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Anomalously large Born effective charges in cubic WO_3

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Within density-functional theory, we compute the Born effective charges of tungsten trioxyde in its reference cubic phase (defect-perovskite structure). For the tungsten atom, the effective charge tensor is isotropic, with $Z^*_{\mathrm{W}} = +12.51$. For the oxygen atoms, the two independent components of the tensor, corresponding, respectively, to a displacement of the atom parallel or perpendicular to the W-O bond, have the values $Z^*_{\mathrm{O}\parallel} = -9.13$ and $Z^*_{\mathrm{O}\perp} = -1.68$. Z^*_{W} and $Z^*_{\mathrm{O}\parallel}$ are anomalously large with respect to the nominal ionic charges ($+6$ on W and -2 on O), but compatible with the Born effective charges found in related ABO_3-perovskite compounds. [S0163-1829(97)01727-X]

Tungsten trioxyde (WO_3) is studied for a long time because of its electro-optic, electrochromic, ferroelectric, and semiconducting properties.[1–3] Between $-180\,°C$ and $900\,°C$, it undergoes five phase transitions. During cooling, the crystal structure, originally tetragonal, becomes successively orthorhombic, monoclinic, which is the stable phase at room temperature, triclinic, and again monoclinic at low temperature.[1] From one phase to the other, only small changes occur in the atomic positions, as well as in unit cell dimensions and angles. Although a bulk cubic phase WO_3 has never been observed at high temperature, it is taken as a reference structure in many works.[2] Recently such a cubic phase was obtained in thin films by the sol-gel process.[4]

The cubic phase has a very simple unit cell where the W atom lies in the center of an octahedron of oxygen atoms. At the opposite, one needs eight W atoms to build the unit cell of monoclinic phase. Hjelm, Granqvist, and Wills[3] showed that the oxygen octahedral cage is mainly responsible for the electronic properties of the different phases. Because this oxygen cage is only slightly modified from phase to phase, the calculations performed in the cubic structure will provide information that should remain meaningful for the other phases as well.

In this paper, we present *ab initio* calculations of the Born effective charges in WO_3, within density functional theory (DFT). We also report on the WO_3 electronic band structure, as well as on the high frequency dielectric tensor. For a few years, first-principles techniques have been able to address the computation of the Born effective charges in moderately complex materials.[5,6] Directly connected to the force that an atoms feels due to the imposition of an electric field, or to the polarization created by collective atomic displacements, Born effective charges play an important role in the lattice-dynamical properties of crystals (i.e., the LO-TO splitting of phonon frequencies). In several ABO_3-perovskite materials, the Born effective charges were recently observed to be much larger than the nominal ionic charges.[7–11] By considering WO_3, we now continue to fill the database, with a structure that extends naturally upon the family of perovskites already investigated. We find that the effective charges along the W-O bond are even larger than the values observed in these materials. MoO_3 and CrO_3 would have been interesting to study also, but they do not crystallize in a defect-perovskite structure.

A detailed account of our computational techniques can be found in Refs. 6,12,13. We used the local density approximation (LDA).[12] Responses to the homogeneous electric field were obtained using a variational approach to density-functional perturbation theory.[6,13] Spin-orbit coupling was not included in our study, as in Ref. 3. We needed a mesh of $10\times10\times10$ points to sample the Brillouin zone with sufficient accuracy. The all-electron potentials were replaced by extended norm conserving, transferable pseudopotentials.[14] We have considered $5s$, $5p$, $5d$, and $6s$ as valence states to build the W pseudopotential and $2s$, $2p$ as valence states for the O pseudopotential. The use of pseudopotentials enables the expansion of the wave functions in a reasonable number of plane waves. The kinetic energy cutoff was 30 hartrees which corresponds to about 2700 plane waves.

We obtained the lattice constant from a minimization of the energy. We found a value of 3.73 Å, in good agreement with experimental values (3.714 Å from Ref. 4, and 3.84 Å from Ref. 3).

Next, we calculated the electronic band structure (see Fig. 1). The computed indirect band gap is 0.73 eV. It is quite small compared to an experimental value of 2.62 eV in the monoclinic phase.[15] The monoclinic distortions seem to induce an increase of the band gap with respect to the cubic phase,[16] but part of this underestimation could also come

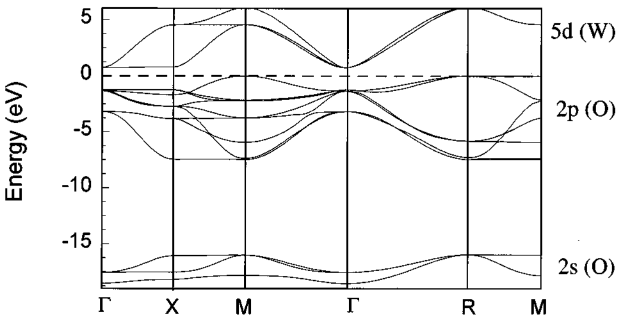

FIG. 1. Electronic band structure of cubic WO_3.

0163-1829/97/56(3)/983(3)/$10.00

from the DFT band-gap problem[17] (in $BaTiO_3$, the difference between the LDA band gap and the experimental band gap is on the order of 1.3 eV). The maximum of the valence band is situated at the R point in the Brillouin zone and the minimum of the conduction band is at the Γ point. The width of the $2p$ valence band is equal to 7.49 eV which shows reasonable agreement with the value calculated in Ref. 3 (about 7.1 eV). Charge density plots reveal that the upper part of the valence band is dominated by O $2p$ states, while W $5d$ states mostly contribute to the conduction band. Moreover, there exists a non-negligible hybridization between the O $2p$ and W $5d$ orbitals (Refs. 3 and 18).

Then, we computed Born effective charge tensors. We found a value of $+12.51$ for Z^*_{W}. For the oxygen atoms, we have to consider two different directions. $Z^*_{\mathrm{O}\parallel}$ (-9.13) and $Z^*_{\mathrm{O}\perp}$ (-1.68), respectively, correspond to displacements of the O ions parallel and perpendicular to the W-O bond, respectively. The charge neutrality is fulfilled within 0.02, which gives an idea of the precision of the calculations. The electronic (high frequency) dielectric tensor, isotropic in our case, is quite large, and equal to 8.01 within the LDA.

The value of Z^*_{W} and $Z^*_{\mathrm{O}\parallel}$ largely exceed the nominal ionic charges ($+6$ and -2, respectively). Large Born effective charges were also recently observed in several ABO_3 compounds (cubic structure),[7–11] among which the most closely related to WO_3 (with respect to their crystallographic structure, their band structure, and their bonding) are those with the pair of A and B elements chosen either in the IIa and IVb columns, or in the Ia and Vb columns. The nominal charges of the B ion, as well as the Born effective charges along the B-O direction are summarized in Table I, for WO_3 and closely related ABO_3 compounds. One observes that the choice of the A atom has a rather limited influence on the reported values. While the nominal ionic charge of Ti and Zr is $+4$ in these compounds, the Born effective charge is between $+7.08$ and $+7.56$ for Ti, and approximately equal to $+6.03$ for Zr. For Nb, the ionic charge is $+5$, while the Born effective charge is between $+9.11$ and $+9.37$. Going now to W, the ionic charge increases to $+6$, while the Born effective charge reaches the much larger value of $+12.51$. The trends are clear, and indicate that WO_3 is indeed in line with the ABO_3 compounds. In Table I, we computed the ratio $Z^*(B)/Z(B)$. This ratio is roughly constant and close to 1.8 for all materials presented, even if slight deviations are observed for WO_3 and $BaZrO_3$ (2.085 and 1.5075, respectively).[19] Born effective charges of the oxygen atom, along the B–O bond, are closely related to those of the B atom, and are much more negative than -2.

TABLE I. Born effective charges in the direction of the bond for WO_3 and related ABO_3 cubic perovskites, compared to the reference ionic charge of the B ion (Z_B). The theoretical lattice constant (in bohr) is also mentioned (Ref. 19).

ABO_3	a_{cell}	Z_B	Z^*_B	$Z^*_{\mathrm{O}\parallel}$	Z^*_B/Z_B	
$CaTiO_3$	7.19	4	7.08	-5.65	1.77	Ref. 8
$SrTiO_3$	7.30	4	7.12	-5.66	1.78	Ref. 8
		4	7.56	-5.92	1.89	Ref. 11
$BaTiO_3$	7.46	4	7.16	-5.69	1.79	Ref. 8
		4	7.25	-5.71	1.78	Ref. 9
$BaZrO_3$	7.85	4	6.03	-4.74	1.51	Ref. 8
$NaNbO_3$	7.40	5	9.11	-7.01	1.82	Ref. 8
$KNbO_3$	7.47	5	9.13	-6.58	1.83	Ref. 7
		5	9.23	-7.01	1.85	Ref. 8
		5	9.37	-6.86	1.87	Ref. 10
WO_3	7.05	6	12.51	-9.13	2.09	Present work

Recently, the origin of the large Born effective charges in ABO_3 compounds[9,21,22] was explained in connection with dynamic changes of hybridization between O $2p$ and B d states. This model can likely be transferred to the WO_3 case. It is well established[3,18] that the W–O bonds are not purely ionic: they present a certain amount of covalency materializing in a non-negligible hybridization between O $2p$ and W $5d$ orbitals. Similarly to what happens in ABO_3 compounds, the change of this hybridization with respect to the interatomic distance may produce a dynamic transfer of electrons between the W and O ions. Following the model introduced by Harrison,[23] this can explain the large value of Z^*. A band-by-band analysis could reveal the real contribution of each band to Z^* and should confirm the predominant role of the W $5d$ and O $2p$ bands in the dynamic charge transfer.

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