

Structural and Electronic Properties of TiO₂ Polymorphs: a Wannier Functions Approach

Michel Posternak

Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The one-particle description of the electronic structure of periodic crystalline solids is usually based on extended Bloch functions (BF's). An alternative description can be derived in terms of localized Wannier functions (WF's), which are defined in real space via a unitary transformation performed on the BF's. By imposing the further condition of maximal localization, the problem of the nonuniqueness of WF's has been mostly resolved by Marzari and Vanderbilt [1], and their method has now become a standard tool for practical applications. In contrast to BF's, WF's are useful in visualizing chemical bonds, and provide furthermore complementary informations regarding dielectric properties. As an illustration of this aspect of the WF's description, we analyze here the microscopic origin of differences in structural and electronic properties of the four natural TiO₂ polymorphs, *i.e.*, rutile, anatase, brookite, and the monoclinic TiO₂ (B) form. Indeed, because of the similarity of the local crystal environment in these phases, the use of a delocalized-basis approach (BF's) precludes a conclusive explanation of the subtle differences observed in their physical properties. In the case of rutile and anatase, physical properties have been commonly analyzed in the literature assuming that the basic building units are TiO₆ octahedra, which are distorted and assembled differently [2]. In contrast, our WF's analysis for these two phases has shown that the OTi₃ triangular complex is in fact the relevant building unit for understanding their electronic properties [3]. WF's differences between the two phases are directly related to the opposite distortion from equilateral shape that the isosceles Ti₃ coordination triangle has in these structures. In particular, this explains quantitatively the opposite anisotropy of the calculated dynamical Born charge tensors. We have extended these results to the case of brookite [4], where the corresponding (non-planar) OTi₃ structural units break up into an equal number of rutilelike and anatase-like units. The WF's of the two non-equivalent O sites display an anisotropy which is in line with the structural data, and this trend applies also to the case of the Born dynamical charge tensor. Physical properties of brookite are expected to be intermediate between those of rutile and anatase. A further phase, TiO₂ (B), which coexists with, and derives from natural anatase has been recently identified [5]. It is monoclinic with C_{2h}^3 space group, and its conventional cell contains 8 TiO₂ formula units. At variance with the three cases discussed above, the 16 O atoms in TiO₂ (B) are *not* all threefold coordinated: indeed, 12 O atoms belong to anatase-like OTi₃ structural units, and the remaining 4 O atoms are twofold coordinated. The outcome of structural differences on electronic properties of these various TiO₂ phases is analyzed.

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