Measures of ionicity of alkaline-earth oxides from the analysis of *ab initio* cluster wave functions

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We present an analysis of the M-O chemical bonding in the binary oxides MgO, CaO, SrO, BaO, and Al_2O_3 based on *ab initio* wave functions. The model used to represent the local environment of a metal cation in the bulk oxide is an MO_6 cluster which also includes the effect of the lattice Madelung potential. The analysis of the wave functions for these clusters leads to the conclusion that all the alkaline-earth oxides must be regarded as highly ionic oxides; however, the ionic character of the oxides decreases as one goes from MgO, almost perfectly ionic, to BaO. In Al_2O_3 the ionic character is further reduced; however, even in this case, the departure from the ideal, fully ionic, model of Al^{3+} is not exceptionally large. These conclusions are based on three measures, a decomposition of the $M^{q+}-O^{q-}$ interaction energy, the number of electrons associated to the oxygen ions as obtained from a projection operator technique, and the analysis of the cation core-level binding energies. The increasing covalent character along the series MgO, CaO, SrO, and BaO is discussed in view of the existing theoretical models and experimental data.

INTRODUCTION

Metal cations in oxide compounds assume very different oxidation states ranging from one in Na_2O or two in MgO to eight in OsO_4. Of course, the formal oxidation state may have little in common with the real charges of the ions in the bulk oxide. The determination of the degree of ionicity or, in other words, of the extent to which the metal and the oxygen orbitals form covalent bonds, is of fundamental importance. In fact, the ionicity of an oxide affects several physical properties such as the surface electrostatic potential, the electric-field gradient at the surface, the mode, and the extent of surface reconstruction due to the Madelung instability, etc. Further, the ionicity of an oxide surface has direct consequences for the reactivity of chemisorbed species in the preliminary steps of the catalytic processes.[1] For example, the charge asymmetry due to the presence of cations and anions on an oxide surface results in a strongly modulated electronic potential which can lead to the heterolytic dissociation of H_2 with formation of M^+-H^- and O^--H^+ surface complexes. On the other hand, on metal surfaces the H_2 molecule undergoes a homolytic dissociation. The ionic character of the surface may also increase the sticking probability of molecules with permanent dipole moment, like CO, water or ammonia, because of the electrostatic interaction between the electric field at the oxide surface and the multipole moments of the adsorbed molecule.[2,3] Finally, the ionic character of a material has important consequences for the understanding of its electronic properties. For instance, it has been suggested that the chemical bonding in the high-T_c superconducting oxides is strongly influenced by the large fields induced by the very ionic cations like Sr or Ba and that the presence of these cations is a necessary requirement for superconductivity.[4]

Experimental measurements of the net charge of the ions in a metal oxide have been based on the determination of the electron density from x-ray diffraction data[5-8] and on x-ray photoelectron spectroscopy (XPS).[9-11] The interpretation of the results of both of these types of measurements involves approximations which may limit the accuracy of the determination of the ionicity. For example, in x-ray diffraction measurements the boundaries of the ions are assumed to correspond to the minimum of the electron density and the ion charge is obtained by integrating the electron density within this region. Thus, the accuracy of the charge depends on the validity of the assumptions done in partitioning the electrons among the ions. A method for estimating the ion charges based on XPS measurements was proposed by Broughton and Bagus.[9] The difference between the core-level binding energies (BE's) of the O^{2-} and the M^{2+} ions in the solid and in the gas phase depends on two terms, the lattice Madelung potential and the final-state extra-atomic relax-

ation which, in turns, are functions of the ionic charge. This method has limitations, in particular, connected to the accuracy of the measured BE's; however, it provides theoretical criteria which give a useful qualitative guide to the ionicity in similar compounds.

Other measures of bond ionicity in metal oxides have been based on optical transitions,[12-19] fundamental IR modes,[20] dielectric[20,21] and elastic[21] constants, electron-energy loss,[22] Born-Haber circle computations,[23] and ionic polarizabilities.[24] Despite the large amount of data reported, the degree of ionicity in alkaline-earth oxides is still controversial. While there is no doubt that these oxides must be regarded as highly ionic, the extent of covalent mixing is still unclear. Some estimates indicate that MgO is almost perfectly ionic,[5,6] others suggest that the charge associated to each oxygen is -1 and that one entire electron is shared between Mg and O.[7]

Not only is the absolute value of the ionic charges controversial, but also the trend of the ionicity for closely related compounds is not well established. Two opposite views coexist. Chemical arguments based on electronegativity scales[25-27] extended to bulk crystals by Phillips, Van Vecthen, and Levine[28-31] suggest that the ionicity should increase as one goes from MgO to BaO. Other arguments, on the other hand, are in favor of a decreasing ionicity as one moves from MgO to BaO. These arguments are (a) the O^{2-} ion, which is unstable in the gas phase,[32] is stabilized in ionic lattices by the Madelung potential, V_{Mad}; V_{Mad} is larger in MgO than in BaO and the O^{2-} ion becomes less stable in the heavier oxides, thus favoring the covalent mixing; (b) the participation of the empty d orbitals of the metal cation into the covalent bonding with the oxygen increases with the atomic number.[33] While no empty d states exist near the Fermi level in MgO, the s-d excitation energy for a free Ba^+ ion is only 0.6 eV.[34] Both these views are supported by some experimental data; they will be discussed at length below.

In this paper we present the results of ab initio cluster-model[35] calculations on a series of alkaline-earth metal oxides, MgO, CaO, SrO, and BaO. Calculations have also been performed on a model of Al_2O_3 to compare the behavior of largely ionic oxides like the group-IIA oxides, with that of alumina, an oxide which is believed to have a large degree of covalency. We have determined Hartree-Fock self-consistent-field (SCF) wave functions for cluster models $[MO_6]^{10-}$ for M = Mg, Ca, Sr, Ba, and $[AlO_6]^{9-}$; it is important to stress that the calculations are parameter-free and that the degree of covalent mixing in these oxides comes out as the direct consequence of the self-consistent nature of the wave function. The analysis of the wave function allows us to identify the relative importance of ionic, covalent, and polarization contributions to the M-O interaction.

The results can be summarized as follows. (1) The bonding is largely ionic in all alkaline-earth oxides. (2) The covalent mixing due to the ns and np empty levels of the metal dication is small and not too different for the four alkaline-earth oxides considered. (3) There is a small but increasing involvement of the low-lying empty d levels of the cation in the covalent bonding with the oxygens; this contribution follows the trend Mg($3d$)

$\ll$ Ca($3d$) $<$ Sr($4d$) $<$ Ba($5d$). (4) As a consequence, the importance of covalency increases by increasing the atomic number of the cation, MgO being less covalent (more ionic) than BaO.

These conclusions are based on three measures: (1) A decomposition of the interaction energy between M^{2+} and O^{2-} ions allows one to obtain an estimate of the relative energetic importance of the covalent interaction in the oxides considered; (2) a projection operator technique provides a measure of the number of electrons associated with the oxygen anions in the clusters hence of the net charge on the cation; (3) the analysis of the core-level BE shifts is used to extract information about the importance of the $O^{2-} \rightarrow M^{2+}$ charge transfer. None of these measures alone can give definitive information about the trend of the covalent mixing in the series. However, the fact that all the measures are consistent with an increasing, although small, $O^{2-}(2p)$-$M^{2+}(nd)$ covalency as the atomic number increases, indicates that this effect is real and not simply related to artifacts in the calculations.

CLUSTER WAVE FUNCTIONS AND BASIS SETS

The clusters used contain one metal atom and the six nearest-neighbor oxygen ligands and the number of electrons explicitly involved in the calculations is that corresponding to M^{2+} in $(n-1)p^6ns^0$ configuration and to six O^{2-} ions in $1s^22s^22p^6$ configuration. The M-O distances were taken from the respective crystals; O_h symmetry was assumed for the $[MO_6]^{10-}$ cluster model of alkaline-earth oxides, see Fig. 1; C_3 symmetry was used for the $[AlO_6]^{9-}$ model of Al_2O_3. For alkaline-earth oxides, a grid of 343 point charges (PC's) placed at the lattice positions was used to reproduce the Madelung potential in the cluster region.[36] For the cluster model of Al_2O_3 an array of 248 PC's wa used; this array was determined following the same strategy used to obtain the Madelung field of the alkaline-earth oxides.[36]

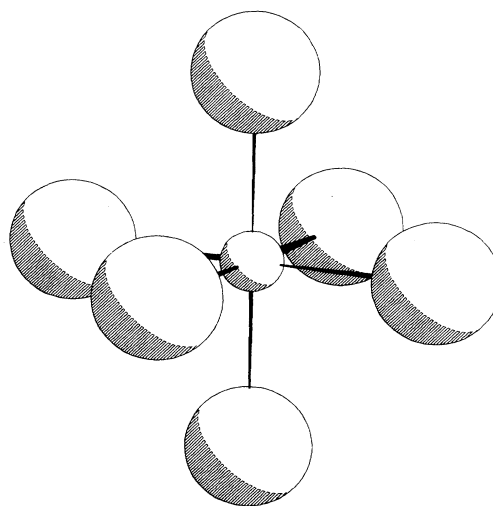The cluster wave functions were determined by per-

FIG. 1. Schematic representation of the MO_6 cluster model (M=Mg, Ca, Sr, Ba) used to represent the alkaline-earth oxides.

forming all electron SCF calculations within the molecular-orbital–linear combination of atomic orbitals (MO-LCAO) approximation. The MO's have been expanded in terms of Gaussian-type orbitals (GTO). The basis set for the O^{2-} ions[3] is of nearly triple-ζ quality, $[11s7p/5s3p]$. This basis set was optimized for the O^- free ion. As an alternative, one could optimize the oxygen basis set on a OMg_6 cluster; this would result in more contracted orbital exponents. However, we believe that the choice of the oxygen basis set is not going to affect in a serious way the conclusions of this work. The basis sets for the alkaline-earth atoms, optimized for the dications, have been taken from Ref. 37. Two diffuse s and one diffuse p functions were added to these basis sets to provide a representation of the outer ns and np orbitals of the metal cations. The resulting basis sets are Mg^{2+} $[9s5p/6s3p]$, Ca^{2+} $[12s8p/8s5p]$, Sr^{2+} $[15s11p4d/10s8p2d]$, Ba^{2+} $[18s14p7d/12s10p4d]$, and Al^{3+} $[11s8p/6s4p]$. Hereafter, we denote this group of basis sets as basis A. These basis sets should give a comparable description of the different ions in the clusters. However, the choice of the basis set is critical. In fact, the incompleteness of the basis set causes the occurrence of the basis set superposition error (BSSE);[38] the BSSE may lead to an overestimate of the importance of the O^{2-}-M^{2+} charge transfer.

Besides basis A, two additional basis sets were used. Basis B was obtained from basis A by removing the two outer s and the most diffuse p functions. In this way there is no representation of the outer ns and np orbitals on the cation and, in principle, no covalent bond can be formed with the O^{2-} ions. Basis C was obtained from basis A by adding to the metal cation basis set two extra d functions to represent the empty d orbitals, $3d$ for Mg and Ca, $4d$ for Sr, and $5d$ for Ba. The exponents of these orbitals, optimized for the dications, were taken from Ref. 37: Mg $\alpha(d)=8.344$, $\alpha(d')=1.724$; Ca $\alpha(d)=1.378$, $\alpha(d')=0.446$; Sr $\alpha(d)=0.779$, $\alpha(d')=0.266$; Ba $\alpha(d)=0.445$, $\alpha(d')=0.141$. Five d components were always used. Other d exponents have also been used to establish the dependence of the results on the basis set choice.

ENERGY DECOMPOSITION: Al_2O_3

Before presenting the results for the alkaline-earth oxides, it is important to discuss in detail the major features of the energy decomposition used to estimate the degree of the covalent mixing in metal oxides. We analyze at length the case of the $[AlO_6]^{9-}$ cluster model of Al_2O_3. In particular, we will examine different ways to perform the decomposition as well as the effect of different Madelung potentials on the results. We choose to study Al_2O_3 first because covalent effects may be more important for the formally Al^{3+} oxidation state than for the formally M^{2+} oxidation state of the alkaline-earth oxides.

In the constrained space-orbital variation (CSOV) method,[39–41] the cluster wave function is determined with some constraints in order to identify the relative magnitude of the electrostatic and electronic terms which determine the stability of a compound. It is reasonable to

start the analysis assuming that the crystal is formed by ions with appropriate formal charges. Thus, we have determined separately the wave functions for the Al^{3+} and the $[O_6]^{12-}$ fragments, both embedded in the field created by the PC's. The six neighboring O^{2-} ions around Al^{3+} were replaced by -2 PC's; in the $[O_6]^{12-}$ cluster the central cation was replaced by a PC of $+3$. The PC's used to represent the Madelung potential, see above, were also included. The initial step of the CSOV, the frozen orbital step (FO), is determined by computing the interaction energy of the two units, $Al^{3+}+$PC's and $[O_6]^{12-}+$PC's, at the $[AlO_6]^{9-}$ nuclear positions. Electronic relaxation is not allowed at this FO step and the total energy accounts for the large electrostatic interaction between the O^{2-} anions and the Al^{3+} cations but includes also the repulsive interaction due to the superposition of the Al^{3+} and $[O_6]^{12-}$ frozen-charge distributions (Pauli repulsion). Therefore the FO step includes effects due to the finite size of the anions and cations explicitly included in the AlO_6 cluster. The total energy at this step, which is taken as zero reference, already includes the Coulomb interaction between the ions which is by far the most important term for the stability of an ionic crystal. To reduce the initial FO repulsion, the Al^{3+} and the O^{2-} ions polarize. We first allow the Al^{3+} polarization and we indicate this variation within the space of the occupied and virtual Al orbitals as $V(Al;Al)$, see case 1 in Table I. The $V(Al;Al)$ energy contribution is negligible; this is consistent with the very small polarizability of Al^{3+}.

The next CSOV step measures the extent of charge transfer from the occupied Al^{3+} orbitals to the virtual O^{2-} orbitals, $V(Al;all)$ step. This mixing has no physical meaning and can only arise from a BSSE; indeed, the very small energy change found at this step, <0.01 eV, indicates that there is no significant BSSE due to the Al^{3+} cation basis set, see Table I. More important for the reduction of the initial repulsion is the polarization of the bulky O^{2-} anions, the $V(O;O)$ step. The energy contribution from the O^{2-} polarization in $[AlO_6]^{9-}$ is large, about 1.2 eV, in part because of the procedure followed to perform the CSOV. The $[O_6]^{12-}$ unit has been computed in the presence of the external Madelung potential and of a central PC which replaces the Al^{3+} ion. This PC induces a strong distortion of the very polarizable O^{2-} electron cloud towards the center of the $[O_6]^{12-}$ cluster. In the $[AlO_6]^{9-}$ cluster, however, the central position is occupied by a real Al^{3+} ion which has a finite extent; the nonbonding overlap of the "polarized" O^{2-} ions gives rise to a strong repulsion with the central Al^{3+} cation. At the $V(O;O)$ step the oxygen orbitals modify their shape to reduce this large initial repulsion (see case 1 in Table I).

In the following step of the CSOV, $V(O;all)$, the occupied O^{2-} orbitals are allowed to interact and mix with the empty Al^{3+} orbitals, with consequent $O^{2-}\rightarrow Al^{3+}$ charge transfer. *This is the most important step for the purpose of this paper* because it measures the degree of covalency in the oxides. The contribution of the covalent O^2-Al^{3+} interaction in Al_2O_3 is quite relevant, about 1.8 eV, see Table I. The energy lowering at this CSOV step

TABLE I. CSOV analysis of the interaction of an Al^{3+} cation with the surrounding O^{2-} anions in a $[AlO_6]^{9-}$ cluster model of Al_2O_3.

	ΔE_{int}[a] (eV)			
	Case 1	Case 2	Case 3	Case 4
Interacting fragments				
Cation	Al^{3+}+PC's	Al^{3+}+PC's	Al^{3+}+PC's	Al^{3+}+PC's
Anions	$[O_6]^{12-}$ $+$PC's($\times 1$)	$[O_6]^{12-}$ $+$ECP$+$PC's($\times 1$)	$[O_6]^{12-}$ $+$ECP$+$PC's($\times \frac{3}{4}$)	$[O_6]^{12-}$ $+$ECP$+$PC's($\times \frac{1}{2}$)
Point Charges				
Cation	+3.0	+3.0	+2.25	+1.5
Anions	−2.0	−2.0	−1.50	−1.0
First order of variations				
$V(Al;Al)$	0.015	0.004	0.004	0.005
$V(Al;all)$	0.011	0.002	0.003	0.003
$V(O;O)$	1.227	0.153	0.155	0.158
$V(O;all)$	1.795	1.825	1.531	1.414
Additional terms	0.304	0.040	0.043	0.051
Second order of variations				
$V(O,O)$	1.497	0.169		
$V(O;all)$	1.836	1.836		
$V(Al;Al)$	0.015	0.015		
$V(Al;all)$	0.004	0.004		
Additional terms	0.000	0.000		

[a] ΔE_{int} is defined as the energy decrease at each CSOV step with respect to the previous one.

must be compared with the corresponding terms determined for cluster models of alkaline-earth oxides (*vide infra*).

The sum of all these contributions, electrostatic stabilization, interunit polarizations, and O^{2-}-Al^{3+} charge transfer, is close but not equal to the total interaction energy obtained with an unconstrained SCF calculation; in fact, there is an additional stabilization of about 0.3 eV when one goes from the $V(O;all)$ to the final SCF step, see case 1 in Table I. This indicates that some coupling occurs among these bonding mechanisms.

This coupling arises because of the large, unphysical, polarization of the O^{2-} ions when the $[O_6]^{12-}$ unit is computed with a central PC which replaces the Al^{3+} ion. To account for this problem, we have computed the $[O_6]^{12-}$ fragment using an effective-core potential $(ECP)^{42,43}$ to represent the central Al^{3+} ion; the same set of external PC's is used to reproduced V_{Mad} (see case 2 in Table I). The ECP provides a repulsive potential and prevents the tails of the O^{2-} wave functions to penetrate the core region of Al^{3+}. In this way the initial, large, polarization of the O^{2-} ions toward the central PC in $[O_6]^{12-}$ is avoided. Using this wave function for the $[O_6]^{12-}$ cluster, $[O_6]^{12-}$+ECP+PC's, we repeated the CSOV decomposition, see case 2 in Table I. With respect to the previous CSOV analysis, case 1, we found that there are no substantial changes in the $V(Al;Al)$, $V(Al;all)$, and, most important, in the $V(O;all)$ or covalency steps. On the other hand, we found the expected change in the polarization of the oxygens, $V(O;O)$, which is strongly reduced. In this second CSOV, the sum of the

bonding contributions is nearly equal to the interaction energy obtained with an unconstrained SCF calculation.

In principle, the order of the variations in the CSOV is arbitrary, and the choice to vary first the cation orbitals and then the oxygen orbitals is not unique. Therefore, we have repeated the CSOV analysis with a different sequence of variations, first oxygens and then Al, see Table I. Apart from some minor changes, the contributions from the M-O covalency, $V(O;all)$, remain essentially unchanged.

An additional, important, concern about the validity of the present analysis is the implicit assumption of an ionic model in the simulation of the rest of the crystal by PC's. In principle, the use of $+3$ and -2 PC's to represent the Al and the oxygen ions can produce an external Madelung potential which is too large; the PC's are not determined self-consistently and this may artificially favor charge separation in the $[AlO_6]^{9-}$ cluster. It is important to establish how large is the dependence of the results, and, in particular, of the covalency step of the CSOV, on the external electrostatic potential. The CSOV decomposition has thus been repeated with a set of PC's placed in the same lattice positions but reduced by $\frac{1}{4}$ (case 3) and by $\frac{1}{2}$ (case 4), respectively, with respect to the "full" ionic model, see Table I. For this calculation, an Al^{3+} ECP was used in the determination of the $[O_6]^{12-}$ wave function (as in case 2). The results are very satisfactory because they show that the extent of covalent Al-O mixing, as well as of the other electronic mechanisms, depends only moderately on the external field. This makes us confident that the analysis is not biased toward an

artificially high ionicity of the bonding in the cluster by the large field given by the PC's.

ENERGY DECOMPOSITION:
THE ALKALINE-EARTH OXIDES

Following the previous discussion on $[AlO_6]^{9-}$, we consider now similar models of the alkaline-earth oxides. The two units, M^{2+} (M=Mg, Ca, Sr, Ba) and $[O_6]^{12-}$, have been computed in the presence of the PC's, but no ECP was used to represent the central ion in $[O_6]^{12-}$, see case 1 in the previous discussion. The FO step is our starting point. To reduce the initial Pauli repulsion, the M^{2+} and the O^{2-} ions polarize, and we first allow the M^{2+} polarization, V(M;M), see Table II. The energy contribution from the metal polarization is negligible in Mg^{2+}, but increases as the metal cation becomes larger; the Ba^{2+} polarization is of the order of 0.1 eV. The $V(M;$all) step, which measures the charge transfer from the occupied M^{2+} orbitals to the virtual O^{2-} orbitals, shows a very small energy decrease, indicating, as for the $[AlO_6]^{9-}$ case, the occurrence of a negligible BSSE for the cations; the energy changes at this CSOV step have thus been omitted from Table II. The energy contribution from the O^{2-} polarization in MgO is -0.5 eV; in CaO it is about 50% larger, 0.77 eV, and it further increases in SrO and BaO where it is 0.8–0.9 eV. For comparison, the O^{2-} polarization computed in the same way amounts to about 1.2 eV in $[AlO_6]^{9-}$, see case 1 in Table I.

The contribution of the covalent M^{2+}-O^{2-} interaction, V(O;all), which involves charge transfer from the O $2p$ to the M^{2+} ns and np orbitals only, is quite small in MgO, about 0.1 eV, and increases regularly in the heavier oxides, being about 0.40 eV in BaO, see Table II. In $[AlO_6]^{9-}$ the contribution of the Al^{3+}-O^{2-} covalent interaction, 1.8 eV, is 4–5 times larger than in BaO.

These results have been obtained with a basis set, basis A, which includes a representation of the cation outer s and p orbitals but not of the empty d orbitals. It is important to establish to which extent the energy stabilization found at the V(O;all) step is real or is an artifact connected to the BSSE. To measure the importance of the BSSE we have repeated the CSOV with the basis B. In

basis B, the GTO's representing the empty ns and np orbitals of the cation have been removed, so that no O($2p$)-M^{2+}(nsp) charge transfer can occur. Nevertheless, we found that even without the Ba $6s$ and $6p$ orbitals there is still a covalency contribution of about 0.25 eV in BaO. This contribution is most likely due to a BSSE. Because basis A contains diffuse basis functions, it may have a larger BSSE for the $[O_6]^{12-}$ unit; however, we take the M-O contribution obtained with basis B, Table II, as a measure, probably a lower bound, of the BSSE. We subtract this BSSE from the energy changes at the V(O;all) step obtained with the basis A and we obtain an estimate of the O^{2-}($2p$)-M^{2+}(nsp) covalent bonding, see Table II. This is found to be small, 0.1–0.2, and similar in the four alkaline-earth oxides while it remains large, about 1.5 eV, in Al_2O_3.

THE ROLE OF THE M^{2+} EMPTY d ORBITALS
IN THE M-O COVALENT BOND

It has been suggested, based on optical transitions[16] and core-level BE shifts,[33,44] that the empty d levels of the metal cation play an increasingly important role in the M-O mixing as one goes from Mg to Ba. This is supported by the fact that the lowest $s \rightarrow d$ transition in the gas-phase atoms decreases from 5.94 eV in Mg to 1.12 eV in Ba, see Table III.[34] This effect is even more pronounced in the gas-phase monocations, M^+: while the lowest s-d transition in Mg^+ occurs at about 9 eV, the same excitation in Ba requires only 0.6 eV, see Table III.[34]

The CSOV analysis has been performed using the basis C; basis C differs from basis A only for the presence of the extra d functions on the cations. The presence of the d polarization functions on M^{2+} does not alter the extent of intraunit polarization, $V(M;M)$ and V(O;O), whereas it changes the extent of the M-O covalent interaction, V(O;all), see Tables II and IV. Except for MgO, where the $3d$'s on Mg are too high in energy to directly participate into the bonding, in the other alkaline-earth oxides the covalent interaction is reinforced by the presence of the d polarization functions on the metal. This additional stabilization, $\simeq 0.5$ eV, is similar in CaO, SrO, and BaO. This is consistent with the much smaller s-d transi-

TABLE II. CSOV analysis of the interaction of a M^{2+} cation with the surrounding O^{2-} anions in a $[MO_6]^{10-}$ cluster.

	Basis[a]	ΔE_{int}[b] (eV)				
		MgO	CaO	SrO	BaO	Al_2O_3
$V(M;M)$	A	0.01	0.06	0.08	0.10	0.02
V(O;O)	A	0.54	0.77	0.83	0.89	1.23
V(O;all)	A	0.11	0.26	0.30	0.40	1.80
Additional terms	A	0.13	0.19	0.28	0.39	0.30
V(O;all) (BSSE)[c]	B	0.03	0.08	0.19	0.26	0.27
V(O;all, basis A) V(O;all, basis B)		0.08	0.18	0.11	0.14	1.52

[a]Basis A does include representation of the outer ns and np orbitals on M^{2+}; in basis B the outer ns and np orbitals have been removed.

[b] ΔE_{int} is defined as the energy decrease at each CSOV step with respect to the previous one.

[c]Estimate of the basis set superposition error, see text.

TABLE III. Excitation energies (in eV) in gas-phase alkaline-earth atoms and alkaline-earth monocations (from Ref. 34).

	Mg	Ca	Sr	Ba
M $s^2 \rightarrow s^1 p^1$ (^3P)	2.71	1.88	1.77	1.52
$s^2 \rightarrow s^1 d^1$ (^3D)	5.94	2.52	2.25	1.12
M^+ $s^1 \rightarrow p^1$ (^2P)	4.42	3.12	2.94	2.51
$s^1 \rightarrow d^1$ (^2D)	8.86	1.69	1.80	0.60

tion energy in Ca^+, Sr^+, and Ba^+ compared to Mg^+,[34] see Table III. Here the results can also be affected by the BSSE. However, the covalency in MgO, 0.17 eV, is about five times smaller than in BaO, 0.94 eV, see Table IV, and it is likely that this trend is only partially due to the BSSE (Ref. 38) also because the use of different exponents for the d orbitals does not significantly change the importance of covalency.[45]

To summarize, the M-O covalency increases when the empty d orbitals are present on the metal cation; this enhancement is virtually zero in MgO which is an almost perfect ionic crystal, while it is small but non-negligible in CaO, SrO, and BaO.

NET CHARGES ON THE CATIONS: PROJECTION OPERATORS

The previous results indicate an increasing covalent character as one goes from MgO to BaO. However, the absolute value of the covalent contribution as determined from the CSOV analysis depends on several factors, including the basis set employed and the size of the cluster used, and cannot be related in a simple way to the net charge of the cation. A usual way of assigning charges in molecular compounds is based on the Mulliken population analysis;[46] this measure, however, is very basis set dependent and most often fails in giving reliable charges because of the arbitrary partition of the overlap population in equal parts between two adjacent centers. Indeed, the Mulliken charges in the $[MO_6]^{10-}$ clusters are Mg$= +2.05$, Ca$= +2.30$, Sr$= +1.70$, and Ba$= +1.74$. These charges not only do not show a regular trend, but

TABLE IV. CSOV analysis of the interaction of a M^{2+} cation with the surrounding O^{2-} anions in a $[MO_6]^{10-}$ cluster performed with basis C. The basis set on M^{2+} includes representation of the outer ns, np, and $(n-1)d$ orbitals.

	ΔE_{int}^a (eV)			
	MgO	CaO[b]	SrO[b]	BaO
$V(M;M)$	0.01	0.06 (0.06)	0.07 (0.07)	0.10
$V(O;O)$	0.54	0.77 (0.77)	0.83 (0.83)	0.89
V (O;all)	0.17	0.83 (0.96)	0.88 (0.84)	0.94
Additional terms	0.13	0.22 (0.21)	0.30 (0.34)	0.43

[a] ΔE_{int} is defined as the energy decrease at each CSOV step with respect to the previous one.
[b] In parentheses are given the results obtained with a different set of d polarization functions on Ca and Sr, see text and Ref. 45.

are also unrealistic for Mg and Ca where the charges are larger than $+2$.

To avoid this problem we have used a projection operator method.[47,48] Projection operators are constructed from orbitals of the $[O_6]^{12-}$ unit. The expectation values of the projection of these orbitals onto the $[MO_6]^{10-}$ wave function provide information about the change in the shape of the O^{2-} orbitals in the $[MO_6]^{10-}$ cluster due to the O^{2-} polarization, and to the covalent bonding or charge transfer to M^{2+}. The values of the projections of these orbitals, Table V, are always lower than 60; an expectation value of 60 would correspond to six O^{2-} ions, hence to perfect ionicity. The deviation of the projection from the full ionic value of 60 is negligible for MgO, while it moderately but regularly increases in the heavier oxides, see Table V.

With basis C the expectation values of the projection operator are always lower than those obtained with basis A, see Table V, consistently with an augmented charge transfer when d polarization functions are added to the cation basis set. According to these values, MgO is close to be a perfect ionic crystal with a Mg net charge of $+1.95$, while the charge of Ba in BaO is $\simeq +1.8$, with a deviation from perfect ionicity of $\simeq 10\%$. Furthermore, the computed net cation charges with both basis A and C correlate almost linearly with the lattice Madelung potential, see Fig. 2. However, we wish to stress that the estimate of the covalency, or the charge on the metal atom, is almost certain to be an upper limit to the true covalency in the MO crystals. This follows very simply because while the metal to oxygen stoichiometry in the crystal is 1:1, it is 1:6 in the MO_6 cluster. Put very simply, in the cluster six O anions can contribute to the covalent bonding with the metal while this is not the case in the real crystal. A plausible correction for this false stoichiometry is to divide the covalent contribution in MO_6 by 6; this leads to net charges, using basis C, of $+1.99$, $+1.98$, 1.98, and $+1.97$ for Mg, Ca, Sr, and Ba. While this correction for the stoichiometry may overestimate the metal ionicity, it does show that the alkaline-earth oxides are extremely ionic. On the other hand, correlation effects, not included here, are expected to slightly increase the covalent character of the weak function.

CORE-LEVEL BINDING-ENERGY SHIFTS

A measure of the participation of the $O^{2-} \rightarrow M^{2+}$ charge transfer can be obtained from the analysis of the core-level BE's of the cation. When electronic charge is transferred from the O^{2-} anions to the cation empty levels, the increased electron density screens the core levels

TABLE V. Total charge on the six oxygens surrounding the metal cation. Expectation values of the projection of the $[O_6]^{12-}$ wave function onto the $[MO_6]^{10-}$ wave function (see text).

	MgO	CaO	SrO	BaO
Basis A	59.96	59.91	59.89	59.87
Basis C	59.95	59.88	59.85	59.82

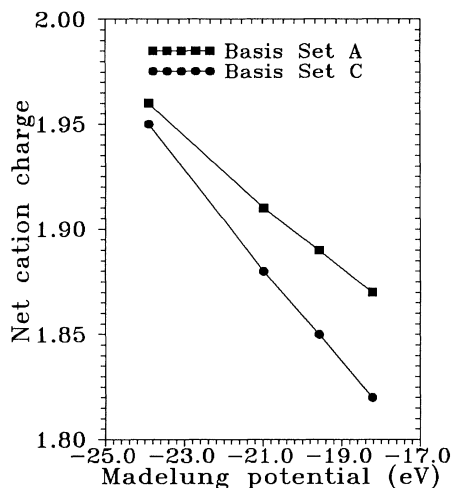FIG. 2. Net cation charges for the $[MO_6]^{10-}$ cluster (M=Mg, Ca, Sr, Ba) determined by means of a projector operator technique with two basis sets, basis A (without empty d orbitals on M) and basis B (with empty d orbitals on M). The cation charges exhibit an almost linear correlation with the Madelung potential, V_{Mad}; $V_{Mad}(Mg) = -23.9$ eV, $V_{Mad}(Ca) = -21.0$ eV, $V_{Mad}(Sr) = -19.6$ eV, and $V_{Mad}(Ba) = -18.2$ eV.

of the metal and leads to smaller BE's, i.e., to negative BE shifts.[44,49] Since the charge transfer is allowed at the $V(O;all)$ step of the CSOV, the change in the core-level BE's at this step can be related in a simple way with the extent of covalent mixing in the initial state. Previous studies have shown that the chemical shift in alkaline-earth oxides, as well as in other materials, is largely due to initial-state effects.[44,49] It is possible to determine the shifts in the initial-state core-level BE's of the metal from the Koopmans' theorem, $BE(nl) = -\varepsilon(nl)$, where ε is the energy of the orbital nl. The shifts for the $2p$ core levels of the cations in MgO, CaO, SrO, BaO, and Al_2O_3, determined with basis C [$\varepsilon(2p)$ CSOV step $V(O;all)$ $-\varepsilon(2p)$ CSOV step $V(O;O)$], are given in Table VI. The shifts are always negative, i.e., toward smaller binding energies, consistent with an increase of the electron density of the metal at the $V(O;all)$ step; the shift increases as one goes from MgO to BaO. In MgO the shift is small, about -0.2 eV, while in BaO it is almost -1 eV. In Al_2O_3 the shift is even larger, -1.5 eV. This trend is fully consistent with the trend of the covalent character MgO < CaO < SrO < BaO < Al_2O_3.

TABLE VI. Koopmans' theorem core-level binding-energy shifts induced by the M-O covalent mixing in MO_6 clusters.

	MgO	CaO	SrO	BaO	Al_2O_3
ΔBE^a, eV ($2p$)	-0.2	-0.6	-0.9	-0.9	-1.5

^{a}The ΔBE shifts are for the $2p$ orbitals of M^{2+} in metal oxides; they are determined at the CSOV step $V(O;all)$ as [$\varepsilon(2p)$; CSOV step $V(O;all)$ $-\varepsilon(2p)$; CSOV step $V(O,O)$]. The results refer to basis C.

THE TREND OF IONICITY
IN ALKALINE-EARTH OXIDES

The true ionic charge of an oxide is not easily available from experimental data and it is common to estimate the ionicity of a compound from electronegativity scales. Pauling[25] defined electronegativity as "the power of an atom *in a molecule* to attract electrons to itself." Various scales of electronegativity have been proposed;[25-27] they all suggest that Ba is more electropositive than Mg. We have computed the gas-phase MgO, CaO, SrO, and BaO diatomic molecules using the same basis sets employed for the MO_6 clusters (basis C) and in fact we found, based on the analysis of the dipole moment curves,[47,48] that the MgO molecule has a largely covalent character while in the BaO molecule the bond is dominantly ionic.[50] Thus, *using the same computational scheme, we found a reverse ordering in the trend of ionicity as one goes from the free molecules to the bulk oxides.* Clearly, the electronegative scale arguments, which are perfectly applicable in the molecular case, may be less successful in the solid state where the lattice electrostatic energy has a large stabilizing effect. Phillips[28,29] and Van Vechten[30] have proposed an extension to bulk systems of the electronegativity concept based on a simple one-gap model for the electronic band structure. The energy of a bond has been divided into a covalent, or homopolar, part, and an ionic, or heteropolar, part. The values of these two contributions can be defined in terms of transition energy between bonding and antibonding states or band gap. The average band gap E_g is then expressed as

$$E_g^2 = E_h^2 + C^2 .$$

E_h is the homopolar energy gap which is assumed to depend only on the distance r and on the position of the two elements in the Periodic Table; C is the ionic energy gap which is related to the electronegativity of the elements. Phillips[28,29] also suggested that one can define the fraction of ionic character f_i as

$$f_i = C^2 / E_g^2 .$$

In the full ionic limit E_h is zero and $f_i = 1$. The values of E_g are obtained from the optical properties of the solids while E_h is extrapolated from values of E_g of elemental solids like silicon or diamond using an empirical relation $E_h = r^{-S}$ where S is an empirical constant. According to this procedure, f_i increases from 0.84 in MgO to 0.93 in BaO, BaO being about 10% more ionic than MgO, see Table VII. The classification of Phillips has the value of being simple (it does not require recourse to accurate quantum-mechanical calculations) and of general applicability and is widely accepted; on the other hand the method makes use of electronegativity as a scaling parameter and suffers from the typical limitations of parametrized approaches.

The idea that the ionicity follows the trend MgO < CaO < SrO < BaO contrasts with the present results but is supported by the interpretation of several experiments like x-ray measures of charge density,[5-7] elastic constants,[21] infrared spectroscopy,[19] and, indirectly, band-structure calculations.[51] In these calculations[51] the

TABLE VII. Electronic and structural properties of alkaline-earth oxides.

	$r(M\text{-}O)$ Å	V_{Mad} eV	E_q eV (Ref. 60)	$O(1s)$ BE eV (Ref. 53)	Estimated ionicity			
					f_i (Ref. 28)	$q(M)$ (Ref. 20)	$q(M)$ (Refs. 5 and 6)	$q(M)$ this work
MgO	2.106	-23.90	7.7	530.9	0.839	1.76	1.9–1.5	1.95
CaO	2.399	-20.98	6.8	529.8	0.916	1.52	1.8	1.88
SrO	2.572	-19.57	5.7	529.0	0.928	1.16	2	1.85
BaO	2.762	-18.22	3.8	528.5	0.931		2	1.82

decrease in the valence-band width as one goes from MgO to SrO has been considered as a sign of a higher degree of localization of the wave function, hence of the fact that SrO is more ionic than MgO; however, the narrowing of the valence band can simply arise from the increase of the O-O distance which in SrO is about 20% larger than in MgO without the necessity to assume a decrease in ionicity.

Recently, a classification of the oxides as covalent oxides, normal ionic oxides, or very ionic oxides based on the $O(1s)$ XPS lines has been suggested by Barr;[52] the metallic oxides, classified as ionic according to the modification of the Phillips/Van Vechten method[28−30] proposed by Levine,[31] exhibit a $O(1s)$ BE in the range 530 ± 0.5 eV, whereas more covalent oxides such as SiO_2 have considerably higher $O(1s)$ BE's, >532 eV. According to this view, BaO is more ionic than MgO because the $O(1s)$ BE in BaO is about 528.5 eV while it is about 530.9 eV in MgO.[52] Several effects contribute to the measured BE's, including final-state screening; however, the observed trend in the $O(1s)$ BE of alkaline-earth oxides can be explained by simple electrostatic arguments without assuming a different charge transfer. In fact, a linear dependence exists between the $O(1s)$ BE's of alkaline-earth oxides and the inverse of the M-O distance;[54] this suggests that the shift in the $O(1s)$ BE as one goes from MgO to BaO is determined, almost entirely, by the change in the Madelung potential and that this shift cannot be related in a simple way to the different ionicity of these oxides. Results of ab initio calculations fully support this view.[54]

The theoretical justification of an increasing ionicity with increasing atomic number is connected only with the electronegativity arguments discussed above. On the other hand, arguments as convincing as the previous ones can be used in favor of a decreasing ionicity as one moves from MgO to BaO. We already mentioned in the Introduction that these arguments are based on two facts: (a) the instability of the gas-phase O^{2-} ion and the stabilizing effect of Coulomb interactions in ionic lattices (which decrease as the distance between ions increases) and (b) the initial-state occupancy of the low-lying d states near the Fermi level which in Ba compounds is definitely larger than in Mg compounds. The importance of this latter mechanism, which implies a decreasing ionicity with increasing atomic number, is supported by the present calculations, as well as by band-structure calculations.[33] The trend in ionicity MgO > CaO > SrO > BaO is also consistent with measures of electronic spectra,[12,13]

dielectric constants,[20] and XPS core-level BE's.[33]

Recently, Torrance et al. have found an almost linear correlation between the optical gap and the degree of ionicity in metal oxides.[55,56] The ionicity has been indirectly inferred through a parameter, $\Delta=(e\Delta V_{\text{Mad}}-e^2/r)-(I\text{-}A)$, which is defined as the energy required to excite an electron from the anion to the cation in the oxide; $e\Delta V_{\text{Mad}}$ is the difference in electrostatic energy (Madelung potential) between the cation and the anion (zero for NaCl-like structures), I is the ionization potential of M^+, and A is the electron affinity of O^-. The degree of ionicity of a compound is determined by the competition between these two contributions and the energy Δ can be used as a quantitative measure of the ionicity. Torrance found[55,56] that the ionic character increases linearly with the optical gap, i.e., MgO is more ionic than BaO. This picture has also been supported by ab initio valence-bond calculations[57,58] of the ground and the excited states involved in the optical-gap transitions of simple M-O-M cluster models of alkaline-earth oxides.

To summarize, the question of the ionicity in alkaline-earth oxides is still open and far from being solved. To the best of our knowledge we have presented for the first time an analysis of the M-O bonding in these solids based on ab initio quantum-mechanical calculations. The accurate analysis of the wave functions has led to the conclusion that the ionic character is larger in MgO than in BaO. The results have been obtained with cluster models of extended solids, and it is important to stress than the main limitation of this approach is related to the use of an external potential which simulates an ideal ionic crystal. However, we have found that the results are quite stable with respect to the use of different external potentials and the previous conclusion does not seem to be seriously affected by the choice of the external potential. This result is supported by recent cluster-model studies using a variety of ab initio wave functions, from the simple ionic model to the nearly exact configuration-interaction wave functions.[57,58] The larger covalency in CaO, SrO, and BaO with respect to MgO arises, in part, from the different involvement of the low-lying d levels of the dication. This mechanism is more sensitive to the local s-d excitation energy rather than to the global external field. Furthermore, periodic Hartree-Fock band-structure calculations on bulk MgO, where the ionic charges are determined self-consistently, indicate an almost full ionicity for this oxide,[59] in agreement with our conclusions based on a local model.

From the previous discussion it is apparent that there

is no simple way to define and to measure the ionic character of an alkaline-earth oxide and, in general, of ionic compounds. A measure of covalent mixing might be provided by x-ray absorption (XAS) at the O(1s) edge. Transitions from O(1s) to O(2p) are not allowed for a fully ionic system where the O(2p) shell is fully occupied, $2p^6$, but they are allowed when covalent bonding reduces the 2p shell occupation below 6. Thus, it may be possible to relate the XAS intensity distribution to the covalent character of the M-O bond. In fact, the O(1s) edges of several transition-metal oxides have been measured and analyzed by de Groot et al.;[60] however, they were not able to completely explain the relative XAS intensities. Measurements of the O(1s) edge combined with cluster-

model calculations of these excitations may provide a direct and definitive measure of the degree of covalent mixing in oxides.

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timal Gaussian functions [$\alpha(d)=0.13$, $\alpha(d')=0.06$]; these orbitals are very diffuse and will strongly overlap with the occupied oxygen $2p$ orbitals. If the BSSE plays an important role, the energy lowering at the $V(O;all)$ step should be considerably enhanced. For the same reason, the use on $[SrO_6]^{10-}$ of a set of very contracted d orbitals for the Sr^{2+} ion [$\alpha(d)=1.25$, $\alpha(d')=0.50$] should give the opposite effect. Indeed, with the d orbitals we found an increased covalency in CaO and a reduced covalency in SrO, see Table IV. The differences, however, are quite small, suggesting that the BSSE due to the $O^{2-}(2p)-M^{2+}(nd)$ overlap is not large.

$dμ/dr=+0.29$ and $d^2μ/dr^2=0.58$, indicating a largely covalent bond. In the other alkaline-earth diatomics, $dμ/dr$ goes from -1.56 in CaO to -2.42 in SrO and -2.40 in BaO, consistent with an increasing ionicity for the heavier diatomics.

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