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Reversed trend in polarity for alkaline earth oxides—an *ab initio* study

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Abstract. First principles calculations show the expected trend of increasing polarity for the alkaline earth oxides MgO, CaO and SrO to be reversed, with MgO being the most ionic substance and SrO the most covalent one. The larger radii for Ca and Sr cations enable an effective hybridization between the p orbitals of O and the metal d electrons of Ca and Sr. In Ca and Sr metal, the 3d and 4d levels are positioned just around the Fermi level, while in the oxides they dominate the cation valence charge. The larger lattice of SrO enables a slightly better p–d hybridization, which makes SrO somewhat less ionic than CaO.

1. Introduction

The concept of ionicity is not entirely clear since there is no absolute definition for it, but the general trends and charge distributions are well known for most substances such as the alkali halides or III–V semiconductors [1, 2]. Naively one expects the alkaline earth oxides to show a similar trend to the alkali fluorides, i.e. the charge redistribution to increase with increasing Z of the cation. They exhibit the same type of rock salt geometry, and the columns in the periodic table has only been moved one step to the centre for the cations as well as the anion. That is, SrO might be expected to be more ionic than CaO, which in turn should be more ionic than MgO. This is in full agreement with the expectations based on simple electronegativity considerations.

Despite this straightforward situation the question of the ionic situation in the alkaline earth oxides has still not been resolved. According to the classical Phillips values [3], the ionic charge is slightly less than ± 1 in these systems, with the heavier cations more ionized. Modern cluster-model calculations on the other hand [4, 5] have found an almost complete ionization of near ± 2 electrons (1.95–1.85) on the cation and anion respectively. The expected trend of increasing ionic character with increasing Z was in addition shown to be reversed compared to what traditionally has been assumed. Still other calculations suggest a more modest ionization of MgO in the area of ± 1.5 electrons [6]. Neither have recent experiments been able to end this controversy [7].

In order to resolve this problem we have employed modern *ab initio* calculations to produce the cation and anion charges as functions of the radii, full charge distributions and careful comparisons to simpler model calculations. The results clearly show a reversed trend in ionicity of the investigated substances with a decreasing oxygen charge for increased atomic number of the cation. The character of the valence charge of Ca and Sr is also fundamentally different from that of MgO, and partly form covalent p–d bonds with the O atoms. MgO on the other hand is found to be highly ionic.

2. Computational details

The wavefunctions and energy eigenvalues were calculated using first principles within density functional theory [8, 9] (DFT). The local density approximation (LDA) as implemented by Ceperley and Alder [10] and Perdew and Zunger [11] was used to describe the exchange correlation function. For the electron–ion interaction, fully separable, nonlocal pseudo potentials (PP) were used [12, 13], based on self-consistent solutions of the relativistic Dirac equation for free atoms [14–16]. The calculations were performed using the plane-wave band structure code fhi94md.cth [17], which is a heavily modified version of fhi93cp [18] concerning the computational methods. The bulk cells of MgO, CaO and SrO were all sampled by plane waves with energies up to 48 Ryd and 19 special Monkhorst–Pack k -points in the irreducible Brillouin zone (IBZ), corresponding to 125 points in the full zone. The theoretical lattice constants of 4.11, 4.69 and 5.11 Å (MgO, CaO, SrO) were used everywhere in the calculations. This is slightly less than the experimental values (4.20, 4.80, 5.16), but should be expected from the PP–DFT–LDA. The numerical procedures to produce the angular and radial charge distribution were identical to that of [19].

To produce the model charge distributions (see below) standard Slater orbitals [20] were used. The radial part of the wavefunctions were adjusted with respect to the ion charges and calculated for ionic charges of ± 2 electrons and ± 1 electrons respectively. Each atomic site was assumed to display spherical symmetry and the electrostatic crystal field neglected in order to simplify the calculations and allow for a straightforward interpretation. The total model charge distribution was achieved by superposition of the individual ions.

3. Results and discussion

When discussing the charge distribution of the alkaline earth oxides it is very useful to realize some simple, but important aspects of the substances in general. Since the anion species is kept fixed, it is much more informative to investigate the charge of the oxygen ions than of the metal ions. In this way any ambiguous definitions of ion radii is avoided. Furthermore will the anion vary very little in size if the ionicity is indeed relatively fixed [3–5], which makes any comparison simple between the different systems.

In addition the oxygen ion will be *spherical* in the first approximation when the electrostatic crystal field is disregarded. Because of the high symmetry in the rock salt geometry, the different p orbitals will be equally occupied. Taking the absolute value of the equally occupied p_x , p_y and p_z atomic orbitals the result becomes angular independent. Since the s electrons already are spherically symmetrical, the entire O ion will be spherical. Hence a spherical integration of the charge is well motivated and should be expected to return most of the important features.

Turning to the results, we immediately note that for any given radius, the anion contains considerably *more* charge in MgO than compared to CaO, see figure 1. In a similar way is the O less charged in SrO than in CaO, but this difference is considerably smaller. It should be noted that for large radii there will be a finite overlap with the cation valence charge. Still, the difference is positive for all radii, i.e. even well inside the oxygen ion. This clearly indicates a reversed trend in ionicity. In fact, in order to claim an increasing ionicity one is forced to assume significantly larger ion radius for the oxygen ion for materials with larger cations even to keep the anion charge constant (see figure 1), something that is obviously unphysical. It should be noted though that the integrated charge does not include the interstitial charge, but only that found within a sphere of the given radius. Thus the total ion charge is in fact slightly

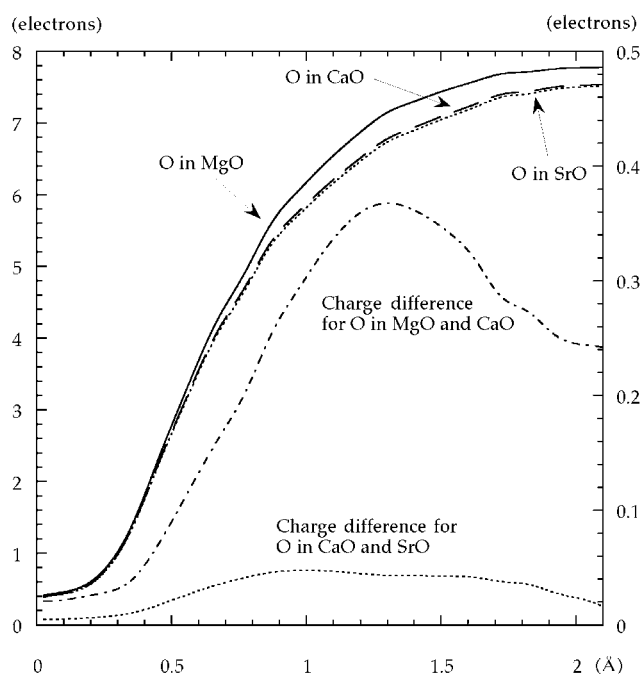


Figure 1. The spherically integrated charge of the oxygen ions in MgO, CaO and SrO for different radii. The differences between the charge of MgO and CaO, and CaO/SrO for identical radii are displayed in the same figure using the vertical axis on the right.

Table 1. The ionicity and ionic radius for the bulk and surface atoms respectively, together with the polarity ratio (in parentheses) and total charge. Radii in Å and charge and ionicity in electrons, the numerical uncertainty is ± 0.01 Å and $<5\%$ respectively. Ionicity δ_i , polarity ratio (P_{ratio}) and ionic radii after the definitions in [19].

Compound	δ_i (P_{ratio})	Cation R_i	Anion R_i	Cation charge	Anion charge
CaO	1.28 (14.18)	1.25	1.30	0.67	6.76
MgO	1.74 (53.58)	0.91	1.31	0.24	7.15
SrO	1.25 (9.60)	1.48	1.30	0.70	6.72

larger [19] than what is shown in figure 1. This does not affect the conclusion of decreasing ionicity with increasing Z , however.

Trying to quantify the results, using the local definitions of ionicity and ion radii in [19], we see that MgO is highly ionic with an ion charge equivalent to ± 1.74 electrons, see table 1. CaO and SrO on the other hand is considerably less ionic (± 1.28 and ± 1.25 respectively) and display a definite degree of covalence. Although different definitions like that of [21] alter the absolute values of table 1 somewhat, the relative quotes of the cation charges remain more or less fixed. (This should be expected from figure 1.)

These large differences in ion charges are directly reflected in the partial density of states (PDOS). While the O atom is completely dominated by s and p electrons, the cations have a finite d-electron-like contribution. In the case of MgO where the Mg ions do not have any d levels lying near in energy to the Fermi level, this contribution is reasonably small, i.e. in the order of 10%, i.e. about 0.02 electrons. The absence of d hybridization is also fully consistent

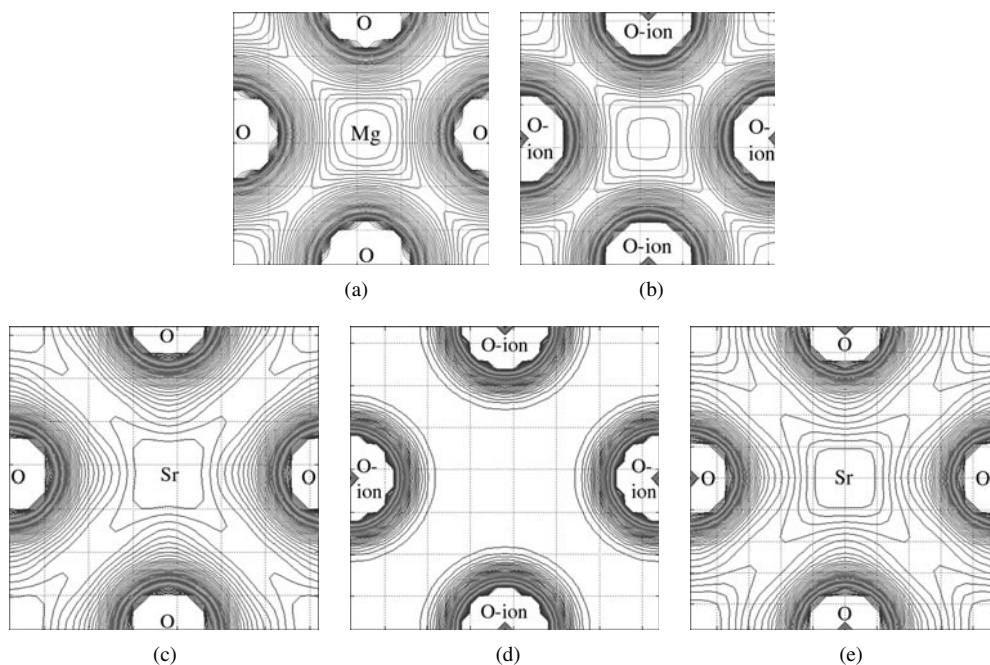


Figure 2. (a) Charge contour plot from the *ab initio* calculation for bulk MgO in the cation–anion plane. The plot has been cut at 20% of the maximum value and each line corresponds to a step of 1/300 of the highest density value. (b) The charge contour plot of the completely ionized model (± 2) calculation for MgO (scale identical to (a)). (c) Same as (a), but for SrO. Note that the larger size of the figure corresponds to the larger lattice constant. (d) Charge contour plot of the totally ionized (± 2) model calculation for SrO (scale identical to (c)). (e) Identical to (d), but with ion charges of ± 1 electrons, where the Sr valence electrons are assumed to be only of d character.

with the very small ion radius of the Mg ion; there is simply no room for large d orbitals. Turning to the charge density contour graph in figure 2(a), this becomes especially evident.

To enhance the understanding even further it turns out to be very rewarding to perform simple Slater based calculations (see section 2 above) and compare the model charge contour plot with the *ab initio* results. By assuming total ionization, i.e. closed shell configuration for the oxygen and no electrons left on the Mg, it is a straightforward task to produce a contour plot that may be compared with the original one, see figure 2(b). Although this simple model plot only contains full shell O ions, the qualitative similarity with the first principles calculation is striking. Only a minor depletion of charge at the Mg site indicates that the system is over-ionized. Apart from that the simple superposition of the O^{2-} ions return almost all notable topologic structures in themselves. This strongly supports the view of MgO as being a basically ionic material.

The Ca and Sr ions on the other hand are dominated by d electrons while the s and p contributions are as low as 25–30%. The presence of d electrons is also easily seen in the charge density distribution since these break the spherical distribution of the s and p shells, see figure 2(c) for the example of SrO. Approximately 70% of the d electrons are made up by $d_{x^2-y^2}$ and d_{z^2} orbitals, while d_{xy} , d_{xz} and d_{yz} only contribute with 30% of the total d DOS. That is, the major part of the d DOS is distributed in orbitals directly directed towards and partly overlapping with the oxygen ions. This makes the charge density around the anion nuclei to become octahedron like rather than spherical, something that is clearly seen in figure 2(c). The CaO exhibit a very similar distribution. The d_{xy} type of charge on the other hand is

directed in between the oxygen ions. Partly this is an effect of the Pauli repulsion, but placing metal ion charge between the anions also stabilize the electrostatic energy since it will make the Ca/Sr appear less charged from the point of the anion than it really is, i.e. on a straight line between the oxygen and the metal ions, the d_{xy} , d_{xz} and d_{yz} orbitals are not visible. Hence the metallic charge of approximately 0.70 electrons is effectively seen as only slightly more than 0.50 electrons by the anions.

A very important question is now whether the octahedron like shape of the charge around the oxygen nuclei indeed is the result of the combination of metallic $d_{x^2-y^2}$ and d_{z^2} electrons and the s and p shell of the anion, or if the result is an artifact stemming from an artificial assignment of the charge. As noted above the anion should be spherical in a first approximation. The presence of the crystal field will try to distort the oxygen charge and shape it towards an octahedron though. This is true for all three systems, however, including the MgO which displays a high degree of ionization and the smallest lattice constant which still results in nearly perfectly spherical anion charge, see above and figures 2(a) and (b). Not even a full ionization will result in a higher field strength in CaO and SrO than that found in MgO. Thus the octahedron shape cannot be explained in terms of crystal fields. Alternatively the anion itself must display a finite d DOS in order to explain the unspherical shape. Because of the low atomic number of oxygen and the nearly closed shell electronic structure this must be considered impossible though. In addition the PDOS for the anion shows no d electrons at all (i.e. less than 10^{-4} which is well beyond the numerical errors). Hence the covalent p-d bond between the Ca/Sr and O is real, and the ionic binding is complimented by covalent bonds.

In order to understand why the otherwise s-dominated valence charge of Sr and Ca exhibits d character within the oxides it is extremely important to realize the consequences of size. Doing the same model calculation for SrO as for MgO (total ionization) results in well separated and isolated anions with large regions of empty space in between, see figure 2(d). The considerably larger lattices of CaO and SrO thus make enough room for the d orbitals. Or differently stated: in SrO and the CaO the ion radii approximately coincide with the radii of the d orbitals for the charges of the metal ions at hand. In addition to this the 3d and 4d electrons are known to be close in energy to the Fermi level in Sr and Ca metal which makes it possible from an energetic point of view to use d orbitals when forming the covalent bonds with the anions. Neither the lattice constant, nor the energy situation allows this hybridization to take place in MgO. It is also important to realize that the directionality of the d electrons promotes the forming of covalent bonds. The s and p electrons have smaller radii (but still too large relatively speaking in the case of MgO), and add up to a spherical shell (see above) that cuts through all the surrounding anions. Electrostatically this is not very favourable and in addition it limits the possibility of forming highly directional covalent bonds, something that in the case of the $d_{x^2-y^2}$ and d_{z^2} electrons overcomes the electrostatic situation.

Making a simple Slater based model (see section 2) of SrO and CaO verifies these results. Using an ionization of ± 1 electrons for simplicity, neglecting the s and p contribution and assuming the same distribution between the two types of d electron as found above, a surpassingly good match between the model charge distribution and the *ab initio* result is found, see figures 2(c) and (e). The general charge density at the cation site is somewhat higher than what is found in the first principles calculation though, but this is fully expected with the choice of ± 1 electrons. Still, the qualitative agreement clearly shows that the metal d DOS and the overlap with oxygen charge are real, i.e. that the SrO and CaO are partly ionic and partly covalent. The small difference in ionicity of the two compounds should be expected from the similarity in electronic structure and electronegativity. The larger lattice in SrO is somewhat more favourable for the d electrons though which is the reason for the slightly lower ionicity compared to CaO.

4. Summary

In accordance with earlier investigations MgO is shown to be highly ionic with a charge distribution of ± 1.74 electrons on the cation and anion respectively. The trend of increasing polarity with increasing cation Z is shown to be wrong, however, and instead the oxygen ion shows considerably less total charge for any given fixed radius with increasing metallic Z . The ion charges of CaO and SrO are found to be as low as ± 1.28 and ± 1.25 electrons, and the metal ion valence charge is dominated by d electrons in these cases. Strong evidence for p–d covalent partial bonds is also found. Approximately 0.15 electrons are in addition distributed in between the anions in order to decrease the effective metal valence charge seen by the oxygen. The driving force of the strong d character and the covalence found in CaO and SrO is the larger lattice size compared to MgO, and the relatively low energy of the 3d and 4d orbitals. The larger size of the SrO lattice gives SrO a slightly lower ionicity than CaO.

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