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Crossover between ionic-covalent bonding and pure ionic bonding in magnesium oxide clusters

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An empirical potential with fluctuating charges is proposed for modeling $(\mathrm{MgO})_n$ clusters in both the molecular (small n) and the bulk ($n \to \infty$) regimes. Vectorial polarization forces are explicitly taken into account in the self-consistent determination of charges. Our model predicts cuboid cluster structures, in agreement with previous experimental and theoretical results. The effective charge transferred between magnesium and oxygen smoothly increases from one to two, with an estimated crossover size above 300 MgO molecules.

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Crystalline magnesium oxide is a purely ionic compound, in which the Mg^{Z+} and O^{Z-} ions carry a charge Z around ± 2.[1] In the gas phase, the oxide anion O^{2-} is unstable and spontaneously decays into $\mathrm{O}^- + e$ due to the strong electron-electron repulsion. As a result, the effective atomic charge in the MgO molecule is much smaller than 2: independent *ab initio* calculations by Ziemann and Castleman[2] and by Recio *et al.*[3] found $Z \sim 0.8$. In the intermediate size regime, $(\mathrm{MgO})_n$ clusters are thus expected to show intriguing properties due to a partially covalent character of the chemical bonding. Beyond condensed-matter or molecular physics, these clusters received some special attention in the astrophysics community, where they have been involved in the nucleation process of dust in circumstellar shells around M stars.

Despite the vast amount of experimental[2,4,5] and theoretical[2,3,6–12] investigations on neutral or charged clusters, the way and the rate at which bonding evolves from ionic-covalent at small sizes to purely ionic in the bulk remains essentially unexplored. Because the electric field created by the ions does not vanish in finite systems, the highly polarizable oxide anion has a deformable outer electron cloud that could be responsible for a partial screening of the repulsion between cations. However, the situation is complicated by the possible coordination dependence of charge transfer.

Theoretical studies of $(\mathrm{MgO})_n$ clusters can be separated into two groups. *Ab initio* or density-functional theory based calculations have been performed on specific geometries, in a rather limited size range.[2,3,6–9] These works predict that small clusters exhibit cuboidlike shapes similar to NaCl rocksalt clusters. The apparent charge transferred, as estimated from Mulliken populations, is indeed size and coordination dependent, and lies between 1 and 1.5 for $2 \leqslant n \leqslant 13$.[3,9] More empirical methods have also been used to predict optimal structures.[2,10,11] Ziemann and Castleman,[2] and more recently, Roberts and Johnston,[11] have used the rigid-ion model with two possible values of the charge transferred. When a charge $Z=1$ is taken, cuboids are preferentially found as the most stable geometries. For $Z=2$, as in the bulk, small clusters show instead hollow, fullerenelike structures. The effects of polarization have been studied by Köhler and co-workers[10] using the Rittner model.[13] Wilson[12] investigated MgO ''nanotubes'' made of stacked hexagonal $(\mathrm{MgO})_3$ rings. For this, he developed a more sophisticated compressible-ion model[14] with explicit coordination-dependent polarizabilities.

None of these empirical potentials account for the different charges transferred in MgO clusters. Only in Ref. 10, the authors explicitly employed a size-dependent value of the charge Z, using an arbitrary law $Z(n) = (2\zeta n + 1)/(\zeta n + 1)$. ζ was taken such that the crossover n^* between ionic-covalent and purely ionic, for which Z equals 1.5, occurs at $n^* = 20$. However, the low-energy structures found by Köhler *et al.* significantly deviate from regular cuboids or stacked hexagons in this size range.[10] Improved electrostatics and charge transfer are provided by fluctuating-charge (fluc-q) potentials[15–17] based on the principle of electronegativity equalization.[18] Such potentials have been used in simulations of water[17,19,20] and molten salts,[21] and have recently proven valuable in describing the heterogeneous bonding in coated fullerenes and nanotubes.[22,23] They have been extended to include dipolar terms and the corresponding polarization.[20] In MgO clusters, atomic polarization cannot be neglected, and we provide here a self-consistent treatment of these effects. Briefly, the system is made of N magnesium and M oxygen ions, each carrying a charge q_i and located at the position vector $\mathbf{r}_i$. The potential energy V of the system is written as $V = V_{\mathrm{rep}} + V_Q$. The repulsion interaction is taken in the Born-Mayer form, namely, $V_{\mathrm{rep}}(\{\mathbf{r}_i\}) = \sum_{i<j} D \exp(-\beta r_{ij})$, where r_{ij} is the distance between ions i and j. The electrostatic energy is expressed as

$$V_Q(\{\mathbf{r}_i\}) = \sum_i \left[\varepsilon_i q_i + \frac{1}{2} U_{ii}^0 q_i^2 - \frac{1}{2} \alpha_i E_i^2 \right] + \sum_{i<j} J_{ij}(r_{ij}) q_i q_j + \lambda \left(Q - \sum_i q_i \right). \tag{1}$$

$U_{ii}^0 = U_{\text{Mg-Mg}}^0$ or $U_{\text{O-O}}^0$ are the respective hardnesses of the magnesium and oxygen ions, respectively, $\varepsilon_i = \varepsilon_{\mathrm{Mg}}$ or ε_{O} their electronegativities, and $\alpha_i = \alpha_{\mathrm{Mg}}$ or α_{O} their polarizabilities. J_{ij} is the Coulomb integral between ions i and j, taken in the Ohno representation,[24]

$$J_{ij}(r) = [r^2 + (U_{ij}^0)^{-2} \exp(-\gamma_{ij} r^2)]^{-1/2}. \tag{2}$$

$\mathbf{E}_i$ is the electric-field vector felt by ion i,

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$$\mathbf{E}_i=\sum_{j\neq i} -q_j\frac{\partial J_{ij}}{\partial \mathbf{r}_{ij}}. \tag{3}$$

Finally, the last term in Eq. (1) includes a Lagrange multiplier λ that accounts for the conservation of the total charge Q of the system. Given an instantaneous set of positions $\{\mathbf{r}_i\}$, the charges $\{q_i\}$ are found by minimizing Eq. (1) above. Due to the quadratic expression of V_Q in q_i's, this minimization can be done readily using linear algebra. The charges are solution of the matrix equation $\mathbf{CX}=\mathbf{D}$, where $\mathbf{X}=\{q_i,\lambda\}$ is a $N+M+1$ vector, $\mathbf{D}$ has components $D_i=-\varepsilon_i$ for $i\leqslant N+M$, and $D_{N+M+1}=Q$. The element (i,j) of matrix $\mathbf{C}$ is

$$C_{ij}=J_{ij}-\sum_k \alpha_k\left(\frac{\partial J_{ki}}{\partial \mathbf{r}_{ki}}\cdot\frac{\partial J_{kj}}{\partial \mathbf{r}_{kj}}\right), \tag{4}$$

with $J_{ii}=U_{ii}^0$. In this simple model, the partial covalent bonding comes from the balance between the short-range Pauli repulsion and the long-range electrostatic attraction. The $U_{ii}^2 q_i^2$ terms are crucial in the expression of V_Q as they prevent the charges from diverging. This model has 11 independent parameters, including D, β, α_i's, U_{ij}^0's, and γ_{ij}'s. Only the difference in electronegativities $\Delta\varepsilon=\varepsilon_{\mathrm{Mg}}-\varepsilon_{\mathrm{O}}$ is physically relevant.[17] For the model to be transferred from the molecular range up to the bulk, some constraints must be imposed on these parameters. In the MgO molecule, the equilibrium distance, charge transferred, and electric dipole are known,[10] and one must minimize the energy function with respect to the Mg-O distance r. After some calculation, we find $V^{\mathrm{MgO}}(r)=De^{-\beta r}+V_Q^{\mathrm{MgO}}(r)$ with the electrostatic term,

$$V_Q^{\mathrm{MgO}}(r)=\frac{1}{2}\,\frac{(\Delta\varepsilon)^2}{(\alpha_{\mathrm{Mg}}+\alpha_{\mathrm{O}})[J'_{\mathrm{MgO}}(r)]^2+2J_{\mathrm{MgO}}(r)-U^0_{\text{Mg-Mg}}-U^0_{\text{O-O}}}, \tag{5}$$

where we have employed the notation $J'_{\mathrm{MgO}}=dJ_{\mathrm{MgO}}/dr$.

In the crystal, the charge transferred Z and lattice constant a are chosen as reference data. Assuming that $J_{\mathrm{MgO}}(a)\sim 1/a$, the binding energy per ion reads

$$\frac{V^{\mathrm{bulk}}(a)}{N}=6De^{-\beta a}+\frac{V_Q^{\mathrm{bulk}}(a)}{N},$$

$$\frac{V_Q^{\mathrm{bulk}}(a)}{N}=\frac{(\Delta\varepsilon)^2}{M/a-U^0_{\text{Mg-Mg}}-U^0_{\text{O-O}}}, \tag{6}$$

with M the Madelung constant. For a set of parameters, the total energies corresponding to the molecule and to the crystal must be minimized numerically with respect to r or a, respectively. The full parametrization of the model can then be achieved by minimization of an error function χ^2 to reproduce the charge transferred and the equilibrium distances in the molecule and the crystal. The following values have been adopted: $D=6056$ eV, $\beta=4.89$ Å^{-1}, $U^0_{\text{Mg-Mg}}=12.5$ eV, $U^0_{\text{O-O}}=30.7$ eV, $U^0_{\mathrm{MgO}}=23.3$ eV, $\gamma_{\text{Mg-Mg}}=0.35$ Å^{-2}, $\gamma_{\text{O-O}}=0.49$ Å^{-2}, $\gamma_{\mathrm{MgO}}=0.36$ Å^{-2}, $\Delta\varepsilon=25.4$ eV, $\alpha_{\mathrm{Mg}}=0.18$ Å^3, and $\alpha_{\mathrm{O}}=4.65$ Å^3. It must be noted that the large value of $\Delta\varepsilon$ is due to the heavy charge transfer in the crystal.

This set predicts the charge transfer to be 0.92 in the MgO molecule and 1.92 in the crystal. The equilibrium distance is 1.86 Å in the molecule and the crystal lattice constant is 1.78 Å, close to the experimentally measured values 1.749 Å and 2.11 Å, respectively. The binding energies cannot be compared with reference values because the present model includes extra self-energy U^0 terms.

The lowest-energy structures of MgO clusters have been searched using the basin-hopping algorithm.[25,26] For each size in the range 2–30, 5000 Monte Carlo steps were performed starting from a random geometry. We also locally optimized the databases of structures found by global optimization of the rigid-ion model with fixed charges ± 1 and ± 2. In many cases, the global minimum was found within the database obtained with $Z=\pm 1$.

The structures of the global minima are represented in Fig. 1. Beyond $n=3$, they are based on small $(\mathrm{MgO})_4$ cubic units. The cuboid picture found here is essentially similar to the results of Roberts and Johnston,[11] obtained with a genetic algorithm, except for the slight distortions due to polarization. We do not find evidences for hollow[2,11] or ''spiky'' geometries.[10] Stacking of $(\mathrm{MgO})_3$ hexagonal units leads to isomers slightly less stable than cuboids of the same size. This partly explains why the global minima at $n=14$ and $n=22$ differ from the results of Roberts and Johnston.[11] Actually, the fact that hexagonal rings are less favored in the present model is not in strong contradiction with experimental results, because most magic number peaks interpreted as the signature of hexagonal stacks are indeed compatible with cuboidlike geometries. Also, experiments have been performed by mass spectrometry on charged species, which may well exhibit different stabilities than neutrals. We have computed the energy difference $\Delta E(Q)=E_{\mathrm{cub}}-E_{\mathrm{hex}}$ between charged $(\mathrm{MgO})_{24}^{Q}$ clusters in hexagonal and cuboid forms. The present model gives $\Delta E=0.824$ eV for anions, 1.039 eV for cations, and 0.975 eV for neutrals. The enhanced stability of cationic cuboids is consistent with the experimental analysis by Ziemann and Castleman.[2]

The variations with size of the binding energy of the lowest-energy structures found with the present polarizable fluc-q model are depicted in Fig. 2. The binding energy E shows a global increase, which can be fitted approximately in a liquid drop fashion as $E(n)=-15.13n+1.83n^{2/3}+0.89n^{1/3}+1.45$. The values of the latter parameters are slightly changed if we include larger cubic clusters such as

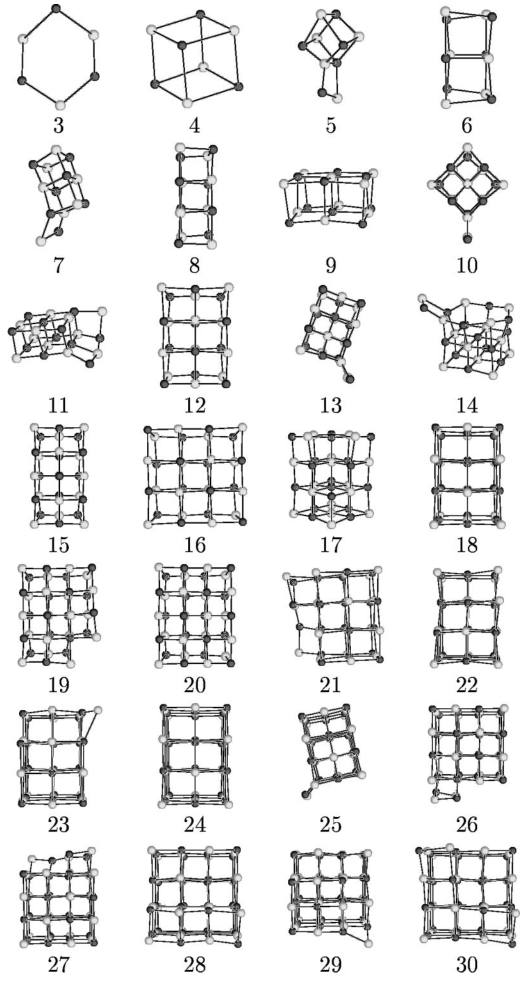

FIG. 1. Lowest-energy structures of $(\mathrm{MgO})_n$ clusters from Monte Carlo minimization using the self-consistent fluc-q model including polarization forces.

$(\mathrm{MgO})_{108}$. By construction, the crystal binding energy found from this expression is close to the numerical minimization of Eq. (6).

As can be noted in Fig. 2, there are some deviations from the smooth behavior of the fitted energy. To see them more clearly, the second energy difference $\Delta_2 E(n)=2E(n)-E(n+1)-E(n-1)$ has been represented in the inset of this figure. This quantity is usually convenient to find the special stabilities of some sizes. The most stable clusters appear here at $n=2$, 4, 6, 9, 12, 18, and 24. The sizes $n=15$, 21, and 27 can be added as relatively stable. All these clusters are perfect cuboids. The magic character of the $n=15$ cluster is less marked due to the fact that $(\mathrm{MgO})_{16}$ is also a cuboid.

We turn now to the problem of charge transfer, and more generally to the ionic or covalent nature of the chemical bonding in MgO clusters. In Fig. 3, we have represented the average charge $\langle q\rangle$ carried by the ions in the cluster, regardless of their position inside the cluster or the coordination number. This quantity is defined as the mean value over all magnesium ions. This definition is somewhat loose and arbitrary, because all ions do not play the same role in the cluster due to the large surface-to-volume ratio. From Fig. 3 we see that the charge transfer is strongly size dependent in the present model, and that the convergence toward the bulk limit is much slower than assumed by Köhler and co-workers.[10] In fact, knowing that the average charge effectively reaches about ±2 at large n allows us to fit the variations of $\langle q\rangle$ with n as $\langle q\rangle(n)\approx 2-a'n^{-1/3}-b'n^{-2/3}-c'n^{-1}$. The effective crossover size between mixed ionic-covalent bonding and pure ionic bonding can then be estimated as n^* such that $\langle q\rangle(n^*)\sim 3/2$. To get more realistic values for n^*, we have included the data corresponding to larger cubic clusters, namely, $(\mathrm{MgO})_{32}$ and especially the $6\times 6\times 6$ cluster $(\mathrm{MgO})_{108}$. Because the size range covered remains quite small, the value for the latter cluster was given a relative weight of 10 in the fitting process. Using this procedure, we find the crossover size to be located at $n^*\sim 300\pm 100$ depending on the presence of the large cluster in the

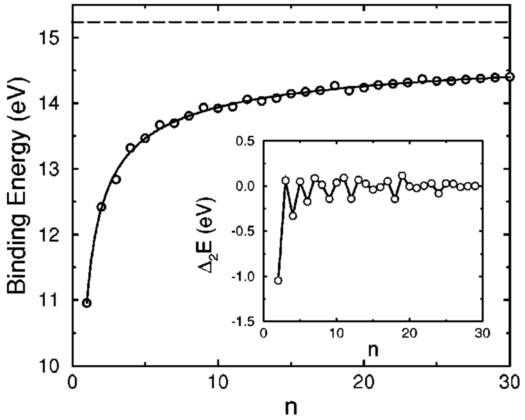

FIG. 2. Binding energy of $(\mathrm{MgO})_n$ clusters in the range $1\leqslant n\leqslant 30$. The horizontal dashed line marks the bulk limit. The open circles correspond to the structures in Fig. 1, and the solid line is a fit of the form $E(n)/n=a+bn^{-1/3}+cn^{-2/3}+dn^{-1}$, with parameters given in the text. Inset: second energy difference $\Delta_2E(n)=2E(n)-E(n+1)-E(n-1)$ versus n.

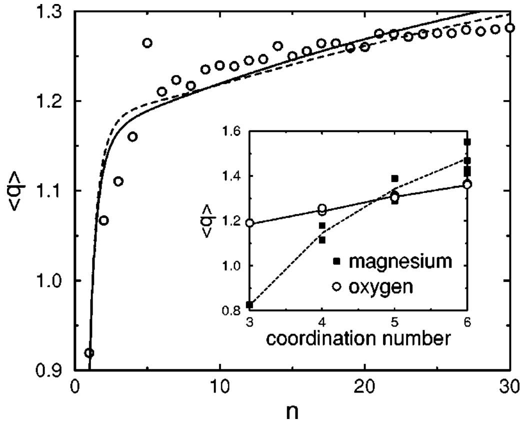

FIG. 3. Average modulus of the charge transferred in $(\mathrm{MgO})_n$ clusters. The lines are fits of the form $\langle q\rangle(n)=2-a'n^{-1/3}-b'n^{-2/3}-c'n^{-1}$, with (solid line) or without (dashed line) the value for the $(\mathrm{MgO})_{108}$ cluster. Inset: effective moduli of the charges carried by magnesium (full squares) or oxygen (empty circles) ions in $(\mathrm{MgO})_{108}$ versus their coordination number. The lines are a guide to the eye.

fit. Including the value for $(\mathrm{MgO})_{108}$ results in an increase of n^*, and including the data for larger clusters should further shift the crossover size toward several hundreds or thousands of MgO molecules.

Within the present empirical model, electrostatic properties are naturally coordination dependent. In the inset of Fig. 3, the modulus of the charge transferred is plotted for each ion in the $(\mathrm{MgO})_{108}$ nanocrystal versus its coordination number. Several features are of interest. First, the magnitude of the charge transferred increases with coordination, as expected from the decreasing intensity of the electric field. This agrees with the electronic structure calculations performed by Recio *et al.*,[3] by Veliah *et al.*,[6] and more recently by Coudray *et al.*[9] Second, the charge carried by Mg ions is more sensitive to coordination than the charge carried by oxygen ions. This is also in agreement with the findings of Veliah *et al.*[6] The above results confirm that conventional potentials with fixed charges are not fully appropriate to describe MgO clusters. This had been addressed by Wilson who considered phenomenological coordination-dependent polarizabilities within the compressible-ion model.[12] Coordination-dependent charges are a natural outcome of the present potential, allowing to study MgO clusters in a wide range of condensed phases. While the present potential is able to treat large clusters beyond the possibilities of the first-principles computations, the needed inversion of a square matrix can be a limiting factor. Fortunately, the extended Lagrangian techniques[17] can reduce the computational cost significantly, making the polarizable fluc-q model valuable in various thermodynamical conditions. Further possible improvements include a more realistic treatment of covalent bonding, higher-order electrostatics, as well as size-dependent hardnesses.

To conclude, we proposed an empirical model to describe ionic-covalent bonding in MgO clusters. This model is based on fluctuating charges and incorporates atomic polarization in a self-consistent way. By fitting it on both molecular and bulk properties we found that small clusters preferentially exhibit cuboid geometries, showing magic numbers in good agreement with experiments. The average charge carried by magnesium or oxygen atoms smoothly increases, and the crossover between ionic-covalent and pure ionic bonding was estimated to be above 300 molecules. The model correctly predicts that the charge transferred depends on coordination.

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