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Theoretical analysis of the O(1s) binding-energy shifts in alkaline-earth oxides: Chemical or electrostatic contributions

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We report results from *ab initio* cluster-model calculations on the O(1s) binding energy (BE) in the alkaline-earth oxides, MgO, CaO, SrO, and BaO; all these oxides have a cubic lattice structure. We have obtained values for both the initial- and final-state BE's. A simple point-charge model, where an O^{2-} anion is surrounded by point charges, accounts for the observed shift in the O(1s) BE by about 2.5 eV to lower energy going from MgO (largest BE) to BaO (smallest BE). This point-charge model only describes the effect of the Madelung potential at the 1s ionized O^{2-} anion; it does not allow any covalent bonding between the metal (M) cations and the oxygen anions. Once the effect of the $O^{2}\rightarrow M^{2+}$ covalent bonding is included explicitly by using O_mM_n cluster models of the MO crystal, the trend in the O(1s) BE to smaller values for heavier metals does not change significantly. This shows that the main contribution to the shift is not the different amount of covalent mixing in the alkaline-earth oxides but rather the change in the Madelung potential along the group.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is one of the most widely used techniques for the characterization of the electronic structure of organic and inorganic materials.[1] When dealing with inorganic compounds such as metal oxides, one of the current uses of XPS is the determination of the oxidation state of a given atom and of the nature of the chemical bonding in the material. To this end, both the metal and the oxygen core-level binding energies (BE) are measured and usually correlated with the amount of charge transfer from the oxygen to the cation, or, in other words, with the extent of the deviation from the nominal ionicity of the ideal ionic crystal. Recently, it has been proposed to classify the metal oxides as covalent, ionic, or very ionic on the basis of their O(1s) core-level BE.[2,3] The ionicity of several oxides has been estimated theoretically using the modification of the Phillips–Van-Vechten electronegativity scale[4,5] proposed by Levine;[6] the ionic character estimated in this way has been correlated with the measured O(1s) core-level BE's.[2] In a similar way, O(1s) BE's of solid-state oxides have been correlated with the effective charges calculated according to Pauling.[7]

The underlying idea is that when the electronic charge around the oxide anion (O^{2-}) is reduced by the bonding overlap with the neighboring cations this will result in a more attractive potential at the oxygen nucleus and in a corresponding increase of the O(1s) core-level BE. According to the classification proposed by Barr and Brundle,[2] normal ionic oxides, with estimated ionicities ranging between 76–89 % according to the Levine model,[6] exhibit an O(1s) BE of 530±0.5 eV. In this class of materials, oxides such as CuO and Cu_2O are found. For oxides such as SiO_2 and Al_2O_3, the O(1s) BE is shifted to higher values, around 531–532 eV. The interpretation of this shift is that these oxides are more covalent and the O(1s) BE is larger because the electron density around the oxygen ion is reduced.[2] There are also oxides such as BaO, where the O(1s) BE is shifted to lower values, about 528–529 eV. In these cases, the oxides are assumed[2] to be very ionic and to have an ionicity around 95%. One of the essential points of this classification scheme is that the shifts of the O(1s) BE's are good measures of the ionicity of an oxide. However, we show in this paper that there is a very different explanation for the O(1s) BE shifts along the series of alkaline-earth oxides from MgO to BaO.

O(1s) chemical shifts have been used also to evaluate the optical basicity[8] or the isoelectric point[9] of a metal oxide. The optical basicity index has been introduced to describe the solvent chemistry of oxide slags for metal ions; it is an empirical parameter, usually measured with a UV spectrophotometer,[10] which reflects the valence charge density surrounding the oxygen ion in the oxide. The isoelectric point of a solid surface is a parameter characterizing the acid-base behavior of oxide surfaces.[9]

As indicated by the analyses described above,[2,3,8,9] there is a widely held belief that the shifts in the O(1s) BE's in metal oxides are mainly the result of changes in the electron density around the oxygen. An immediate consequence of this belief is that the shifts can be directly related to changes in the ionicity of O in the various oxides. However, it neglects a very important contribution to the BE shifts; this contribution arises from the Madelung electrostatic potential of the ionic oxides. The Madelung potential decreases the metal core-level BE's over the value for a free cation and increases the oxygen

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core-level BE's over the value for a free anion.[11,12] Thus, changes in the Madelung potential must be included as part of the analysis of the O(1*s*) BE shifts. There are large changes in the Madelung potential going from MgO to BaO because the lattice constant a_0 increases regularly along this series of cubic oxides. The Madelung potential varies with $1/a_0$ and, hence, it decreases regularly. The different contribution of the Madelung potential to the O(1*s*) BE's for the various oxides is such as to give a monotonic decrease in these BE's going from MgO to BaO. This is, in fact, exactly the trend which is experimentally observed.[2,13]

It is well known that electrostatic effects must be taken into account in order to treat the electronic structure and electronic energy levels of ionic crystals. The simplest model for these effects is to treat the ions as point charges and this model has been applied with considerable success. In 1929, Pauling[14] used a point-charge model to explain the shifts in the K absorption edge for Cl in alkali chlorides. Using such a simple initial-state electrostatic model Citrin and Thomas[15] have analyzed the contributions to the shifts of Na and Cl core levels in NaCl and have obtained a remarkable agreement with the experimental data. Broughton and Bagus[16,17] have used clusters of ions embedded in point charges to model and analyze the core levels of ionic solids such as LiF, BeO, and MgO. More recently, we have used the same approach to account for the shifts in the cation energy levels in alkaline-earth oxides.[11,12]

In the 1970s, Nefedov, Sergushin, and Salyn[18] showed that the O(1*s*) BE's of about 30 oxides were nearly on a straight line when plotted against the inverse nearest-neighbor distance, $1/R_{MO}$. The same is true if one plots only the O(1*s*) BE's of the alkaline-earth oxides,[2,13] see Fig. 1 and Ref. 13. This linear dependence suggests that the shift in the O(1*s*) core-level BE as one goes from MgO to BaO, about 2.5 eV to smaller BE (Table I), is not necessarily due to a change in the *M*-O chemical bonding but rather to the regular decrease in the Madelung potential. On the basis of detailed theoretical analyses[19] of the bonding for MgO, CaO, SrO, and BaO, it has been shown that the bonding is largely ionic for all these alkaline-earth oxides. In the present study, we will show for these largely ionic crystals that the electrostatic term is much more important in determining the shifts in the O(1*s*) core-level BE than differences in ionicity. To verify this hypothesis we have performed quantum-mechanical calculations on a series of cluster models for MgO, CaO, SrO, and BaO. We have determined the O(1*s*) ionization potentials from *ab initio* wave functions for these clusters. This work extends our analysis on the importance of electrostatic effects in determining the core-level BE's of metal cations in alkaline-earth oxides.[11,12] It provides further evidence for the very important contribution of the Madelung potential to the core-level BE's of atoms in ionic crystals, a contribution which is very often underes-

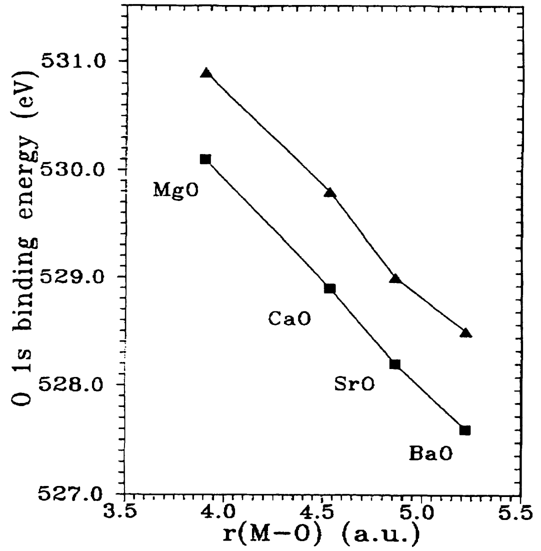

FIG. 1. The O(1*s*) core-level binding energy as a function of the metal-oxygen distance in alkaline-earth oxides with a cubic lattice; (■) Ref. 13; (▲) Ref. 2.

TABLE I. Initial (KT) and final (ΔSCF) state O(1*s*) binding energy BE, binding energy shifts ΔBE, and relaxation energy E_R, in eV for alkaline-earth oxides. The shifts are given with respect to MgO.

		MgO BE/ΔBE	CaO BE/ΔBE	SrO BE/ΔBE	BaO BE/ΔBE
[O/Mad]	KT	561.2/0	560.2/−1.0	559.7/−1.5	559.1/−2.1
	ΔSCF	538.5/0	536.7/−1.8	535.9/−2.7	535.0/−3.5
	E_R	22.7	23.5	23.8	24.1
[OM_6/Mad]	KT	556.0/0	554.0/−2.0	553.7/−2.3	553.2/−2.8
	ΔSCF	534.8/0	532.3/−2.5	531.5/−3.3	530.4/−4.4
	E_R	21.2	21.7	22.2	22.8
[OM_6O$_{12}$/Mad]	KT	559.7/0	558.3/−1.4	557.5/−2.2	556.4/−3.3
	ΔSCF	537.6/0	535.9/−1.7	534.7/−2.9	533.2/−4.4
	E_R	22.1	22.4	22.8	23.2
Experiment	Ref. 13	530.1/0	528.9/−1.2	528.2/−1.9	527.6/−2.5
	Ref. 2	530.9/0	529.8/−1.1	529.0/−1.9	528.5/−2.4

timated in the analysis of XPS spectra of insulating materials.

COMPUTATIONAL DETAILS

The calculations have been performed using the *ab initio* Hartree-Fock method. Nonrelativistic, self-consistent field (SCF) wave functions have been determined for an O^{2-} ion in different environments; these environments model the local surrounding of an oxygen atom in bulk MgO, CaO, SrO, and BaO. Three different models were used. In the simplest one, a single O^{2-} ion is stabilized by an array of 349 point charges (PC's) placed at the lattice positions. The M-O lattice parameters have been taken from experimental bulk values (Mg-O=3.97 bohr, Ca-O=4.54 bohr, Sr-O=4.86 bohr, and Ba-O=5.22 bohr). The set of PC's was fit in order to reproduce the Madelung potential of the ionic crystal in a region around the central O^{2-} ion;[20] the individual PC's are always quite close to ± 2. In this simple electrostatic model, hereafter denoted as [O/Mad], the only effect included is that due to the Madelung potential since the ions which surround the central oxygen are simulated by PC's. Thus, in this model, chemical bonding effects are completely absent.

In a second model, the six nearest-neighbor M^{2+} ions (M =Mg, Ca, Sr, and Ba) of the O^{2-} anion have been included explicitly to form the $(OM_6)^{10+}$ cluster; the notation 10+ refers to the charge of the OM_6 unit resulting from having one O^{2-} and six M^{2+} ions. However, the total system of $(OM_6)^{10+}$ and 343 PC's, or [OM_6 /Mad], is neutral. This second model permits deviations from the ideal ionicity because it allows mixing of the occupied O^{2-} and the virtual M^{2+} orbitals. The [OM_6/Mad] cluster can also include the final-state relaxation of the M^{2+} cations which follows the creation of a core hole in the O(1s) orbital. In a third model, we have also included the next shell of 12 oxygen ions to form the $(OM_6O_{12})^{14-}$ cluster embedded in 331 PC's, [OM_6O_{12}/Mad], see Fig. 2. In this cluster, the M^{2+} cations can form a covalent bond not only with the central but also with the external oxygens, thus providing a more balanced description of this mechanism. In addition, this larger cluster also includes the screening of the O(1s) core hole by the final-state relaxation of the second shell of O^{2-} ions as well as the first shell of M^{2+} ions.

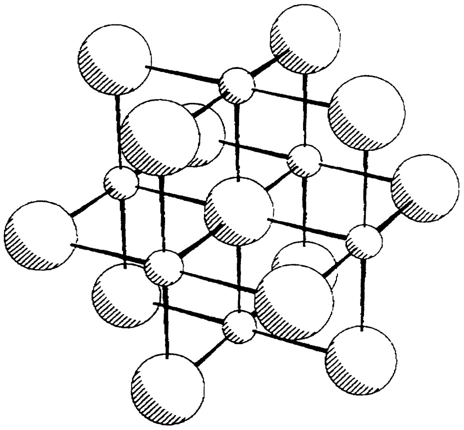

FIG. 2. Schematic representation of the OM_6O_{12} cluster model (M =Mg, Ca, Sr, and Ba) used to represent an oxygen ion in bulk alkaline-earth oxides. The cluster is surrounded by a large set of point charges. In the OM_6 cluster the 12 peripheral oxygen atoms have been replaced by point charges.

The cluster orbitals have been expanded in terms of Gaussian-type orbitals (GTO's). The all electron oxygen basis set, [10s6p/7s3p],[21] has been augmented by one d polarization function with exponent $\alpha_d(O)=1.154$.[22] This polarization function has been included only on the central and not on the peripheral oxygen atoms of the [OM_6O_{12}/Mad] cluster. The Mg ions have been treated at the all electron level using a [7s5p/6s3p] basis set[22] augmented by one d polarization function, $\alpha_d(\mathrm{Mg})=3.444$.[22] For the heavier alkaline-earth metal atoms, Ca, Sr, and Ba, we have used an effective core potential (ECP) to describe the core electrons.[23] This ECP includes an explicit treatment of the outermost, or ns, electrons and also of the $(n-1)s$ and $(n-1)p$ electrons, a 10-electron ECP. A [5s5p/3s3p] GTO basis set was used for Ca, Sr, and Ba;[23] also in this case a d polarization function[22] has been added [$\alpha_d(\mathrm{Ca})=0.986$, $\alpha_d(\mathrm{Sr})=0.640$, and $\alpha_d(\mathrm{Ba})=0.408$]. The inclusion of the extra d functions on the metal atoms is required to correctly describe the participation of the empty d levels of the cations into the M-O chemical bonding, in particular for BaO.[19,24]

The core-level BE of the O(1s) orbital has been determined in two ways. First, we use the Koopmans' theorem (KT) initial-state BE's by simply taking the orbital energy $-\varepsilon_i$ of the shell from which the electron is removed. The KT BE's are significantly larger than the observed core-level BE's because Koopmans' theorem neglects the final-state relaxation.[1,16] However, the shifts of the core-level BE's for atoms in different environments are often dominated by initial-state effects.[25,26] We have also used the ΔSCF method where the BE is given by the difference between the total energies of the final (ionized) and initial states of the clusters. Thus, these ΔSCF BE's take the screening of the metal core hole into account. For the actual oxides, the final state relaxation energy or screening will be larger than for the [OM_6/Mad] or [OM_6O_{12}/Mad] clusters primarily because of the contributions from the long-range polarization of the rest of the crystal.[27] However, we expect that the differential relaxation effects among the various oxides are taken into account, to some extent, with the clusters used in the present study.

RESULTS AND DISCUSSION

We start our discussion from the results of the simplest, purely electrostatic, model, [O/Mad]. When initial state, KT, BE's are considered, we found an excellent agreement with the experimental data in the overall shift of the O(1s) BE as one goes from MgO, taken as reference, to BaO, see Table I and Fig. 3. The computed MgO-BaO KT shift is 2.1 eV to smaller BE; the experimental shift is about 2.4–2.5 eV.[2,13] Also the relative shifts MgO-CaO, CaO-SrO, and SrO-BaO, are well repro-

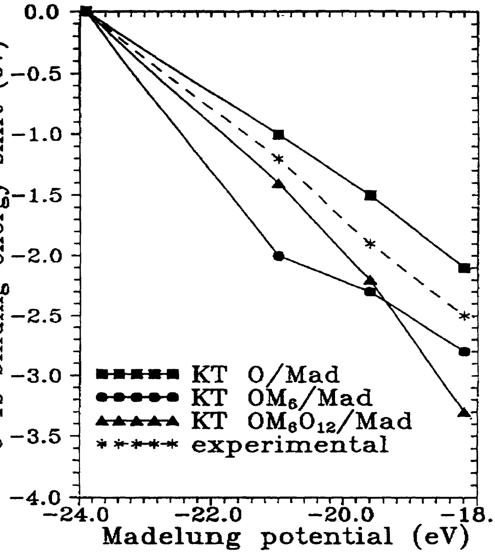

FIG. 3. Koopmans' theorem O(1s) binding energy shifts as a function of the Madelung potential, V(Mad). V(Mad): MgO = −23.9 eV, CaO = −21.0 eV, SrO = −19.6 eV, BaO = −18.2 eV.

duced. The intra-atomic final-state relaxation, see E_R in Table I, lowers the ionization potential by about 23–24 eV; it is largest in BaO and smallest in MgO. As a result, the MgO-BaO ΔSCF BE shift is larger, more negative, than that obtained from experiment by about 1 eV, see Table I. The trend in E_R from MgO to BaO is straightforward to understand for the [O/Mad] cluster model. For this cluster, the final-state relaxation arises, almost entirely, from the contraction of the diffuse O^{2-} valence orbitals, especially O(2p), toward the O nucleus. The PC's used in this model cannot represent the finite size of the cores of the metal cations which are the nearest neighbors of the O^{2-} anion. Therefore, in the initial state, the O^{2-} charge expands too much toward the PC's, up to and even beyond the positions of the PC's. This matter is discussed in Refs. 17 and 28; see also Fig. 5 in Ref. 29 for a graphical view of the polarization induced by a point charge. Thus, an artificial initial-state expansion of the O^{2-} 2p orbital is induced by the PC environment of the anion. This artificial expansion depends on the distance of the PC's from the anion, i.e., on the lattice constant; it increases monotonically from MgO to BaO. When the 2p orbital of the initial state is more diffuse, the final state E_R will be larger. Thus, the increase in the MgO-BaO ΔSCF BE shift to −3.5 eV from the KT value of −2.1 eV is, at least in large part, an artifact of using point charges to represent the extended cation neighbors of the central O^{2-} anion.

The results from the electrostatic [O/Mad] model provide strong, compelling, evidence that there is a dominant contribution to the shift of the O(1s) BE from the electrostatic potential and that the shift is largely an initial-state effect. This is the main conclusion of this paper. In the following, we will show that it does not change even when larger cluster models which explicitly include the first and second shells of atoms surrounding the central O are used to represent the oxides.

So far, we have considered a point-charge model where chemical bonding effects are completely neglected. Although alkaline-earth oxides are highly ionic, with little covalency, some deviation from the nominal ionicity occurs.[19] The covalent bonding is taken into account in the two cluster models [OM_6/Mad] and [OM_6O$_{12}$/Mad], Fig. 2. The degree of covalent character and the charge density around the central oxygen atom are determined self-consistently by the nature of the wave function. In addition to permitting covalent bonding to occur, the finite size of the cations in the first shell of neighbors is taken into account with the [OM_6/Mad] clusters and the finite sizes of the anions and cations in the first two shells are taken into account with [OM_6O$_{12}$/Mad]. With these larger clusters, as with [O/Mad], we distinguish initial- and final-state effects. The experimental trend of the O(1s) BE from MgO to BaO is qualitatively reproduced by the results with these larger clusters; see Table I and Figs. 3 and 4. However, there are significant differences from the results obtained with the point-charge model, [O/Mad].

We consider first the differences for the initial state, KT, O(1s) BE's. For the [OM_6/Mad] clusters, the KT BE is about 5–6 eV smaller than found with [O/Mad]. Covalent bonding between O and M would lead to an increase of the O(1s) BE because it would reduce the O anionicity from the ideal value of −2. Clearly, the change in the [OM_6/Mad] O(1s) BE's to smaller values cannot arise because M-O covalent bonds are formed; we must find the origin elsewhere. To a very good approximation,[11] shifts in the initial state O(1s) BE's are determined by the electric potential at the O nucleus. However, in addition to the Madelung potential arising from the point-charge environment in the [O/Mad] clusters, there are two other important contributions to the potential at the O nucleus.[17,30] The first of these two contributions is due to a compression of the charge distribution of the

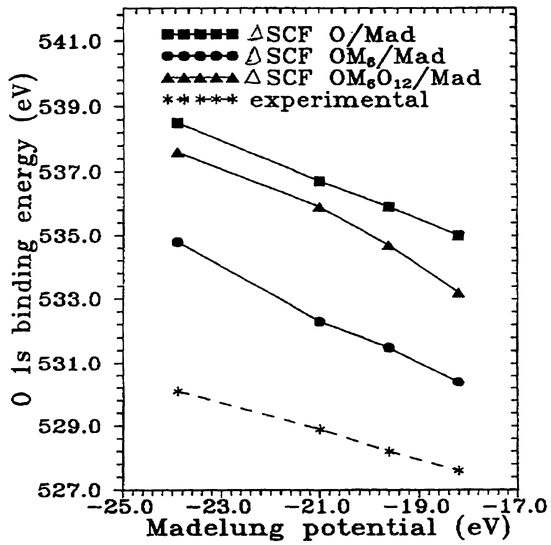

FIG. 4. ΔSCF O(1s) binding energies as a function of the Madelung potential, V(Mad); see the caption for Fig. 3.

central O^{2-} anion because of the finite size of its nearest-neighbor cations. The exclusion principle prevents charge from penetrating the nonbonding cation cores;[29,31] hence, the O^{2-} charge distribution, in particular that from the $2p$ orbital, becomes contracted compared with the distribution in the [O/Mad] cluster. It is easy to work out that the change in the potential at the O nucleus due to this contraction, or compression, leads to a decrease in the O(1s) Be.[17,30] Very clearly, the BE shift arising from this compression is a real physical effect which will occur in ionic oxide crystals. The second contribution to changes in the potential from that given by the point-charge environment is related to the nonspherical polarization of the ions that surround the central O anion in the [OM_6/Mad] and [OM_6O_{12}/Mad] clusters.[17] The nonspherical polarization occurs because these ions do not have a proper cubic environment. In the [OM_6/Mad] clusters, the edge M atoms have only one nearest-neighbor oxygen atom and 5 point-charge neighbors; in the [OM_6O_{12}/Mad] clusters, the 12 edge O atoms have 2 nearest-neighbor M atoms and 4 PC neighbors. Clearly, this polarization contribution to the O(1s) BE shifts is a cluster artifact since in the extended crystal all ions have a proper cubic environment.

The M^{2+} ions are not very polarizable and the potential at the O nucleus arising from a polarized M^{2+} cation is not very different from that arising from a point charge. The polarization effect is negligible for Mg^{2+} and small, but less negligible, for Ba^{2+}; we shall return to this point below. Since the polarization of the M^{2+} ions can be neglected, the shift of the O(1s) BE in the [OM_6/Mad] clusters to 5–6 eV smaller values than for [O/Mad] is due mainly to the compression of the central O^{2-} anions. For the [OM_6O_{12}/Mad] clusters, the O(1s) BE are only 2–3 eV smaller than for [O/Mad]. Thus while the compression of the central O^{2-} anion reduces the O(1s) BE in these clusters, the nonspherical polarization of the 12 edge O atoms acts to raise the BE by about 3–4 eV over the values obtained with the [OM_6/Mad] clusters. The polarization of the edge O atoms creates an effective dipole layer at the perimeter of the cluster which is positive toward the central O anion and negative away from the center.[17] It is well known[32–34] that the potential due to a dipole layer of this sign acts to raise the BE's of atoms inside the dipole layer. We stress that this effect, which is due to the nonspherical polarization of the edge O anions, is a cluster artifact and will not occur in an extended crystal.

One feature which is common to both the [OM_6/Mad] and the [OM_6O_{12}/Mad] clusters is that the KT O(1s) BE shift from MgO to BaO is 0.7–1.2 eV more negative than the shift found with the [O/Mad] point-charge model, see Table I. A simple analysis of this change in the BE shift would appear to suggest that the bonding in MgO is more covalent and less ionic than the bonding in BaO. However, our recent detailed analysis of the bonding in the alkaline-earth oxides[19] has shown that the degree of ionicity actually follows the reverse order; MgO is essentially entirely ionic while BaO is slightly less ionic and has a small covalent contribution to its bond. The resolution of the apparent contradiction is that the reason for the about 1-eV change in the O(1s) BE shift from [O/Mad] to the larger clusters is not because of the covalent bonds that are formed in the [OM_6/Mad] and [OM_6O_{12}/Mad] clusters. The reason for the change in the BE shift from MgO to BaO is likely to be the different magnitude of the nonspherical polarization of the M^{2+} cations in these clusters. The polarization of the cations will generate an effective dipole layer of opposite polarity from that due to the nonspherical polarization of the O^{2-} anions. Thus, the contribution to the 1s BE shift due to the cation polarization will be opposite in sign to the contribution due to the anion polarization; the cation contribution will lower the BE to smaller values. For Mg, the cation polarization is nearly vanishing and it does not significantly lower the O(1s) BE in the MgO clusters. However for Ba, the cation polarization, while small, could easily lead to an additional lowering of the O(1s) BE by about 1 eV in the BaO clusters. This cluster artifact may well be responsible for the more negative MgO-BaO KT BE shift. The important point is that the trends found with the [OM_6/Mad] and [OM_6O_{12}/Mad] clusters are qualitatively similar to that found with the purely electrostatic point-charge, [O/Mad], model. The trend to smaller O(1s) BE for heavier alkaline-earth oxides is dominantly due to the trend of the Madelung potential in these ionic crystals. Cluster artifacts prevent us from determining the less important contribution that covalent bonding in these ionic oxides may make to the trend of the O(1s) BE shifts.

We turn now to consider the ΔSCF O(1s) BE's. Overall, the trend of the BE's is the same for both the ΔSCF and the KT values; the MgO-BaO shift is somewhat larger, about 30%, when the ΔSCF BE's are used. The relatively small differences between the KT and ΔSCF BE shifts show that the origin of the shifts is dominantly an initial-state effect. Of course, the ΔSCF BE's, which include final-state relaxation, are much closer to the measured values than are the KT BE's; see Table I and Fig. 4. In particular, the ΔSCF BE's obtained with the [OM_6/Mad] clusters are reasonably close to experiment. However, the relaxation energy E_R is larger for [O/Mad] than for the more extended models. This result contradicts what one would expect, i.e., a larger E_R for a cluster including not only the intra-atomic but also the extra-atomic relaxation. The result is due to the fact that in the absence of the neighboring M^{2+} ions, the O^{2-} extends toward the PC's and has a bigger size.[17] In other words, the finite size of the M^{2+} ions causes a compression of the O^{2-} anions. Broughton and Bagus[17] have shown that the relaxation energy closely follows the size of the O^{2-} ion: a larger size corresponds to a larger intra-atomic relaxation. This explains the large E_R value obtained with the [O/Mad] model. When, on the contrary, one compares the [OM_6/Mad] and the [OM_6O_{12}/Mad] clusters, where the size of the central oxygen is approximately the same, E_R follows the expected trend: it is larger for the bigger cluster. However, the larger E_R for [OM_6O_{12}/Mad] is not sufficient to compensate the initial-state shift to higher BE's caused by the unphysical polarization of the external oxygens. The result is that the smaller [OM_6/Mad] cluster yields final-state

BE's in better agreement with the experimental values than the [OM_6O_{12}/Mad] cluster, see Fig. 4.

CONCLUSIONS

All the theoretical models considered in this work reproduce the trend found experimentally, i.e., a decrease of the O(1s) BE from MgO to BaO; see Figs. 3 and 4 and Table I. If one assumes that the origin of the O(1s) BE shift is the different amount of O^{2-} to M^{2+} charge transfer, the conclusion would be that the charge transfer is larger in MgO than in BaO. In other words, that MgO is more covalent than BaO. This conclusion is consistent with the classical electronegativity scale for molecular systems[35] but contradicts our recent detailed analysis based on *ab initio* cluster-model wave functions.[19] We found that the trend of ionic character is MgO > CaO > SrO > BaO with the bonding in BaO more covalent than in MgO; this order of ionic character has also been suggested by other authors.[36–38] We have shown that the main reason for this trend of ionicity is the small but increasing involvement of the low-lying empty *d* levels of the cation in the covalent bonding with the oxygens. The ordering arises because for Mg the unoccupied *d* levels are very high in energy while for Ba, the $ns \rightarrow (n-1)d$ excitations occur at low energy.[12,19] However, we have also shown[19] that the bonding is largely ionic in all alkaline-earth oxides.

The main conclusion of the present work is that the strong evidence about the ionic character and the order of ionicity, MgO > BaO, obtained from our earlier theoretical studies[12,19] is completely consistent with the observed trend in the O(1s) BE's. An interpretation of this experimental trend to conclude that BaO is more ionic than MgO is in error. The error arises because the over-simplified correlation of the O(1s) BE shift to the charge on the O, i.e., to the O ionicity, neglects the important contribution to the BE shift due to the Madelung potential of an ionic crystal. In this paper, we have shown that the shift in the O(1s) BE to lower values from MgO to BaO is due, almost entirely, to the decrease of the Madelung potential along the series.

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