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INTERATOMIC FORCES AND BONDING MECHANISMS IN MgO CLUSTERS

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ABSTRACT

We report results from a first-principles local spin density quantum mechanical study of the energetics and elastic properties of a series of magnesium-oxygen clusters of various morphologies. The role of quantum effects, e.g. covalency, in the bonding character of diatomic MgO is determined by comparison of classical and quantum restoring force curves. The dependence of binding properties on geometry and metal to oxygen ratio is determined by comparison of binding energy curves for a series of clusters. Results show that while gross features of the binding curves may be represented by simple interatomic potentials, details require the many body corrections of a full quantum treatment.

INTRODUCTION

Quantitative simulation of sintering or defect and surface properties of MgO requires the use of accurate interatomic potentials. The forces must be properly modeled over a wide range of atomic separations and neighboring geometries, including situations of greatly reduced symmetry where interactions among relatively few atoms may be important, e.g. as in one species diffusing over the surface of another. Traditionally shell models have been used to describe the interatomic interactions in bulk MgO. These potentials are extracted from the experimentally known bulk crystal properties. They are then used to calculate quantities not utilized in the empirical fitting. Their accuracy is judged upon the prediction of these "unknown" properties. When found to be lacking in accuracy the coefficients are adjusted until this unknown property is also predicted to the desired degree of accuracy.

A widespread effort is underway among many groups [1] to use methods of electronic structure theory to improve the basis for derivation of these interatomic potentials. Work based on the local density approximation (LDA) is of particular interest in this regard since rather large-scale calculations are feasible, allowing considerable refinement and completeness in treatment. Within such schemes, a large database of first principles results can be generated so that reliable parametrized interatomic potential functions can be derived. Another use for these first-principles calculations is to check the results of predictions from simplified models as interatomic potentials are applied to a specific test case.

It is within the former category that we report results from our calculations for the MgO system. While our ultimate goal is to generate first-principles interatomic potentials for use in simulation calculations for MgO, in this paper we limit our discussion to the results of calculations for some MgO fragment clusters which are components of bulk MgO. We show that in the few-atom cluster regime the interatomic separation dependence of the energy and restoring forces, and the way these properties depend upon cluster morphology, show marked departures from simple ionic models.

METHOD

Force and binding energy curves for small clusters were calculated within the local spin density approximation to density functional theory. Specifically the augmented gaussian orbital method [2] was used to calculate cluster cohesive energies and interatomic forces. The quantum mechanical forces are determined independently of the energy calculation using gradient techniques [3], providing a highly precise determination of the forces, and allowing a cross check for the energy calculation. This overall method has several advantages. There are no restrictions on atom type or cluster geometry, the results are parameter free and fully self consistent, and an essentially exact solution of the LDA equations is obtained, within basis set limitations. The one-electron solutions provide a simple framework for interpretation of the results in chemical bonding concepts.

The clusters considered were the diatomic, linear and right angle triatomics, and the octahedron. These are geometries which make up the bulk crystal as can be seen in Fig. 1. All possible combinations of atom types were considered for each cluster as part of our investigation of the dependence of bonding properties on cluster morphology. The binding energy and force curves were calculated as a function of bond lengths within each cluster.

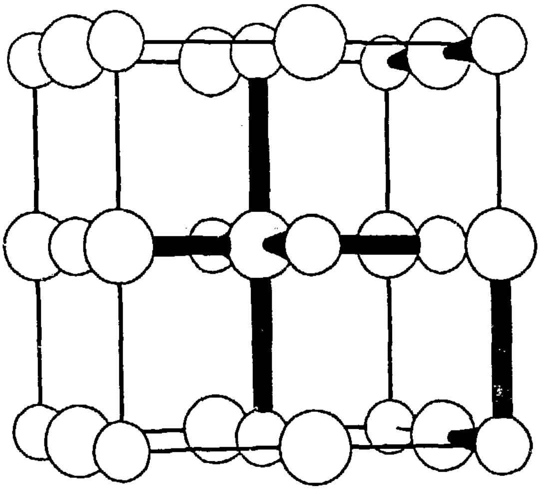

Figure 1: Some cluster geometries present in the NaCl structure of MgO: the linear trimer, the right angle trimer, and the octahedron

RESULTS

Diatomic

The LDA binding energy and restoring force curves for the MgO dimer are given in Fig. 2 where energies are plotted as they depend on MgO bond length (D). We note that the equilibrium separation is at 3.27 bohr, with a binding energy of $-3.55eV$ with respect to the atomic total energies. The experimental values [4] given for diatomic MgO are 3.31 bohr and $-3.53eV$, respectively. The LDA gradient force curve (Fig. 2) shows repulsive behavior for compressed bond lengthes with a Hooke's law dependence near equilibrium, and a maximum restoring force value near $D \approx 4.2$ bohr (a 27% bond stretch). Beyond this critical value the restoring force drops off with further bond elongation somewhat more rapidly that D^{-2}. A classical force curve with this dependence is also given in Fig. 2 for comparison with the LDA dependence. The classical curve has a separation dependence of

$$F(D) = \frac{-Q^2(D)}{D^2}\,. \qquad (1)$$

where $Q(D)$ is the separation dependent net charge associated with the atomic sites as determined by a Mulliken population analysis of the orbital solutions. There is the usual ambiguity associated with the definition of charge per site, particularly when the atoms are as close as they are in this case. Within this picture, the charge $Q(D)$ steadily decreases from a value of $\sim \pm 0.75$ for $D \approx 3.0$ bohr to $\sim \pm 0.57$ for $D \geq 5.0$ bohr. The charge transfers by this definition are much smaller than the nominal ± 2 values associated with bulk MgO.

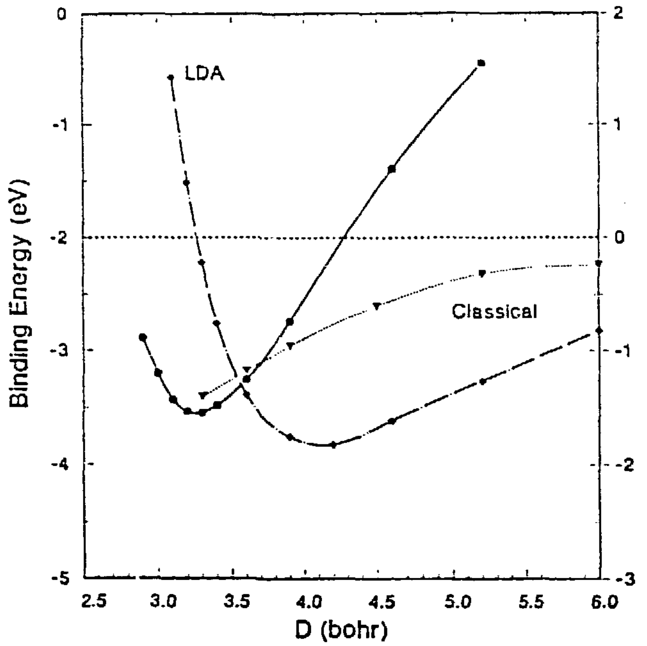

Figure 2: The binding energy and LDA force is shown as a function of separation for an MgO dimer. The classical Coulomb force curve for charge transfer is given by the result of a Mullikan population analysis of the LDA curves. Energy is plotted relative to the left ordinate, forces relative to the right ordinate.

What could be the origin of the enhanced force calculated in the LDA? Certainly the "covalent" components of the diatomic bond, with their bond-oriented directionality, contribute to the restoring force. Higher moments of the charge distribution are not, however, present in any spherically-averaged charge model. Such polarization terms, which contribute attractively and can be an appreciable component of the Coulomb energy [5], can not be ignored in such an asymmetrical case as the dimer. The significance of the polarization terms is apparent on inspection of Fig. 3 where the MgO difference density defined as

$$\delta\rho = \rho_{cluster} - \sum \rho_{atoms} \qquad (2)$$

is plotted in a plane passing through both Mg and O sites. Aside from some secondary differences inside the atomic spheres (grey circles), the charge difference lobe about the O site is negative and that about the Mg site is positive. But it is clear from Fig. 3 that the charge shifts extend far outside the nominal atomic spheres and the shifts are neither point charge-like nor spherically symmetric. Since reducing the Mulliken atomic density to effective point charge form enhances the Coulomb interaction, the LDA force is more than twice as large as the classical extended charge force over the region $D \geq 4.2$ shown in Fig. 2.

DISCLAIMER

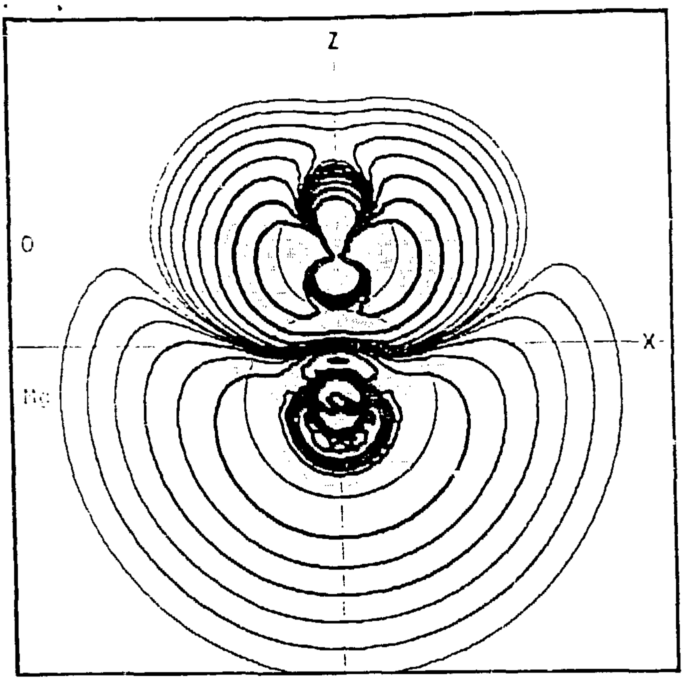

Figure 3: The charge difference density as defined in Equation 1 is shown in the plane containing both atoms. The upper lobe about the oxygen atom is negative or electron rich, the bottom lobe about the magnesium is positive.

Triatomic

We have treated the triatomic clusters MgO_2 and Mg_2O in right isoceles triangular form and $OMgO$ and $MgOMg$ in linear form. These are fragments of bulk MgO, and intercomparison of results for them yields information about the role of bond-angle bending and composition-dependence in modeling the bonding by more approximate means. Binding energy curves for these four cases are given in Fig. 4

There are striking similarities on a course scale - all triatomics are bound between 6.5 and $7.5eV$ with equilibrium bond lengths of 3.4 to 3.5 bohr, and can be crudely modeled by doubling the MgO diatomic energy dependence (dotted curve, Fig 4). The triatomic binding energies are roughly twice that of diatomic MgO, and the bond lengths are slightly increased, showing the general trend for contracted bonds in small clusters to expand to the bulk limit (3.97 bohr) with increasing cluster size. But there are differences in detail both with respect to scaled diatomic results and among themselves. The curve slopes (and therefore the restoring forces) are all nearly the same for $D > 4.0$ bohr. This slope is not, however, the same as the addition of forces for two dimers given by the slope of the dashed line. The three-body interaction is clearly not merely a sum of two two-body interactions.

The oxygen-rich MgO_2 and $OMgO$ triatomics are more stably bound (by 0.3 to $1.0eV$) than the Mg-rich species. In addition the linear cases are more strongly bound than their right triangle counterparts. The linear $OMgO$ case is the most stable, and we can consider it as an MgO with an oxygen atom added end-on (bound by $3.85eV$) with a 0.2 bohr bond length expansion. It is interesting to note from these quantities that the reaction

$$2MgO + O_2 \rightarrow 2OMgO \tag{3}$$

would be energetically allowed (by $0.16eV$) within the LDA.

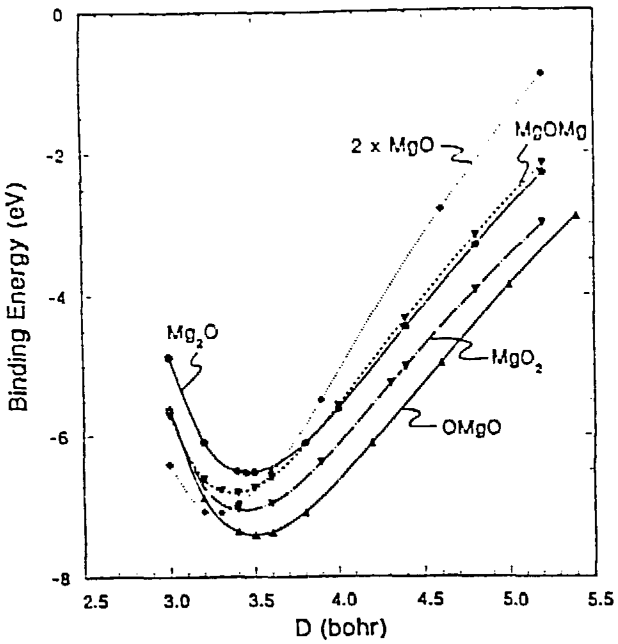

Figure 4: The binding energy as a function of separation for triatomic MgO . The dashed line is the binding energy curve of diatomic MgO, multiplied by two.

Octahedron

In Fig. 5 we present binding energy curves for a variety of clusters including the octahedral cases Mg_6 and Mg_6O. The equilibrium $Mg - O$ bond length for the latter case ($\sim$ 4.10 bohr) has slightly exceeded the bulk (3.97 bohr) value. The binding energy of the Mg_6O cluster is about a factor of 2.7 that of diatomic MgO. Calculations for an MgO_6 cluster (not shown) give a binding energy of $\sim -14.61eV$, the most stable of all the clusters treated. Indeed if we fix the interatomic separation in Mg_6 and O_6 host clusters to the MgO bulk value, an O atom binds in the Mg_6 host by $\sim$ 8.0eV whereas the O_6 host binds Mg by $\sim$ 10.0eV.

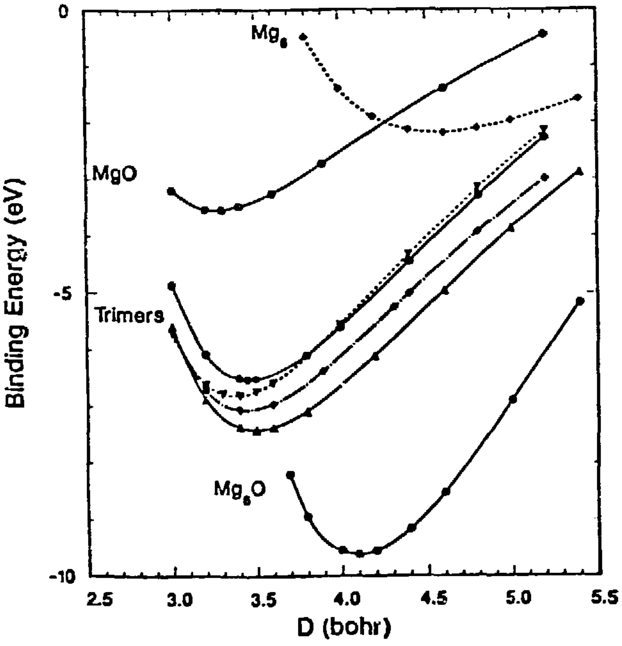

Figure 5: The binding energy as a function of interatomic separation for the Mg_6 and Mg_6O octahedra. The diatomic and triatomic curves are repeated from the previous figures for comparison of scale.

CONCLUSIONS

The results of this study show that the modeling of $Mg - O$ systems involving small atomic configurations requires many-body corrections to simple interatomic potentials of point ion or scaled diatomic form. Energetics and restoring forces depend upon composition and geometry in a way that appears beyond the scope of simple ionic models; certainly those using nominal ionic charges. It has been cautioned [5] that the observations that an ionic model determines crystal properties adequately does not confirm the physical existence of parameters (e.g. ionicity) used in the model. We would add that the regime in which the models apply is probably restricted to systems with high symmetry bulk coordination. These quantum results reflect that some sophistication is required to accurately model interatomic interactions in low symmetry and few atom situations. This finding is not surprising in view of the refinements required [6] to describe lattice dynamics in even simple ionic solids.

ACKNOWLEDGEMENT

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