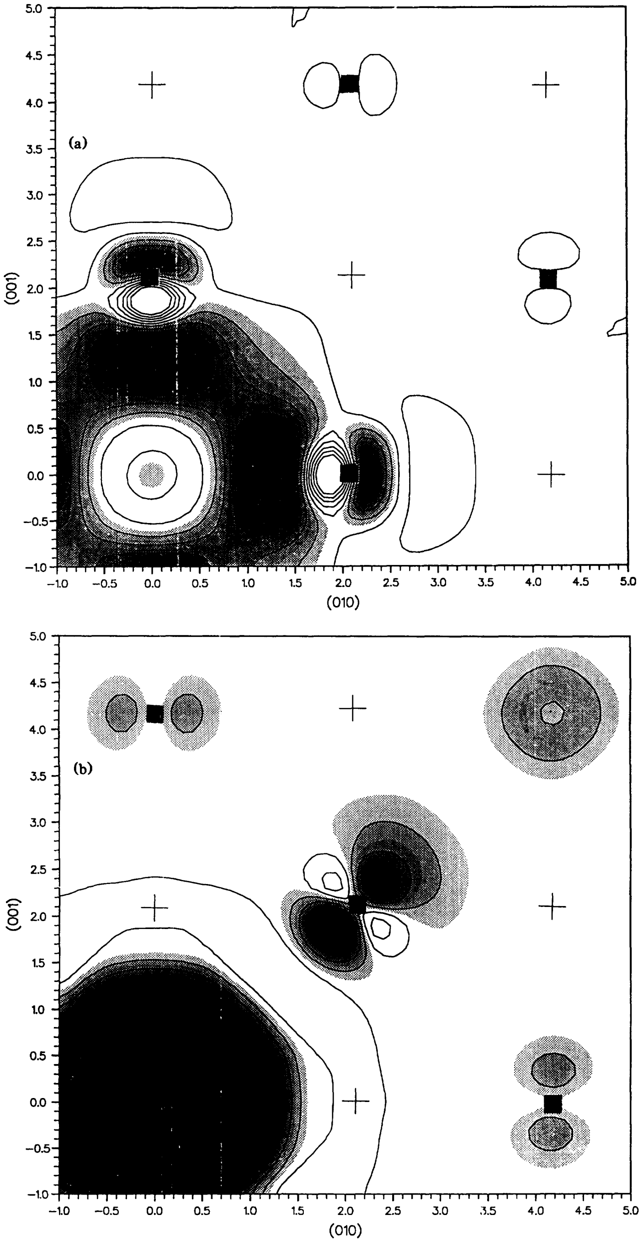

FIG. 1. The response of the valence electron density to the formation of (a) a Mg vacancy and (b) an O vacancy in MgO. Contours show the change of density (unrelaxed vacancy system minus perfect crystal) on the (100) plane, in units of 10^{-2} electron per Å^3, with the interval between contours equal to 2.0. Negative regions are shaded. Vacancies are at the coordinate origin (axis scales in Å); Mg and O ions are marked by crosses and squares, respectively.

In conclusion, we have performed fully *ab initio* calculations on defect energetics in two important oxide materials. The ability of such calculations to produce reliable results is demonstrated by the close agreement with experiment for both formation and migration energies in MgO and Li_2O. We have also used the calculations to study defect-induced electronic polarization in these materials and have found that polarization effects are considerably more complicated than would be expected from simple models. Work on more complex oxides such as Al_2O_3 is now under way. We believe that calculations of the present kind will be an important source of information for improving empirical modeling, as well as providing reliable values for defect energies which are not available from experiment.

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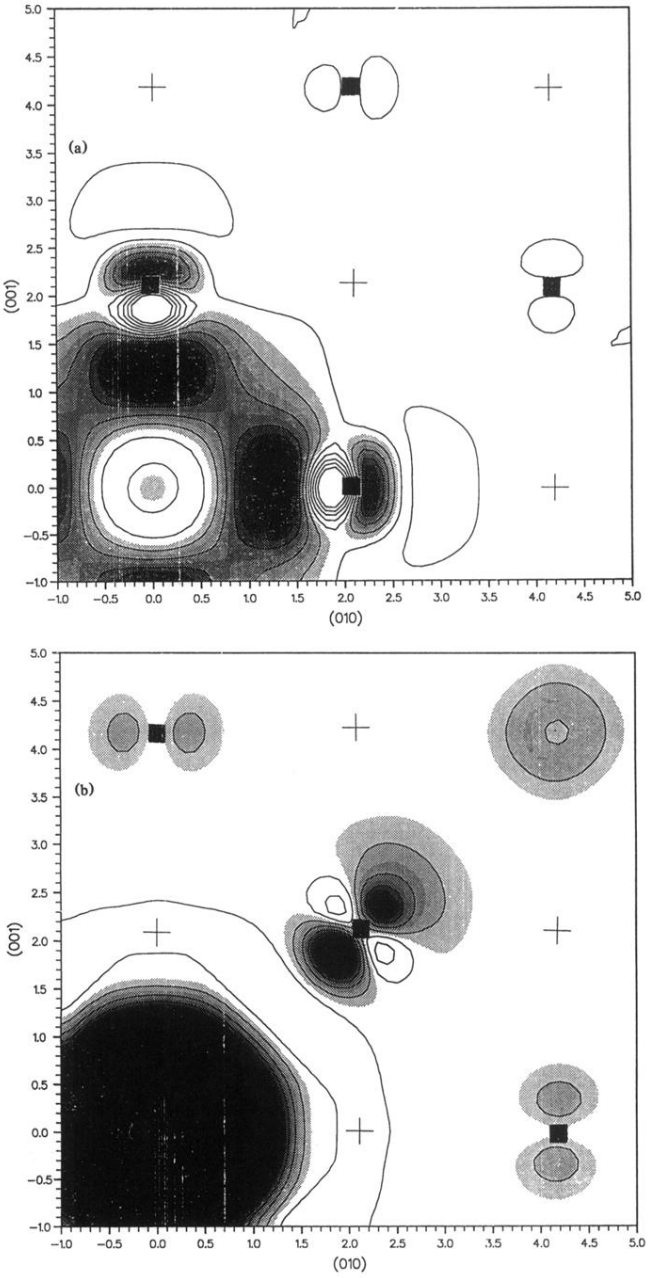

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