Electronic and Optical Properties of Yttria

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The electronic structure and bonding in the Y_2O_3 crystal is completely elucidated by first-principles self-consistent band-structure and optical calculations. Results agree well with experiments. The unique type of bonding in Y_2O_3 is emphasized; it does not support the fully ionic picture and is best described as $Y_2^{+2.16}O_3^{-1.44}$.

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Yttria (Y_2O_3) is an important ceramic oxide with many practical applications. It is an important ingredient for high-temperature superconductors and has also been used as a substrate material for thin-film growth. Little is known about the electronic bonding in this oxide. The lack of microscopic understanding is hindering many aspects of material development in modern technology involving yttria. Fundamental optical-absorption studies in single-crystal Y₂O₃ were carried out in the 1960s¹ and late 1970s.² More recently, an accurate optical spectrum on single-crystal Y_2O_3 in the vacuum-ultraviolet region up to 42 eV has been measured.³ Optical-absorption edges in sputtered Y₂O₃ films were also studied by optical emission spectrometry.⁴ Only very recently, x-ray photoemission and absorption measurements on stoichiometric yttria have been attempted and compared with semiempirical cluster calculations.⁵ The interpretation of these data is incomplete because of the lack of knowledge about the band structure of Y_2O_3 . The optical data were usually interpreted in terms of the energy levels of free ions.^{2,3} The presence (or absence) of possible excitonic lines and the nature of band-edge absorption in Y_2O_3 remain unclear. The high melting point of yttria (2683 K) makes it difficult to produce single crystals of high purity. Possible contamination of impurities and defects as well as the poor surface quality tend to make these measurements less precise.¹⁻³

The lack of theoretical calculations for Y_2O_3 is not accidental. Yttria crystallizes in a very complicated bixbyite structure in which the cubic cell contains sixteen molecules.⁶ The Y-O bond lengths range from 2.25 to 2.34 Å. In a somewhat simplified picture, one may think of the Y atom as being in a highly distorted octahedral environment while the O atom has a distorted tetrahedral coordination. The aluminum oxide (α -Al₂O₃) has a slightly less complicated corundum structure and YAlO₃ has a distorted orthorhombic perovskite structure (GdFeO₃ type). Yttrium aluminum garnet (YAlG), Y₃Al₅O₁₂, an important laser host material with 160 atoms in the cubic cell, is probably the most structurally complicated of all known oxides.

In this Letter, we present the results of a detailed electronic-structure and optical calculation of Y_2O_3 , us-

ing the first-principles self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method. The OLCAO method in the local-density approximation (LDA) has been successfully applied to study the fundamental properties of a variety of condensed-matter systems with great success. The use of atomic orbitals in the basis expansion enables us to study the electronic states of crystals of extreme complexity.⁷ In the present study, a minimal basis including all the core orbitals and Y-5s, Y-5p, Y-4d, O-2s, and O-2p orbitals is used. To facilitate the evaluation of multicenter integrals, the potential and the charge density of the crystal are numerically fitted by atom-centered Gaussian functionals. The quality of the fit is checked by comparing the integrated charge of the unconstrained fit to the actual number of electrons in the crystal. We have achieved an accuracy of limiting this difference to less than 0.002 electron out of a total of 192 valence electrons in Y_2O_3 . Selfconsistency is achieved in about thirty iterations when the energy eigenvalues stabilize to less than 0.001 eV.

The calculated band structure is shown in Fig. 1. All the bands are rather narrow and flat with the exception of the single lowest conduction band (CB). A direct



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LDA band gap of 2.0 eV at Γ is obtained. The electron effective mass m_e^* of the CB at Γ is quite isotropic and is about $1.05m_e$. The components of the hole effective mass m_h^* of the valence band (VB) at Γ are estimated to be 1.6 m_e along ΓP and are much larger (> 11 m_e) along the ΓN and ΓH directions. The flat VB and the large m_h^* in Y₂O₃ indicate that the intrinsic conduction in yttria, if any, has to be with electrons rather than holes. The total density of states (DOS) and the orbital-projected partial DOS (PDOS) are shown in Fig. 2. The VB is 3.9 eV wide and is mainly from the O-2p orbitals. The CB which consists of two pieces separated by a gap of 0.3eV, has a total width of a little less than 5 eV. The significant interaction is the Y-4d orbitals with the O-2porbitals with some participation from the Y-5s and -5porbitals. The lowest CB at Γ is derived from a combination of Y-4d orbitals of the symmetry type $x^2 - y^2$ and $3r^2 - z^2$ at the 24 d Y sites in the cubic cell with a space group of T_h^7 . Contrary to what has been speculated,² the Y-4s electron plays no role in the state near the CB edge. The centers of gravity of the two pieces of the CB are separated by 2.3 eV. This is in good agreement with the x-ray near-edge measurement⁵ which shows a two-peak CB structure α and β separated by 2.2 eV. We have further projected the Y-4d CB into five symmetry types of Γ_{25} and Γ_{12} . We find the Γ_{25} states distribute rather evenly over the two CB pieces, while the Γ_{12} states make a preponderant contribution to the lower CB. Thus the separation of the CB into two pieces in Y₂O₃ may have its origin in the crystal field. The O-2p VB width is only about 4 eV. However, the measured x-ray photoemission VB spectra show⁵ a single major peak with a smaller intensity tail extending down to more than 10 eV. It is likely that the low-intensity peak comes from the defectrelated structure rather than the intrinsic VB states in Y_2O_3 . This view is supported by the optical-spectra calculation to be discussed later.

To further delineate the bonding in Y_2O_3 , the charge density along a Y-O bond (2.261 Å) and the contour map containing such a bond are shown in Fig. 3. There is a minimum of zero charge along the Y-O bond at about 0.3 Å from the Y center. If this is taken as the boundary for a Y ion, then Y has very little valence charge left and is thus close to being fully ionized to Y^{3+} . However, a close look at the contour map in Fig. 3(b) shows something different. Well-defined nearspherical regions of charge distribution are evident around both the Y and the O ions. From this charge map, the ionic radii for Y and O can be estimated to be 0.88 and 1.27 Å, respectively. This means that within the Y ionic sphere of charge, there exists a ring distribution of almost zero charge, followed by another concentric ring of broad charge maxima centered at about 0.55 Å. This outer ring of Y charge participates in a covalent type of bonding with the O ions. This is a very unique feature in the Y-O bonding and cannot be simply described as partially ionic, partially covalent in character.



FIG. 2. DOS and PDOS of Y_2O_3 . (a) Total; (b) Y-5s; (c) Y-5p; (d) Y-4d; (e) O-2s; (f) O-2p.

Similar calculations for α -Al₂O₃ and MgO (Ref. 8) show that the Al-O bond is somewhat similar (but not exact) while the Mg-O bond is close to being fully ionized. Our experience with many other oxides leads us to believe that the Y-O bond may be the only one showing such a feature. Careful analysis of atomic wave functions of Y (Ref. 9) reveals that this is due to the fact



FIG. 3. (a) Charge density $\rho(r)$ along the Y-O bond. The dashed arrow indicates the region of zero charge density and the solid arrow represents the most likely boundary of the Y and O ions. (b) Contour map of charge density on a plane containing the Y-O bond. The contour lines are from a minimum of 0.01 to 0.25 (in intervals of 0.005) in units of electron/cell.

that the third node of the Y-5s and the first node of the Y-4d wave functions happen to coincide at about 0.3 Å from the nucleus. Integration of charge within the Y and O effective ionic radii gives effective charges of 0.80 and 7.38 electrons for Y and O, respectively, with the remaining 1.40 electrons (0.7%) distributed over the interstitial regions of the unit cell. Hence our calculation does not support the well conceived notion² that Y₂O₃ is best described as an ionic compound Y₂⁺³O₃⁻²; rather it should be close to Y₂^{+2.16}O₃^{-1.44}.

To further investigate the electron states in Y_2O_3 , we have calculated the interband optical transitions in Y_2O_3 for photon energies up to 11 eV. The calculation is based on the energy eigenvalues and wave functions at 91 regularly spaced **k** points in the irreducible portion of



FIG. 4. Calculated (solid line) and measured (dashed line, from Ref. 3) curves for $\varepsilon_2(\omega)$. A shift of 2.7 eV has been applied to the theoretical curve.

the Brillouin zone; and takes full account of the dipole transition matrix elements.^{7,10} The calculated $\varepsilon_2(\omega)$ curve is shown in Fig. 4 along with the experimental data from Ref. 3. The experimental major peak at 7.2 eV is aligned with the calculated one by shifting the theoretical curve upward by 2.7 eV. There is good agreement in the general shape and the structures of $\varepsilon_2(\omega)$. The fact that the major absorption is within an 8-eV region is consistent with the calculated VB width of 4 eV and the CB width of 5 eV. Tomiki et al.³ had identified eight absorption structures in this region. The same structures can be identified from the theoretical curve, as indicated by the dotted lines in Fig. 4. Although the relative intensities of the peaks are somewhat off, the relative separations of the peaks are in quite good agreement. Of more importance is the absorption near the band edge. A sharp peak at 6 eV in the experimental curve was tentatively assigned² as an excitonic peak and was further supported by the measurements of Tomiki et al.³ Our calculation is consistent with this interpretation because there is no sharp absorption peak of the interband type in the theoretical curve anywhere near this energy. However, the existence of an excitonic peak may modify the absorption spectrum near the band edge considerably and the comparison between theory and experiment in this region is not straightforward. A general observation is that in oxide materials, in which the excitonic peak exists, the absorption edge is greatly sharpened.¹¹ Although our calculated direct band gap at Γ is only about 2.0 eV, it is well known that the LDA, which is more appropriate for the ground state of the system, underestimates the band gap in insulators and semiconductors. However, according to our calculation, the absorption becomes appreciable only for photon energy 0.6 eV above the intrinsic gap. This is because the optical absorption near the intrinsic band edge is negligibly low



FIG. 5. The absorption curve (data points) near the edge from Ref. 4 compared with the calculated one (solid line) on a logarithmic scale. A shift of 2.7 eV has been applied to the theoretical curve.

due to the low DOS of the lowest CB and the associated matrix effect for the transitions. This kind of situation is quite common in many insulators. For example, in the case of the Cu₂O crystal, the optical transition is directly forbidden at Γ and the optical band gap is much higher than the intrinsic gap.¹⁰ On the other hand, determination of the band gap by optical methods is by no means an easy task because of the presence of the low absorption tail. In general, the optical gap is estimated by some kind of extrapolation based on the absorption data near the edge. Kwok, Aita, and Kolawa⁴ have measured the optical-absorption coefficient of a sputtered film of cubic Y₂O₃ and observed a two-step type of absorption edge in the energy range of 5-6 eV. The data are shown in Fig. 5. This observation agrees with the calculated absorption in the threshold region which also shows a two-step type of absorption after an initial sharp rise. Since the sputtered film is polycrystalline and may not even be stoichiometric, excitons are not likely to be observed in such samples because of the scattering by defects or grain boundaries. The general feature of the absorption profile in such a sample is expected to be in closer agreement with the calculation for transitions near the band edge.

In summary, we have carried out a detailed study of the electronic structure and bonding in Y_2O_3 . It is shown that the traditional notion of Y_2O_3 being fully ionic is incorrect and the bonding between Y and O is peculiar in the sense that there is a region of zero charge within the Y ion. The result on the optical spectrum agrees well with past and present experimental data. The result is also consistent with the interpretation of excitons at 6 eV in the Y_2O_3 crystal. A two-step absorption increase near the absorption edge observed in the sputtered film is reproduced. It is anticipated that this work will stimulate further studies on the electronic states of other laser materials such as AlYO₃ and YAlG, and in the defect and impurity states in Y_2O_3 .

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