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Visualizing electronic structure changes across an antiferroelectric phase transition: Pb_2MgWO_6

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Pb_2MgWO_6 is an ordered perovskite or elpasolite that undergoes a phase transition from a cubic paraelectric phase to an orthorhombic antiferroelectric phase below 310 K. Through an analysis of the electronic structures of both the high and low temperature phases using high level band structure methods, the nature of the changes in the bonding across the phase transition has been examined. The key stereochemical rôle of the lone pairs on the lead atoms has been examined by use of the Electron Localization Function. While the lone pairs on the lead atoms are smeared out by the near octahedral symmetry of the lead sites in the high temperature phase, at low temperatures they localize into the traditional lobes. These changes have been visualized.

While the challenging task of accurately computing the electronic structures of crystalline solids has seen increasing success in recent years, methods for visualizing the results of such computations have also been receiving attention. Particularly in the chemistry and materials communities, there has been increasing emphasis towards the development of tools that permit the electronic structures of inorganic solids to be examined in real space, in terms of bonding between atoms rather than through dispersion relations in *k* space.[1] Simultaneously there has been sustained effort to arrive at more precise guidelines as to what defines a chemical bond.

Bader and Stephens[2] have emphasized the importance of the pair probability of electrons of like spin in the characterization of electron localization, and thereby of chemical bonding. This has been extended by Becke and Edgecombe[3] who suggest the electron localization function (ELF) as a means to map the space around atoms in molecules into core, binding and lone-pair regions. The ELF is a measure of the local influence of Pauli repulsion on the behavior of electrons. Using techniques prevalent in the study of stabilities of dynamical systems, Silvi and Savin[4] have used maxima in the localization to define attractors, of which there are three kinds; bonding, non-bonding and core. Domains of localization can then be defined that are irreducible and contain only one attractor, or reducible and contain more than one attractor.

In the world of extended inorganic solids, the ELF has seen considerable recent use in extracting information from calculations at both semi-empirical as well as *ab initio* levels. The uses have included the visualization of bonding in the carbon group elements,[5] of unusual valence states in some Rb compounds,[6] and for the simulation of STM images.[7] Some of these applications have been reviewed recently.[8] Here we use the ELF to visualize, in real space, the *ab initio* electronic structure of the elpasolite (ordered perovskite) Pb_2MgWO_6. This compound undergoes a phase transition at 310 K from a cubic, paraelectric ($Fm\bar{3}m$) structure to an orthorhombic, antiferroelectric structure ($Pmcn$).[9] This and related compounds are important from the technological viewpoint because of the close relation they bear to so-called relaxor ferroelectrics.[10] Through an examination of the electronic structures calculated from the crystal structures determined at 350 K (cubic) and 80 K (orthorhombic), we shall show that the lone pair on the divalent Pb atom plays a significant rôle in influencing the structure. While the lone pair as visualized from the ELF in the cubic phase is split by symmetry over a number of sites, it is allowed to localize into the more traditional single lobe in the low-temperature phase. The phase transition can thus be described as a tendency of the lone pairs to localize.

Crystal structures and details of the calculations

The calculations on Pb_2MgWO_6 made use of reported structures refined to high precision simultaneously using X-ray and neutron diffraction data from powders.[9] The cubic and orthorhombic structures of Pb_2MgWO_6 are displayed in Fig. 1.

First principles electronic structure calculations were performed using the linearized muffin-tin orbital (LMTO) approach within the atomic sphere (ASA) and local density (LDA) approximations. The scalar-relativistic LMTO program package[11] was made use of for the calculations, employing 1240 and 1183 irreducible *k* points respectively in the primitive Brillouin zones of the cubic and orthorhombic compounds. The basis sets consisted of 6s and 6p orbitals of Pb, 3s and 3p orbitals of Mg, 6s, 6p and 5d orbitals of W and 2s and 2p orbitals of oxygen. The following orbitals, 6d and 5f of Pb, 3d of Mg, 5f of W and 3p of O, were treated using the downfolding technique. The calculations rely on the partitioning of space into atom-centered spheres as well as so-called empty spheres in the interstitial regions. The positions and radii of the empty spheres were determined using an automated procedure.[12] The empty spheres were described using a 1s orbital basis with 2p downfolding.

Results and discussion

Bond Valence Sum (BVS) calculations[13] for Pb in the two phases indicated that while divalent Pb in the cubic phase (with Pb 12-coordinated by O) had a BVS of 1.7, in the orthorhombic phase the BVS was nearly 2. Fig. 2 displays selected results of the electronic structure calculations on the cubic and orthorhombic phases of Pb_2MgWO_6. From the BVS, we anticipate that the significant changes in the electronic structure across the transition might involve Pb, and therefore

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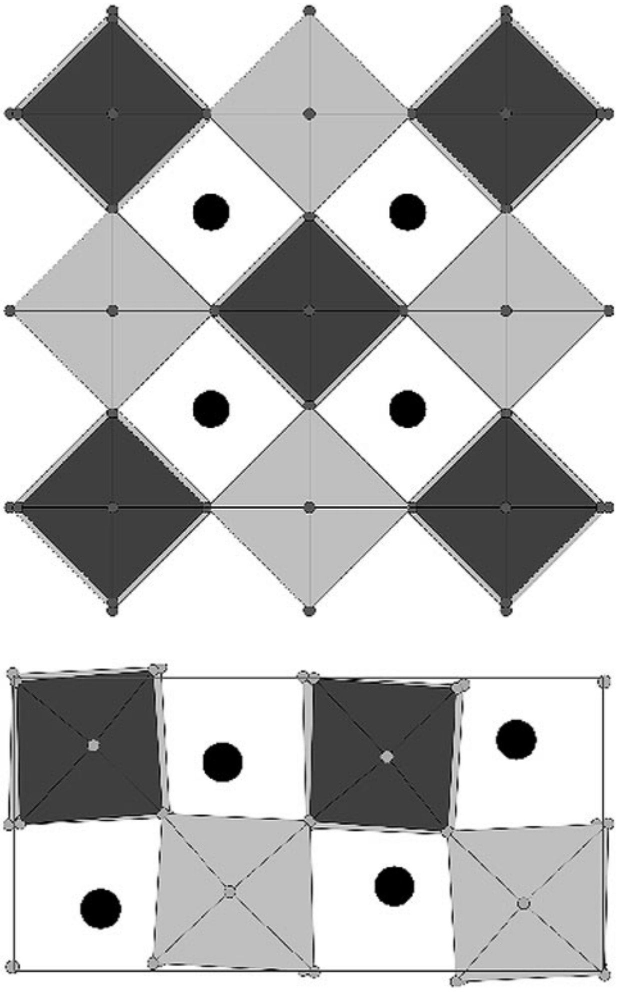

Fig. 1 Crystal structures of Pb_2MgWO_6 in the cubic (upper) and orthorhombic phases (lower). The darker octahedra surround W while the lighter ones surround Mg. Black spheres are Pb. The view is down [100] in both cases. For the orthorhombic phase the lattice parameters are approximately $2a_P$, $\sqrt{2}a_P$, $2\sqrt{2}a_P$, while for the cubic phase the parameter is approximately $a_E = 2a_P$, where a_P is the perovskite cell parameter.

we display in the two upper panels of this figure, the s and p orbital projected densities of state (DOS) of Pb per formula unit for the two phases. The s states are pulled down to 7 eV below the Fermi energy due to relativistic effects. There is some minimal hybridization of Pb s with other states yielding a small peak around −1 eV with respect to the Fermi energy. Considering the p states of Pb, there are significant changes on going from the cubic to the orthorhombic structure. Specifically, one finds more states derived from Pb p in the cubic phase than in the orthorhombic phase, just below the Fermi energy. The presence of some filled Pb p states must arise because of hybridization with oxygen, since in the ionic limit of Pb^{2+}, one expects a filled Pb 6s (the inert-pair effect) and empty Pb 6p.

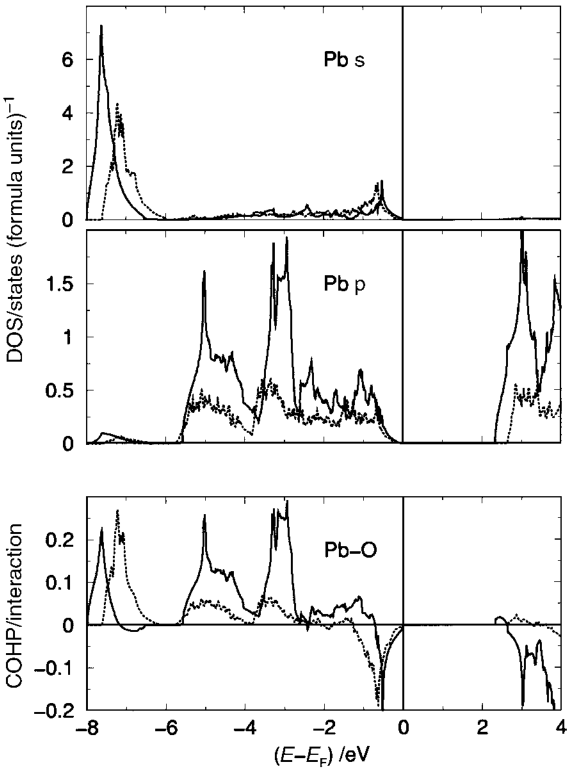

Fig. 2 Orbital projected Densities of States (DOS) and Crystal Orbital Hamiltonian Populations (COHP) of the Pb–O interaction for the cubic (continuous lines) and orthorhombic (dotted lines) phases of Pb_2MgWO_6.

The lowermost panel of Fig. 2 displays the scaled Crystal Orbital Hamiltonian Population (COHP) for the Pb–O interaction in the two phases. The COHP[14] is the density of states weighted by the corresponding Hamiltonian matrix element, and is indicative of the strength and nature of a bonding (positive COHP) or antibonding (negative COHP) interaction. COHPs are similar to the COOPs introduced by Hoffmann and coworkers,[15] though the opposite sign convention is used. From this panel, it is seen that Pb–O interactions just below the Fermi energy actually decrease in the orthorhombic phase. In fact, while for the orthorhombic phase the Pb–O COHP displays nearly closed shell behavior, with the bonding and antibonding interactions below the Fermi energy almost cancelling each other out, the same COHP in the case of the cubic compound is net bonding. Purely from a knowledge of the shortest Pb–O distances in the two phases, 2.8 Å in the cubic phase and 2.4 Å in the orthorhombic phase, this is rather unusual.

Insight into these differences can be obtained from the electron localization functions projected in planes, as displayed in Fig. 3 and 4. The bar (a) in Fig. 3 displays the colour coding for the extent of localization with deep blue (left) indicating poor localization through white (right) indicating complete localization. The three panels in (b) and in (c) display sections of the unit cell along [100] showing the localization in the cubic

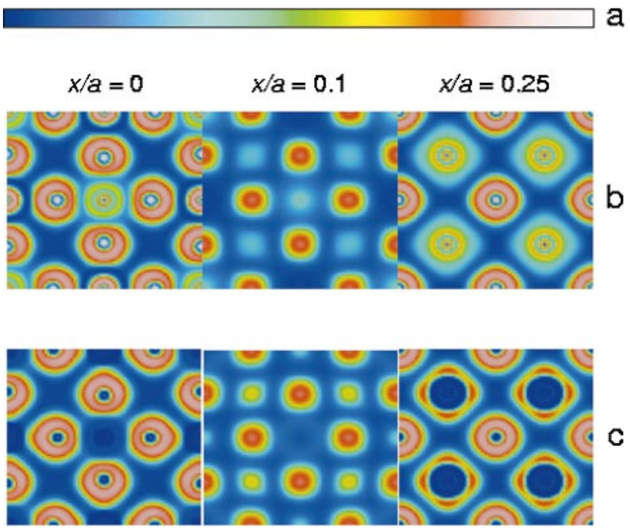

Fig. 3 Total and valence-only ELFs of the cubic phase projected in the unit cell. (a) is the scale bar for the extent of localization, (b) shows the total ELF for different planes along [100] of the cubic unit cell and (c) shows the valence-only ELF for the same planes.

phase projected on planes whose depths are indicated. While (b) corresponds to the total localization, *viz.* core and valence electrons, (c) corresponds to the valence-only localization. From the section corresponding to $x/a=0$ in (b), we can identify strong core localization around W at the centers and corners of the squares, while the localization around Mg atoms which are at the edge-centers, is a little weaker. The localization around O atoms, which surround W and Mg, is clearly polarized with a tail towards Mg. Considering the same level in the valence only localization (c), the W and Mg are now seen to have been stripped of their valence electrons and the polarization of the O is more clearly seen. Going to the level $x/a=0.25$, which has Pb at the positions (0.25,0.25), the core localization in (b) shows up some of the atomic shell structure. An interesting feature is the cyan square around the Pb atoms. Stacking the different levels on top of each other we see that this region of localization forms something like an octahedron surrounding Pb.[16] This near-octahedron is clearly visible as a strongly localized (yellow-orange) region in the valence-only ELF in the panels in (c). This feature arises dues to the lone pair around Pb, forcibly split by the symmetry of the high-temperature phase.

Total and valence-only ELFs for the orthorhombic phase are displayed in the panels of Fig. 4. The section chosen is $b \times c$ on side and projected for the plane $x/a=0$ where the parameters correspond to the orthorhombic cell. The bar (a) has the same meaning as in the previous figure, (b) corresponds to the total localization in the plane and (c) is the valence-only localization. In the plane displayed, only Pb and O atoms are present, arranged alternately with Pb at the bottom left, *etc.* The localization around O in this and other sections is seen to be much more isotropic than what was found in the cubic phase. From the total ELF in panel (b), some displacement of the Pb atoms towards some of the oxygen is seen. This displacement leaves a tail of localization (cyan) on every Pb atom in the opposite direction. In the valence-only ELF in panel (c), the tails are strongly localized forming lobes on every Pb atom. These lobes are the lone pairs, permitted by the low symmetry of the low-temperature phase to localize. Note that the arrangement of the lobes already suggests the antiferroelectric nature of the phase. Pairs of lobes are arranged in an opposed manner such that any resulting polarization of the structure cancels out.

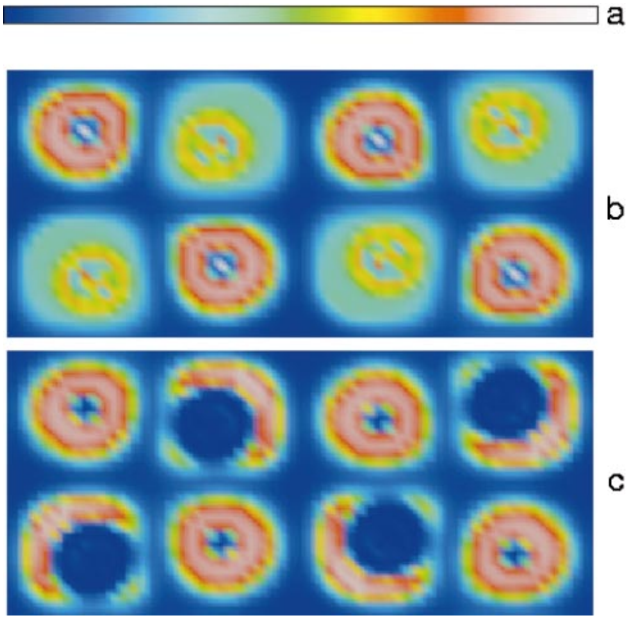

Fig. 4 (a) Scale bar, (b) total and (c) valence-only ELFs of the orthorhombic phase projected in the plane $x/a=0$. This plane contains only O and Pb.

Going back to the COHP displayed in Fig. 2, we can now interpret the presence of the bonding Pb–O states in the COHP of the cubic phase as arising due to the lone pair being degenerate over a number of sites. In the orthorhombic phase where the lone pair is localized, this interaction is no longer possible.

Concurrent with the submission of this manuscript, Watson and Parker[17] have examined the relative stability of α-PbO over PbO in a hypothetical CsCl structure using high level electronic structure calculations, including structural optimization through the use of gradients. In the CsCl structure, symmetry forces the lone pairs to be split, as in the cubic phase of Pb_2MgWO_6, while in α-PbO, the lone pairs can form lobes. They suggest that the stability of the α-PbO arises not from the ability of the lone pairs to form lobes but from the mixing of Pb 6p into antibonding states formed by Pb 6s and O 2p. This argument is consistent with the observation of a slight stabilization of antibonding states in the orthorhombic structure as seen in the COHP in Fig. 2. We make no claim that this is what causes the phase transition in the present case.

Conclusions

The phase transition in Pb_2MgWO_6 can be described as being driven by two propensities—of the oxygen atoms to lose their polarization and of the lone pairs on the lead atoms to localize. In the language of Silvi and Savin,[4] the non-bonding attractor corresponding to the lone pair on lead is reducible in the high temperature phase and becomes irreducible below the structural transition. Analogies from the molecular world are found in the differences between the localized lone pair attractors in H_2O and the delocalized lone pair in HF.[4] The key feature of the present work is the demonstration that such changes can be visualized even in complex materials of technological significance. While the present contribution deals with the phase transition in a single compound, it is our opinion that the insights obtained could be generalized to other systems as well—and particularly to those in which lone pairs are stereochemically important.

Acknowledgements

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