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Bonding of Guest Molecules in the Tubes of Nanoporous Cetineite Crystals

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ABSTRACT

A theoretical study of the optical excitation processes in cetineites is presented. This new exciting class of crystals with tubular structures displays photoconductivity, which strongly depends on the presence of guest molecules within the tubes. Based on self-consistent electronic structure calculations we present calculated dielectric function and photoelectron spectra of the (Na;Se) cetineite with the tube filled with different guest molecules. Calculations are performed with the extended linear augmented plane wave **kp** method. The configuration and the arrangement of the filling molecules is derived from available crystallographic data and from heuristic arguments on chemical binding.

INTRODUCTION

The electronic structure of various pure cetineite compounds has been previously studied extensively, see Ref. [1] and references therein. The general composition formula is $A_6[Sb_{12}O_{18}][SbX_3]_2 \cdot (6-mx)H_2O{\cdot}x[B^{m+}(OH^-)_m]$, where $A = Na^+$, K^+, Rb^+; $X = S^{2-}$, Se^{2-}; and $B = Na^+$, Sb^{3+}. The crystal formulae are abbreviated by $(A;X)$. These materials present an extremely attractive and promising subject owing to their single crystal porous structures with tube diameter of about 0.7 nm (see Figure 1) and their semiconducting properties. Potential applications are similar to those of the zeolites with the additional feature of controling their function in an application by electric power. To date, only in the case of $K_6[Sb_{12}O_{18}][SbSe_3]$ homogeneous single crystals can be grown entirely free of guest molecules within the pores (in the form of needles of about 0.5 mm diameter and 2 mm length along the axes of the pores).

Geometrical and electronic properties of the cetineites are discussed in Ref. [1]. In that paper *ab initio* band structure calculations were presented for A = Na, K; X = S, Se. The bonding mechanisms have been explained by the hexagonal aggregation of the tubes consisting of SbO_3 tetrahedra – netted to form the tube walls. The tubes are stabilized by the presence of singly ionized alkali atoms close to the walls inside the tubes and the negatively charged SbX_3 pyramids between the tubes (see Figure 1). In Ref. [1] the anisotropy of the photoconductivity has been explained in terms of the band structure of the guest-free crystals. Two qualitatively different conduction processes can be deduced from the bandstructure results, namely, hopping between the SbO_3 tetrahedra and

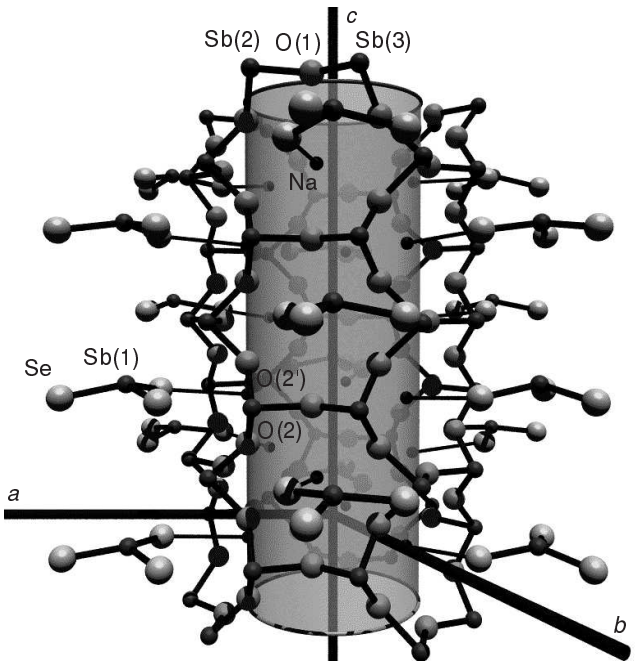

Figure *1: Crystal structure of the cetineites. (Figure from Ref. [1].)*

traveling inside the tube. The latter mechanism is most interesting; by the condition of the orthogonality of the conduction band wave functions to the valence band ones, conduction band states can be formed that have negligible overlap with the orbitals of any of the atomic constituents. Owing to the nanoporosity the conditions for the formation of delocalized states of that nature exist in the cetineites, and we indeed observed an energetically well separated state confined to the tube in our calculation for (K;S). [1] (Similar nearly free electron like states have been observed in calculations on boron nitride nanotubes [2].) It should be, however, noted that this feature of the electronic structure is very sensitive to the atomic composition (e.g., in other cetineites the state was more strongly hybridized with the wall orbitals) and can be easily destroyed by the guest molecules.

Because the guest free material possesses the most attractive features, it has to be understood why in the majority of cases of crystallization water and some other ions of the solution are relatively strongly bound to the interior of the tubes. A direct theoretical approach would require a geometry optimization procedure based on the *ab initio* total energy minimization within the Density Functional Theory (DFT). That would imply considering supercells of large volume and low symmetry, that is beyond our computational abilities.

In this paper we restrict ourselves to a few configurations with assumed geometry of water octahedra where adsorption data are available [3] and the configuration may be fixed by symmetry arguments. The actual *ab initio* calculation then covers the bandstructure

determination, as well as optical and photoelectron spectra. It is hoped that by this procedure one obtains, first, a confirmation of the assumptions through a comparison with experiment, and second, an insight into the bonding properties of the guest molecules which may eventually lead to synthesizing guest free (dry) crystals.

COMPUTATIONAL METHOD

We have considered the following possibilities to fill the tubes with the water (or water-derived) molecules: 1) Inert water cluster $(H_2O)_6$ with symmetrically arranged oxygen atoms (their positions are deduced from x-ray diffraction measurements [4]), which are kept together by hydrogen bonds. 2) The oxygen atoms of the water molecules are connected to the oxygen atoms belonging to the wall via hydrogen bonds. This leads to weaker hydrogen bonds between the oxygen atoms of the water cluster. 3) The center of the cluster is occupied by an antimony atom and there are only hydrogen bonds to the wall, which leads to the $Sb_2(OH)_6$ configuration. The configurations keep the symmetry of the crystal the same as in the case of empty tubes, whereby the symmetry of the molecules might be higher than the actual one, and which has a technical advantage of strongly reducing the computer time. It should be also noted that in nature an incomplete filling of the tubes may occur.

The calculations were performed with the full potential extended linear augmented plane wave **kp** method [5]. The basis set of this direct variational method describes the wave functions in the interstitial by plane waves (the energy cutoff of 9 Ry was used in this work) and inside the muffin-tin spheres by linear combinations of orbitals with several radial functions per angular momentum channel. This leads to a Hamiltonian matrix of dimension 3615. The density-of-states (DOS) curves, dielectric function, and photoelectron spectra were obtained with the tetrahedron method by interpolating the electron eigenenergies, l-projected partial charges, and momentum matrix elements between 12 irreducible **k**-points, which corresponds to the division of the Brillouin zone into 324 tetrahedra, 42 of which are inequivalent.

The resulting self-consistent crystal potential and the band structure agree well with our previous calculations [1], however, our increased computer power and recent methodological progress have made it possible to achieve considerably better numerical accuracy at all stages of the calculation and to treat the more complicated unit cells. In particular, in evaluating the photoelectron spectra the explicit calculation of the optical interband transitions between ~ 150 occupied and ~ 300 unoccupied bands became feasible, owing to our using the plane wave (PW) expansion of the all-electron wave functions instead of the original augmented plane wave (APW) representation. The PW procedure (see Ref. [6]) scales as n^3 with the number of atoms in the unit cell in contrast to the straightforward calculation in terms of APWs, which scales as n^4.

RESULTS AND DISCUSSION

In order to visualize the implications of the guest molecules for the optical excitation

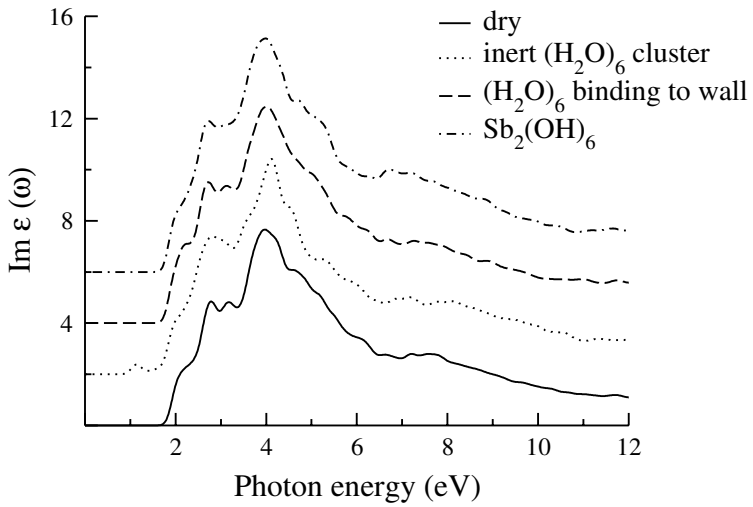

Figure *2: The imaginary part of the dielectric function of the (Na;Se) cetineite with different guest molecules.*

processes, we present in Figure 2 the imaginary part of the dielectric function $\varepsilon(\omega)$ for the four crystals. It can be seen that the guest molecules have no dramatic effect on the optical absorption over the low photon energy region. In other words, the initial and the final states of important optical transitions have apparently the same nature irrespective of the filling of the tubes. However, that does not mean that there is no effect on the photoconductivity: the energy distribution of the mobility of the carriers changes more significantly with the filling of the tubes. (The mobility is proportional to the averaged group velocity of the electrons at a given energy and denoted by ω_p^2 in Ref. [1].) To conclude on the implications for the photoconductivity one needs a plausible approximation for the distribution function of the carriers – this work is in progress.

For the (Na;Se) crystal a photoemission experiment has been performed [1] for the photon energy 21.22 eV, but in Ref. [1] the measured spectrum has been compared only to the theoretical DOS function. In the present work we have calculated the angle-integrated photoelectron energy distribution curves (EDCs) in the framework of interband optical transitions between bulk states for a number of photon energies around 21.22 eV. The calculation is free from adjustable parameters and it takes into account the crystal momentum conservation and the dipole matrix elements. In the photon energy region considered the theoretical spectrum changed only slightly with the photon energy; thus, the uncertainties due to our using the DFT-derived one-particle solutions, which neglect self-energy effects, are apparently small. The EDCs for the pure (Na;Se) and for three different configurations of the guest molecules are shown in Figure 3.

The electron emission from the valence band is seen to be reproduced with excellent quality by the pure (Na;Se) calculation. However, the well-defined experimental maximum at -12 eV has no counterpart in the theoretical curve. The filling of the tubes has a strong effect on the EDC – our results suggest that none of the configurations we have tried is likely to occur in reality. On the other hand, it can be seen that the guest molecules may

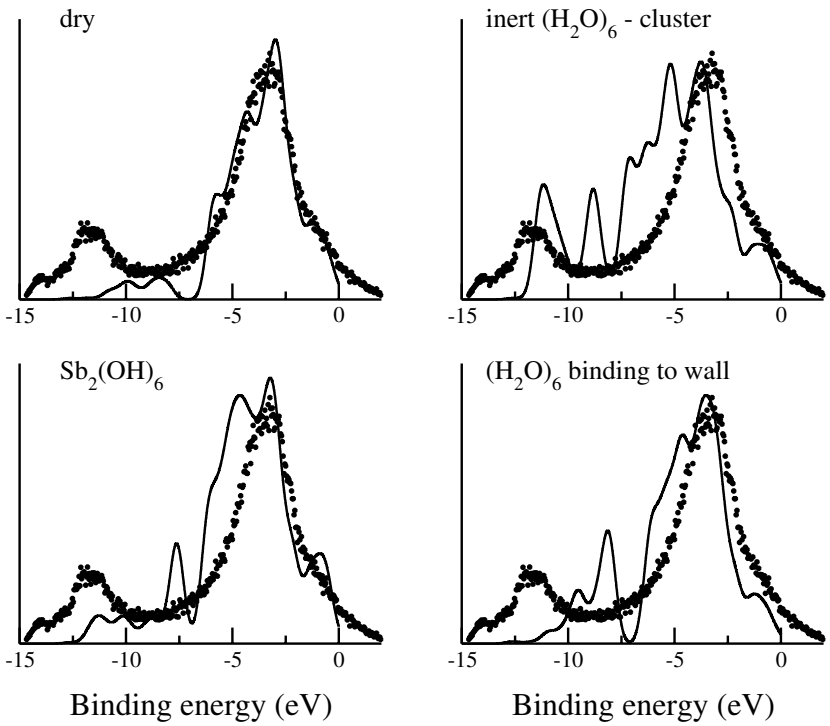

Figure *3: Comparison of the theoretical angle-integrated UPS spectra of the (Na;Se) cetineite with different guest molecules (solid lines) with the measurements of Ref. [1].*

give rise to relatively strong emission at binding energies deeper than -10 eV. The maximum at -12 eV may arise from the presence of alkali atoms in the tubes or may be the effect of contamination. However, in view of the surface sensitivity of the photoemission experiment, the possibility cannot be excluded that this structure comes from surface effects not described by the bulk band structure.

Another interesting effect is observed in the (K;S) compound in the presence of the water molecules in the inert water cluster $(H_2O)_6$ configuration: owing to their small binding energy the $3p$ states of potassium hybridize with the SbO_3 tetrahedra orbitals of the walls to form a satellite DOS maximum about 1 eV higher in energy (see the right panel of Figure 4).

CONCLUSIONS

We have performed *ab initio* calculations of the energy band structure, dielectric function, and photoelectron energy distribution curves for the (Na;Se) cetineite with various configurations of the guest molecules filling the nanotube. The guest molecules have been found to only slightly affect the optical absorption in the visible and UV photon energy range. At the same time, according to our calculations, their effect must be well seen in the photoemission experiments. The experimentally observed influence of guest molecules on the photoconductivity is apparently caused by changes in the mobility of the carriers rather than by changes in the optical excitation process.

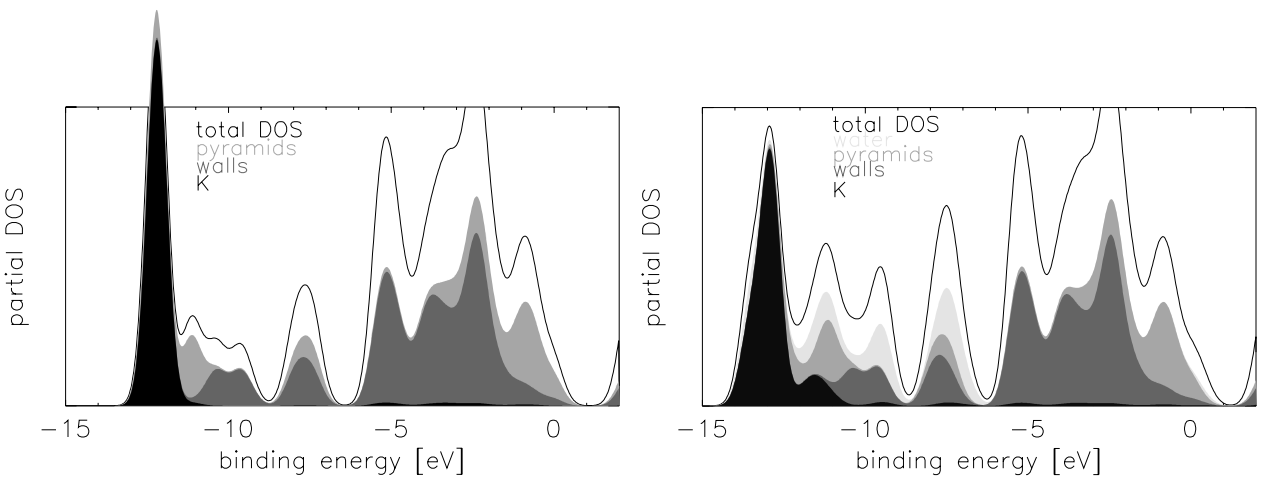

Figure *4: Atom-resolved partial DOS curves for the pure (K;S) compound (left panel) and with the tubes filled with inert water* $(H_2O)_6$ *clusters (right panel). The contributions from* $(H_2O)_6$*-water (right panel only),* SbS_3*-pyramids,* $Sb_{12}O_{18}$ *tetrahedra, and potassium atoms are shown by shaded areas, with the darkness increasing in that order. Thereby the white region shows the contribution from the interstitial region and the solid line gives the total DOS. The DOS at the potassium atom is seen to have a satellite at about* -12 *eV in the presence of water molecules.*

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