

Electronic structure of Cs₂KSb and K₂CsSb

A.R.H.F. Ettema

Delft Institute for Microelectronics and Submicronotechnology, Delft University of Technology, Department of Physics, Lorentzweg 1, 2628 CJ Delft, The Netherlands

R.A. de Groot

Research Institute of Materials, University of Nijmegen, Department of Physics, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
(Received 22 January 2002; published 3 September 2002)

Alkali antimonide compounds perform well as photoemissive materials in photodetectors. A number of band-structure calculations have been reported in recent years on binary compounds; however the ternary alkali antimonides (those that involve two different alkali metal atoms) were most successfully applied. The band structure reported here explains the properties of the K₂CsSb compound in ultraviolet light detectors, and discusses the properties of Cs₂KSb for potential use as a detector cathode in the visible light region.

DOI: 10.1103/PhysRevB.66.115102

PACS number(s): 71.20.Nr, 85.60.Ha, 78.66.Li

I. INTRODUCTION

Alkali antimonide compounds are an interesting class of material with different stoichiometries (MSb and M_3Sb , with M an alkali metal) and with a semiconducting behavior.¹⁻⁴ The semiconducting behavior is even preserved in the molten state.⁵⁻⁸ It has been shown by a small-angle scattering study that the local structure of these compounds remains upon melting, which may be the origin of the maintained semiconducting properties. These compounds also show a metal-nonmetal transition as a function of the alkali metal content.⁹ Moreover, the good optical absorption in the visible region of the light spectrum and the low electron escape energy make the alkali antimonide compounds very suitable as photoemitters.¹⁰ Therefore, this class of compounds has been studied extensively for many years.

From a technological point of view knowledge of the electronic structure is essential in order to understand the photoemissive properties of the alkali-antimonide compounds. The octet compounds with the M_3Sb stoichiometry are most important due to the strong optical absorption and the low work function. Such properties make these materials very suitable in photon detection systems.^{10,11} The conversion of photons into detectable electrons occurs by the excitation of a valence-band electron to a conduction-band state after the absorption of a photon and the subsequent emission of a photoelectron.

The electronic band structure of the hexagonal Na₃Sb and K₃Sb compounds show a discrepancy of the reported band-gap values deduced from optical absorption with respect to the values found from temperature-dependent conductivity measurements.^{10,11} The calculated band structure reported in these compounds by different methods showed a very low density of electron states at the bottom of the conduction band. A strong dispersive band dominated by the alkali metal s states in the center of the Brillouin zone (BZ) reduces the band gap considerably and contributes only a little bit to the state density.^{1,12-14}

Most of the electronic band-structure calculations focused on the binary alkali-antimonide compounds whereas the ternary compounds have been applied most successfully in pho-

todetectors. Therefore it is very interesting why ternary compounds have more beneficial properties than binary compounds for use in photocathodes. Alkali photodetectors, that have a Na₂KSb cathode, are known to have higher quantum efficiencies than the detectors with Na₃Sb or K₃Sb cathodes. It was shown recently that this mixed alkali compound Na₂KSb has a less dispersive band at the bottom of the conduction band, resulting in a better cathode performance.

The two distinct phases for K₃Sb, a cubic phase with the antimony atom surrounded by eight alkali atoms in a CsCl coordination and a hexagonal phase with fivefold coordination, appear to have both a strong dispersive band at the bottom of the conduction band.¹³ Therefore, the local structure seems not to have a major influence on the band-gap discrepancy. The factor that does influence the band gap considerably has been shown to be the packing density of the Sb ions and the relativistic effects of Cs.¹²

The introduction of a new bialkali photocathode based on K₂CsSb with high quantum efficiencies for ultraviolet light detection indicates a low electron affinity and a relatively large band gap. In this paper electronic band structure calculations are presented for Cs- and K-based mixed alkali antimonide compounds Cs₂KSb and K₂CsSb and discussed with respect to its properties as a photocathode in UV light detectors.

II. CRYSTAL STRUCTURE

The arrangement of the atoms in the cubic phase of the alkali antimonide compounds with stoichiometry M_3Sb is highly symmetric.¹⁵ The unit cell has a face-centered space group $Fm\bar{3}m$ (No. 225) or O_h^4 in Schoenflies notation. The antimonide atoms occupy Wyckoff position $4a$ (0,0,0) and the alkali metal atoms are positioned at $4b$ (1/2,1/2,1/2) and $8c \pm$ (1/4,1/4,1/4). The two symmetrically inequivalent alkali atom positions indicate the stoichiometric possibilities Cs₂KSb and K₂CsSb for the ternary compounds with K and Cs. The antimony atoms have an eightfold CsCl coordination by the nearest-neighbor alkali atoms at position $8c$.

The length of the unit cell axis of K₂CsSb has been measured with an x-ray-diffraction experiment on a thin poly-

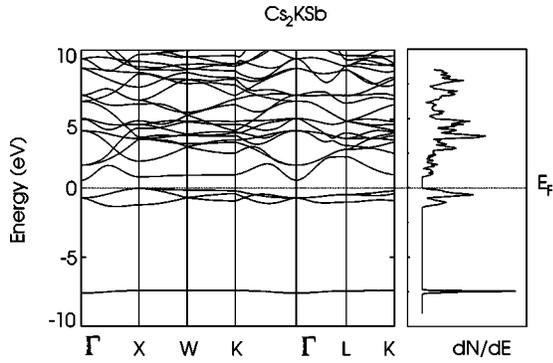


FIG. 1. The dispersion of the energy bands in Cs_2KSb (left-hand side) and the corresponding state density (right-hand side).

crystalline film.¹⁶ The value found for K_2CsSb is $a = 8.61 \text{ \AA}$. The length of the unit cell axis of Cs_2KSb has not yet been determined, and is obtained in this study from interpolation of the reported values of K_3Sb , K_2CsSb , and Cs_3Sb . The experimental values for K_3Sb and Cs_3Sb were determined respectively at 8.49 and 9.15 \AA .¹⁶ The lattice parameter of Cs_2KSb estimated from this interpolation yields 8.88 \AA .

III. BAND-STRUCTURE CALCULATIONS

The calculations were performed with the localized spherical wave method (LSW).¹⁷ This method is based on the augmented spherical wave method but is more efficient in using computing time.¹⁸ Exchange and correlation were treated within the local-spin-density approximation.¹⁹ Scalar relativistic effects were included.²⁰ In the LSW method the radial part of the wave functions is described by a numerical solution of the Schrödinger equation within the spheres and augmented by Hankel functions outside the spheres. On neighboring spheres the Hankel functions are expanded in series of Bessel functions centered on the neighboring spheres. Around each atom a cluster is formed with wave functions that fall off rapidly with increasing distance from the central atom.

The basis functions of the K, Cs, and Sb sites were composed of s , p , and d Hankel functions and s , p , d , and f Bessel functions representing the $4s$, $4p$, and $3d$ states on the K sites, the $6s$, $6p$, and $5d$ states of the Cs atoms, and the $5s$, $5p$, and $5d$ states of the Sb atoms. No empty spheres were included.

IV. RESULTS

A. Cs_2KSb

The calculated dispersion of the bands along the high-symmetry lines in the BZ and the corresponding density of states in Cs_2KSb are presented in Fig. 1. The different element and orbital contributions to the total density of states is shown in Fig. 2. For clarity the state densities are scaled differently for each contribution, and the numbers along the y axis of each frame indicate the scale in states/eV.

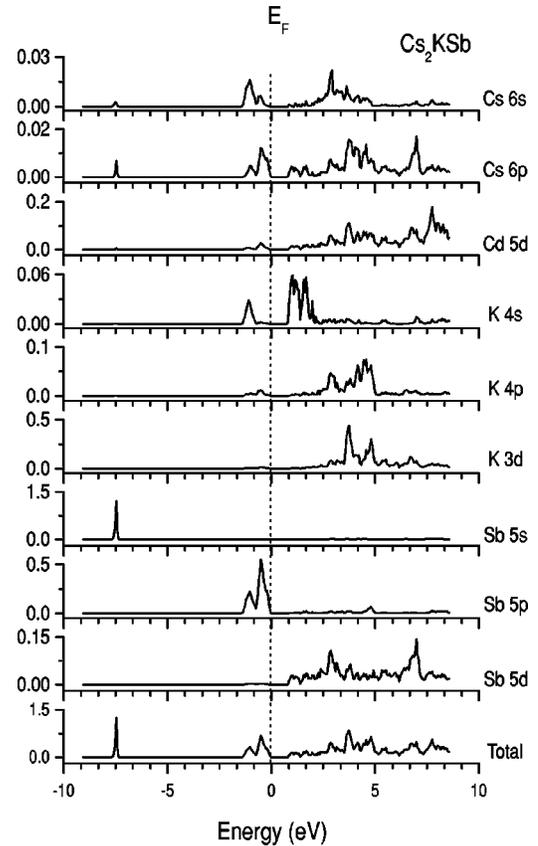


FIG. 2. Element and orbital constituents to the density of states in Cs_2KSb . The numbers along the y axes of the frames indicate the state density in states/eV.

The lowest band at -7.59 eV in Γ is a Sb $5s$ band which is very localized and hardly dispersive. The Sb $5p$ states form three bands just below the Fermi level. These bands are the valence bands, and form initial states in the photoabsorption process. Unlike binary alkali antimonide compounds with lighter alkali metals such as Li, Na and K, Cs_2KSb has its valence-band maximum at the edge of the BZ in point X. The band gap is determined by the energy difference of the upper Sb $5p$ valence bands and the lowest K $4s$ conduction band. The K $4s$ states are low in energy due to the weak crystal field of the neighboring Cs ions. The band-gap value found from this calculation is 0.58 eV. The density of states of the lower conduction band region has a sharp cutoff at the conduction-band minimum. This is in contrast with other alkali-antimonide compounds, that have a small state density at the conduction band minimum. The higher conduction bands are composed of d states from all of the elements involved, however those of Sb and K dominate the bands in the energy range where the conduction band states correspond to the final states in the optical absorption process with visible light.

B. K_2CsSb

The results from the calculation for the compound where the antimonide atoms are surrounded by eight K atoms are

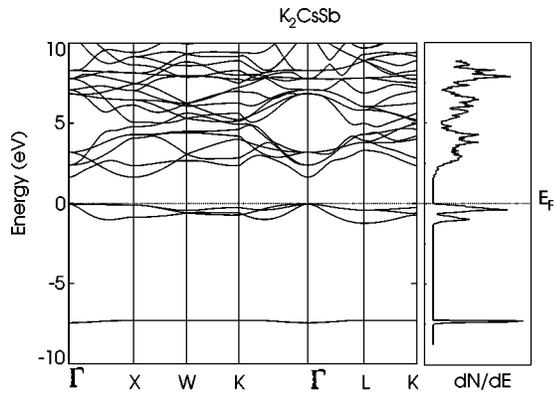


FIG. 3. The dispersion of the energy bands in K₂CsSb (left-hand side) and the corresponding state density (right-hand side).

shown in Figs. 3 and 4. Although most features appear to be similar, there are some important differences. The valence-band maximum is in the center of the Brillouin zone. The twofold-degenerate Sb 5*p* band at the valence-band maximum along the Γ X line does not disperse upward as in Cs₃Sb or downward as in K₃Sb. The conduction-band minimum is determined by a band of K 4*s* states in Γ . There is a second conduction-band minimum of a band composed of Cs 5*d* states with *t*_{2g} symmetry at the edge of the BZ in X; however this minimum is slightly higher in energy. Like many other binary alkali antimonide compounds, K₂CsSb has a very low density of states in the lower region of the conduction band, but the state density becomes appreciable at higher energies where the *d* bands contribute to the state density.

V. DISCUSSION

Band-gap values obtained from local-density-approximation band-structure calculation generally underestimate the experimentally observed band-gap values;^{21,22} therefore, the band-gap values presented here have a relative meaning. In the case of alkali antimonides it should further be considered that in some cases the state density at the bottom of the conduction band is very small and that optical methods generally overestimate the band gap. Unfortunately not much temperature-dependent resistivity data are available for these compounds, which would give more appropriate band-gap values to compare with those values obtained from the calculations. Especially in the context of the electron affinity, values determined for the band gap and the work function need to be treated with great care.

The crystal field of the antimonide atoms in these octet compounds is mainly determined by the nearest neighbors *M*(II). The alkali metal *M*(I) is filling the spatial holes in the framework of chemical bonds between the Sb and *M*(II) atoms. Besides the spatial filling of the unit cell, the alkali metal *M*(I) also donates its valence electron to the valence band in order to fulfill the octet rule for the *M*(I) and Sb atoms. The alkali metal *M*(I) seems to be interchangeable with other alkali metal atoms or metals that appear with a valence of 1+ without having much effect on the electronic

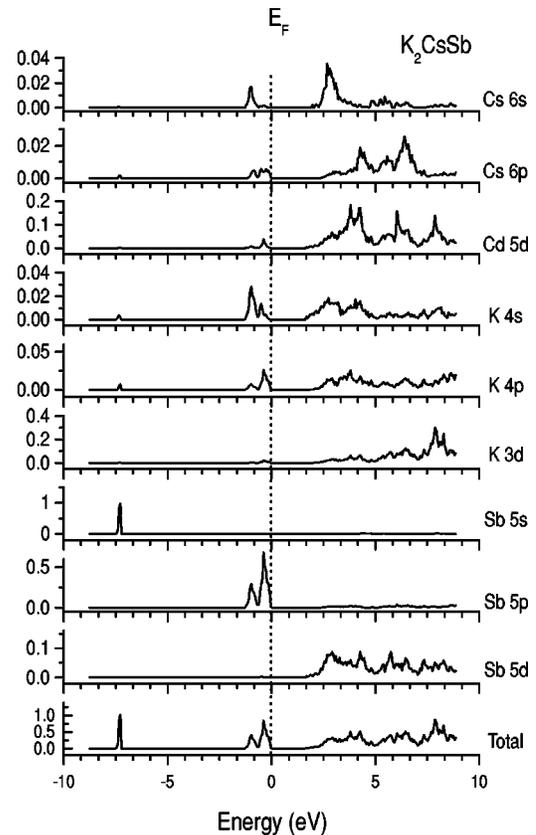


FIG. 4. Element and orbital constituents to the density of states in K₂CsSb. The numbers along the y axes of the frames indicate the state density in states/eV.

structure; however, this is not the case.

It has been shown that the relativistic effects of Cs moves the Cs 6*s* band to a higher energy, causing a relatively large band gap.¹² The less relativistic K atoms have their 4*s* states at a much lower energy. It becomes apparent from the calculations on Cs₂KSb that the band gap is determined by the energy separation of the K 4*s* band and the Sb 5*p* band. Although this compound has an indirect band gap (the valence-band maximum is at X and the conduction-band minimum is at Γ) the density of states does not have a slow increase at the low-energy side of the conduction band but a steep edge with a moderate density. This is a feature for a steep absorption edge as well. The band-gap values obtained from optical data and temperature-dependent measurements should give the same value in the case of Cs₂KSb.

The results for K₂CsSb do show a small state density at the bottom of the conduction band, increasing to a substantial density at energies of 3 eV above the valence-band maximum. This is in agreement with the yellow-transparent color of the K₂CsSb photocathode in UV photodetectors. Also in this case the band-gap value from optical data can be overestimated. This should be borne in mind when the band gap and the work function are measured in order to determine the electron affinity of this material.

Although the compound Cs₂KSb is currently not used in any photodetector, it has promising optical properties for the

visible light region. The steep edge of the state density at the conduction band and the band-gap value around 1 eV are beneficial features for light detection in the visible and UV regions.

In conclusion, we mention that the electronic band structures of Cs₂KsB and K₂CsSb are presented. The results explain the observed properties of the bialkali photocathode based on K₂CsSb, and show that Cs₂KsB has promising properties for use as a cathode in visible light detectors.

ACKNOWLEDGMENTS

This work was supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and by the Technology Foundation STW, applied science division of NWO and the technology program of the Ministry of Economic Affairs.

-
- ¹M. Tegze and J. Hafner, *J. Phys.: Condens. Matter* **4**, 2449 (1992).
²K. Seifert-Lorenz and J. Hafner, *Phys. Rev. B* **59**, 829 (1999).
³K. Seifert-Lorenz and J. Hafner, *Phys. Rev. B* **59**, 843 (1999).
⁴N.E. Christensen, *Phys. Rev. B* **32**, 207 (1985).
⁵W. Freiland and G. Steinleitner, *Inst. Phys. Conf. Ser.* **30**, 488 (1977).
⁶H. Redslob, G. Steinleitner, and W. Freyland, *Z. Naturforsch. Teil A* **27**, 587 (1982).
⁷W. van der Lugt, *J. Phys.: Condens. Matter* **8**, 6115 (1996).
⁸R. Winter, in *Thermodynamics of Alloy Formation*, edited by Y. Chang and F. Sommer (Minerals, Metals, and Materials Society, London, 1997).
⁹J. Robertson, *Phys. Rev. B* **27**, 6322 (1983).
¹⁰A.H. Sommer, *Photoemissive Materials* (Wiley, New York, 1968).
¹¹A.H. Sommer, *J. Appl. Phys.* **29**, 1568 (1958).
¹²S.H. Wei and A. Zunger, *Phys. Rev. B* **35**, 3952 (1987).
¹³A.R.H.F. Ettema and R.A. de Groot, *J. Phys.: Condens. Matter* **11**, 759 (1999).
¹⁴A.R.H.F. Ettema and R.A. de Groot, *Phys. Rev. B* **61**, 10035 (2000).
¹⁵R.W.G. Wyckoff, *Crystal Structures* (Wiley, New York, 1960), Vol. 2.
¹⁶P. Dolizy, O. De Luca, and M.A. Deloron, *Acta Electron.* **20**, 265 (1977).
¹⁷H. van Leuken, A. Lodder, M.T. Czyzyk, F. Springelkamp, and R.A. de Groot, *Phys. Rev. B* **41**, 5613 (1990).
¹⁸A.R. Williams, J. Kübler, and C.D. Gelatt, Jr., *Phys. Rev. B* **19**, 6094 (1979).
¹⁹L. Hedin and B. Lundqvist, *J. Phys. C* **4**, 2064 (1971).
²⁰M. Methfessel and J. Kübler, *J. Phys. F: Met. Phys.* **12**, 141 (1982).
²¹A. Zunger and M.L. Cohen, *Phys. Rev. B* **18**, 5449 (1978).
²²J.P. Perdew and Z. Zunger, *Phys. Rev. B* **23**, 5048 (1981).