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1D Conductance in Cetineites: A New Class of Chemically Synthesized Nanoporous Semiconductors

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Cetineites are crystalline nanoporous oxochalcogenoantimonates with photosemiconducting host lattice. The conduction band, which predominantly carries the photoconduction, results from the interaction of chemically different subunits in an alternating sequence along the crystallographic *c*-axis. We show that it is possible to obtain an exact analytical expression for the conductance for such a one-dimensional periodic system with a complex unit cell, were we consider the case of small extent of each individual potential as compared to any other typical lengths of the system. By means of this basic consideration we can qualitatively describe the characteristics of the experimentally observed wavelength dependent photoconductivity, obtained from single crystals of this new material.

Introduction The chemical synthesis of nanostructured materials has become an important field in fundamental research as well as from the technical point of view. Cetineites belong to this class of materials. They are oxochalcogenoantimonates with zeolite-like channel structure, and they can be synthesized chemically by hydrothermal preparation techniques [1]. Most recently they have been identified to be the first nanoporous crystalline solids with photosemiconducting host lattice [2], the general composition of which is

$$A_6(Sb_{12}O_{18})(SbX_3)_2, \text{ with } A = Na^+, K^+ \text{ and } X = S^{2-}, Se^{2-}.$$

In these structures tubes of composition $[Sb_{12}O_{18}]$ are formed by linking $[SbO_3]$ pyramids, which are arranged in a hexagonal rod packing, held together by ionic bonds between one-dimensionally stacked chains of $[SbX_3]^{3-}$ pyramids and the A^+ ions lining the tube walls. The free diameter of the tubes is approximately 0.7 nm, making the inner surface accessible for small molecules or ionic guests (see Fig. 1).

By means of the linear augmented plane wave (LAPW) method on an ab-initio basis the electronic structure has been obtained for the highly complex unit cell of the cetineites, consisting of 44 atoms with an empty sphere centered in the tube. These calculations indicate that the conduction band, which predominantly carries the photoconduction, results from an overlap of d_{xz}- and d_{yz}-orbitals of the Sb(1) atoms in the stacked pyramids with sp-orbitals of the Sb(2) and Sb(3) atoms in the tube walls [3]. This results in a high conductance anisotropy with a conductance thirty times higher along the *c*-axis. Thus, the photoconductivity is assumed to appear along the crystallographic *c*-axis in independent one-dimensional channels with an alternating sequence of chemically different subunits, i.e. $[Sb(1)X_3]^{3-}$ and $[Sb(2,3)O_3]$ pyramids (see Fig. 2).

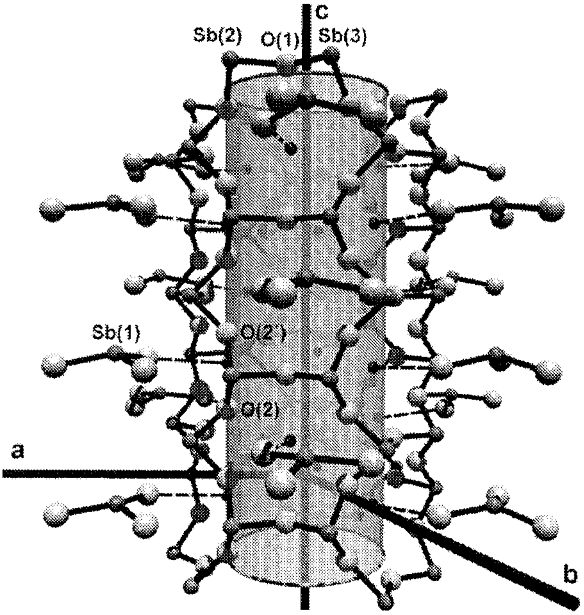

Fig. 1. Structure of cetineites in perspective view [3]. The shaded cylinder is just for the illustration of the three-dimensional view

Method of Calculation In this work we will show that it is possible to obtain an exact analytical expression for the conductance in cetineites along the crystallographic *c*-axis. Our aim is to reduce the problem to the determination of the coefficient of transmission or the Landauer conductance of an electron through a one-dimensional (1D) periodic system [4] with a complex unit cell, i.e., the two chemically different subunits, which constitute the conduction band. Here, we consider the case where the extent of each individual potential is small as compared to any other typical lengths of the system. The geometrical parameters characterize the distance between the potentials in the unit cell, the lattice period as well as the potential height and they are given by the

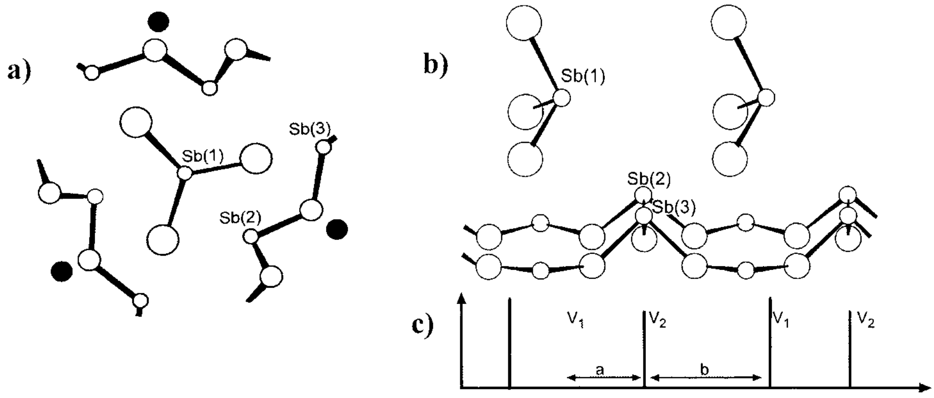

Fig. 2. a) Top view onto the *ab*-plane (just segments are shown). b) Illustration of the conduction paths along *c*. c) Kronig-Penney chain along *c* with distance between V_1 and $V_2 = a$ and periodicity d $(= a + b)$

crystal structure of the cetineites and the value of the fundamental gap, respectively.

The total potential is of the form

$$V(x) = V_1 \sum_{m=1}^{M} \delta[x - (x_1 + md)] + V_2 \sum_{m=1}^{M} \delta[x - (x_2 + md)]\,; \tag{1}$$

d is the lattice period, and M is the number of cells. For cetineites the Sb(1) atoms form the potential V_1 and the Sb(2) and Sb(3) atoms, respectively, form the potential V_2. Both are repulsive for injected charges and similar in height due to chemical arguments. This leads to the well known energy spectrum condition ($\hbar = 2m = 1$, m is the electron free mass and $k = \sqrt{E}$)

$$\cos \beta d = \cos kd + \left(\frac{V_1}{2k} + \frac{V_2}{2k}\right) \sin kd + 2 \left(\frac{V_1}{2k}\right) \left(\frac{V_2}{2k}\right) \sin\ ka \sin k(d - a) \tag{2}$$

with

$$\beta d = \frac{\pi n}{M}, \qquad (n = 1, \cdots, M - 1). \tag{3}$$

According to $|\cos \beta d| \geq 1$, the fundamental gap at 0.5 eV, which has been determined experimentally from the temperature dependence of the conductivity, and the known lattice constants lead to $V_1 \approx 1$ and $V_2 \approx 1$, for $a = 1$ and $d = 2.9$.

Thus, the Landauer conductance $G(E)$ for a 1D structure coupled to two perfect leads, which is related to the transmission coefficient $T(E)$ by the expression $G(E) = 2e^2 T(E)$, is given by

$$G = |D_{M2}|^{-2} = \left\{1 + (|D_2|^2 - 1)\,\frac{\sin^2 (M\beta d)}{\sin^2 (\beta d)}\right\}^{-1} \tag{4}$$

with

$$D_2 = \begin{vmatrix} 1 + iV_1/2k & iV_2/2k\,\mathrm{e}^{ika} \\ iV_1/2k\,\mathrm{e}^{ika} & 1 + iV_2/2k \end{vmatrix} \tag{5}$$

and it reflects the characteristics of the DOS as well as of the energy dependent photoconductivity.

Results and Discussion Figure 3 shows the conductance $G(E)$ for a Kronig-Penney chain with $V_1 = V_2 = 1$, $a = 1$, $b = 1.9$, calculated for eight potentials as well as the energy dependent photocurrent. The calculated curve reflects a fundamental first gap below approximately 0.6 eV, which corresponds to the experimentally obtained fundamental gap of 0.5 eV (not marked in the graph). Above, the conductance rises up to its maximum value, followed by a fine structure with further peaks. At 1.6 eV the conductance drops to a new minimum, i.e. a second gap appears between 1.6 eV and 2 eV. The appearence of a second gap qualitatively coincides with the experimentally observed drop of the energy dependent photoconductivity of cetineite with A = K^+ and X = Se^{2-}. These data were measured at constant voltage on a single crystal along the c-axis at room temperature, which was irradiated with variable photon energy in the range of 1.68 to 5.0 eV [5]. Above the second gap both curves rise again to a maxiumum value, which appears in the experiment as well as in the calculationn at the same energy, i.e. 2.5 eV. While the calculated conductance drops again at energies above

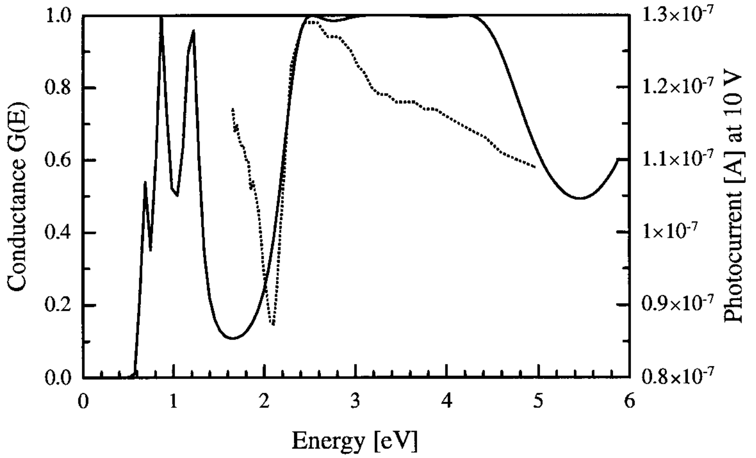

Fig. 3. Conductance $G(E)$ (full line) for a Kronig-Penney chain with $V_1 = V_2 = 1$, $a = 1, b = 1.9$ for eight potentials, and energy dependent photoconductivity (dotted line) of cetineite with A = K^+ and X = Se^{2-}, measured at room temperature on a single crystal along c

4.5 eV, reflecting a third gap, the photocurrent decreases with increasing energy above 2.5 eV, since the penetration depth for light decreases for photons with energies larger than the optical gap. Thus, the appearance of a third gap cannot imediately be derived from the experimental data.

In conclusion, the qualitative agreement of the experimental data, i.e. the fundamental gap at 0.5 eV and the spectral photoconuctivity with the spectra obtained from the calculated data shows that by means of this basic consideration most of the interesting features of the photoconductivity along c can qualitatively be described by the model developed here. This means that due to the high conductance anisotropy, which results from the interaction of just two chemically different subunits, i.e. the $[Sb(1)X_3]^{3-}$ pyramids and the $[Sb(2,3)O_3]$ pyramids, the qualitative description of electronic structure can be reduced to the description of a 1D system consisting of two sublattices, in spite of the complex structure of the material observed.

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References

[1] F. LIEBAU and X. WANG, Beih. Eur. J. Mineral **7**, 152 (1995).

[2] U. SIMON, F. SCHÜTH, S. SCHUNK, X. WANG, and F. LIEBAU, Angew. Chem. Int. Ed. **36**, 1117 (1997).

[3] F. STARROST, E. E. KRASOWSKII, W. SCHATTKE, J. JOCKEL, U. SIMON, X. WANG, and F. LIEBAU, Phys. Rev. Lett. **80**, 3313 (1998).

[4] V. GASPARIAN, U. GUMMICH, E. JODAR, J. RUIZ, and M. ORTUÑO, Physica B **233**, 72 (1997).

[5] U. SIMON, J. JOCKEL, F. STARROST, E.E. KRASOWSKII, and W. SCHATTKE, Nanostructured Materials **12**, 447 (1999).