Journal of Solid State Chemistry **148,** 513–516 (1999)
Article ID jssc.1999.8455, available online at http://www.idealibrary.com on IDEAL®

BRIEF COMMUNICATION

Structural Visualization of α-SnSe by Atomic Force Microscopy

Julián Morales,[1] Luis Sánchez, and Jesús Santos

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Córdoba, Avda. San Alberto Magno s/n, E-14004 Córdoba, Spain

Received July 6, 1999; accepted July 22, 1999

The surface structure of SnSe was studied by atomic force microscopy (AFM). The measured periodicities in the (100) and (101) planes as obtained from AFM images are consistent with those derived from the theoretical SnSe crystalline cell. The slight differences observed are the likely result of surface relaxation induced by the friction forces between the tip and the substrate. © 1999 Academic Press

INTRODUCTION

In this decade, scanning probe microscopic technique have emerged as powerful tools for structural visualization at the atomic level. This accounts for the increasing use of these methods to examine the intimate structure of many materials (1). In this context, chalcogenide compounds such as TiS_2 (2), TaS_2 (3), PbS (4), α-SnS (5), and SnS_2 (6); misfit layered compounds such as $(PbS)_{1.18}(TiS_2)_2$ (3, 7); and transition metal di-tellurides (8, 9) have received special attention; their images have accurately revealed salient features hardly detected by alternative techniques.

In the past few years, intensive research has been conducted on the chalcogenides formed 14 element groups of interest as semiconductor materials, photovoltaic materials, and intercalation electrodes for secondary rechargeable lithium batteries. This communication reports the characterization of the α-SnSe phase structure from atomic force microscopy (AFM) images that were interpreted in accordance with its three-dimensional structure. The results testify to the efficiency of AFM for elucidating the surface structure of this chalcogenide.

EXPERIMENTAL

SnSe was prepared by direct synthesis from its elements (Strem products, purity > 99.99%), which were homogeneously mixed in a 1 : 1 stoichiometric ratio. The mixture was pressed onto pellets (4 tons pressure), placed in a vacuum sealed quartz tube, and heated at 900°C for a week. The SnSe compound was obtained as brilliant metallic gray pearls that were cut with a razor blade to obtain different crystals.

Topographic AFM examinations were performed by using a Nanoscope IIIa contact-mode AFM (Digital Instruments) in the repulsive force range, with a type load of ca. 4 nN. Type NP cantilevers (Digital Instruments) with Si_3N_4 tips and a spring constant of 0.12 N/m were employed. The reported atomic scale resolution images are representative of many observations on multiple crystals and are small subsets of images selected from defect-free regions of the surface. After subtracting a background plane to remove specimen tilt, the two-dimensional fast Fourier transform (FFT) filter was used to remove random noise in some images. This procedure is used to enhance those features that are apparent in the raw data. AFM images for the samples were obtained from cleaved fresh surfaces. To ensure that the observed structures were real and self-consistent mica was used as the calibration sample. The periodicity of the hexagonal rings recorded was 5.19 ± 0.04 Å, in fairly good agreement with the unit cell dimension of muscovite along *a* direction.

RESULTS AND DISCUSSION

Under the experimental conditions used, the crystals obtained crystallized exclusively in the α-SnSe form, as confirmed by the consistency of X-ray powder diffraction (XRD) pattern with the presence of a single phase. The XRD pattern was indexed in the orthorhombic system, with the following unit cell parameters: $a = 11.477_8$ Å, $b = 4.18_1$ Å, and $c = 4.351_4$ Å. These values are coincident with those listed in the JCPDS card (10).

The structure of SnSe is highly affected by the stereochemical effect of the inert pair, which prevents the low-temperature form, α-SnSe, from adopting a high-symmetry

---

[1] To whom correspondence should be addresses. Fax: 34-957-218606; E-mail: iq1mopaj@lucano.uco.es.

0022-4596/99 $30.00

structure such as that of NaCl. In fact, α-SnSe possesses a layered structure that can also be regarded as a highly distorted version of the NaCl structure in which Sn(II) has three pyramidal Se atom neighbors (11), two located in the plane of the layer and one at a short distance normal to this plane. The atomic positions were examined in the *Pnma* space group also adopted by α-SnS, which is isostructural with α-SnSe, as they have the same cation and anions of similar radii ($r_{\mathrm{Se}^=}$: 1.98 Å and $r_{\mathrm{S}^=}$: 1.84 Å). In this group, the Sn and Se atoms are located at 4*c* positions with coordinates (x, 1/4, z) and ($1/2 + x$, 1/4, $1/2 - z$) where $x_{(\mathrm{Sn})} = 0.1194$; $z_{(\mathrm{Sn})} = 0.1198$, $x_{(\mathrm{Se})} = 0.8505$, and $z_{(\mathrm{Se})} = 0.4793(3)$.

The layered structure of α-SnSe is depicted in Fig. 1a; the projected structures on the (100) and (101) planes are shown in Figs. 1b and 1c. These graphs were obtained by taking into account the above considerations and using the Crystal92 program (12). Figures 1b and 1c include three directional vectors intended to facilitate the study of interatomic distances in this structure. The profiles in the γ direction in Fig. 1b show the differential heights of the atoms and reveal the protusion of the tin atoms out the layer. The actual interatomic distances are defined by parameters α and β; on the other hand, γ is the distance between Se and Sn atoms (this latter element as projected on the Se plane).

Figure 2 shows an enlargement of the AFM image obtained for a fresh surface corresponding to the (100) plane in the SnSe compound recorded at a scan size and the rate of 400 × 400 Å and 30 Hz, respectively. The figure also shows the distances measured along the α, β, and γ directions, on the bright spots in the image (a filtered AFM image for easier visualization). However, the interatomic distances

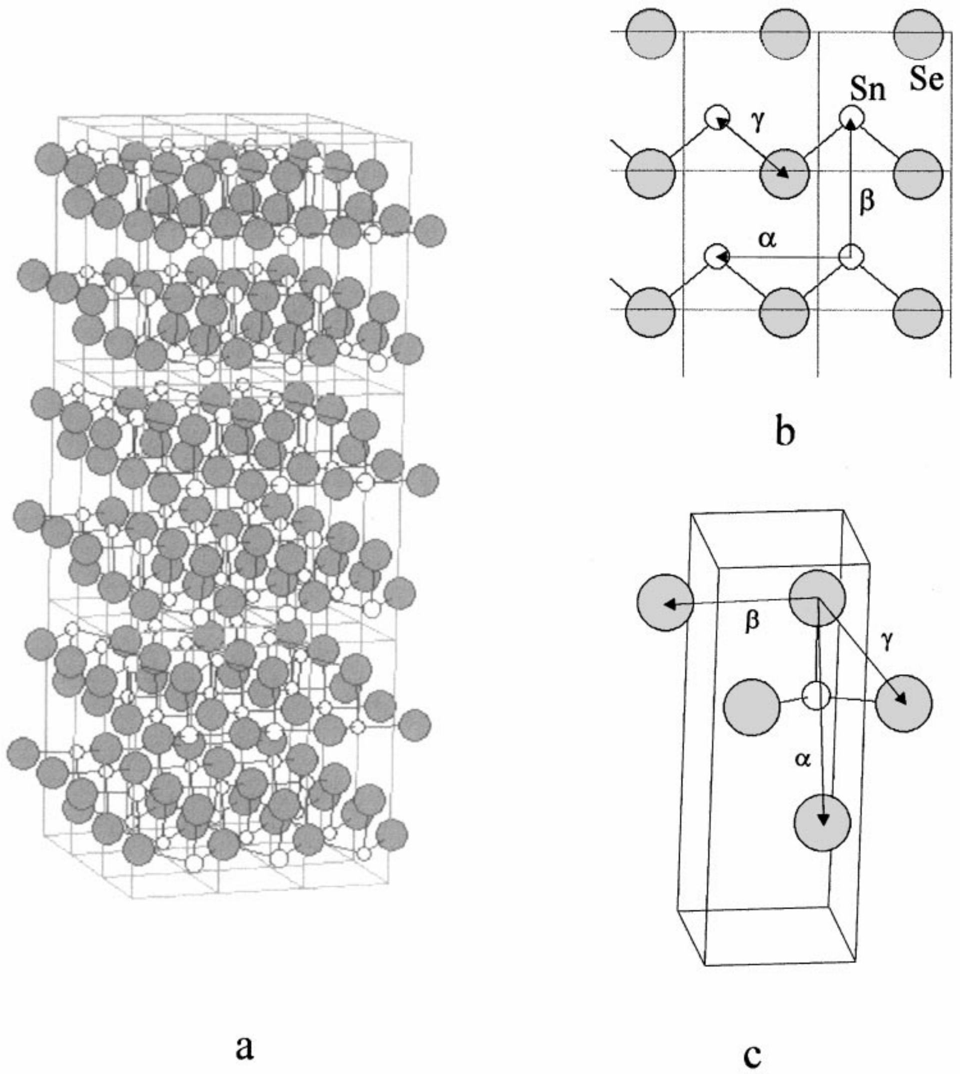

FIG. 1. (a) Orthorhombic crystal structure of α-SnSe, (b) layered structure of α-SnSe projected on the (100) plane, and (c) tridimensional view of the (101) plane.

shown were the result of several measurements in various unfiltered images. The topographic image contains a pseudo-centered rectangular structure, with a distance of 4.27_4, 4.5_3, and 2.70_5 Å in the α, β, and γ direction, respectively. These values are very close to the calculated interatomic distances ($\alpha = 4.18$ Å, $\beta = 4.35$ Å and $\gamma = 2.72$ Å). Figure 2 allows one to evaluate the height difference along the a-axis between Se and Sn atoms. The calculated value, 0.21 Å, is 0.09 Å smaller than that obtained from geometrical considerations, which can be explained in two ways. First, exfoliation of the crystal surface leads to a (100) plane in which the atoms lose coordination with adjacent atoms above them (5). This may cause the structure to relax and hence introduce slight changes in its interatomic distances. Alternatively, this subtle structural modification may be induced by an interaction between the sample and the tip, as reflected in the nonuniform brightness of the different spots in the AFM image.

Although most of the crystal images recorded were fairly consistent with the atom arrangement of the (100) plane, Fig. 3 shows a filtered AFM image recorded at 35 × 35 Å and 128 Hz that reveals a different crystal face. In fact, the image shows a centered rectangular structure for Se atoms. This atom arrangement can only be correlated with the ($h0l$) plane. The three-dimensional view of a (101) plane in Fig. 1c is consistent with the atom distribution observed in the AFM image. The theoretical interatomic distances in this plane are $\alpha = 6.07$ Å, $\beta = 4.18$ Å, and $\gamma = 3.79$ Å. Also, Se and Sn atoms in this plane differ by 0.43 Å in height. The distances measured over the spots in this topographic image correspond to 6.07_9, 4.16_5, and 3.90_5 Å along the α, β, and γ directions, respectively (Fig. 3). Moreover, Se atoms protrude over Sn atoms along the α direction. The calculated distance between both atoms was 0.46 Å. The good agreement between the theoretical and the calculated interatomic distances justifies assuming that the working

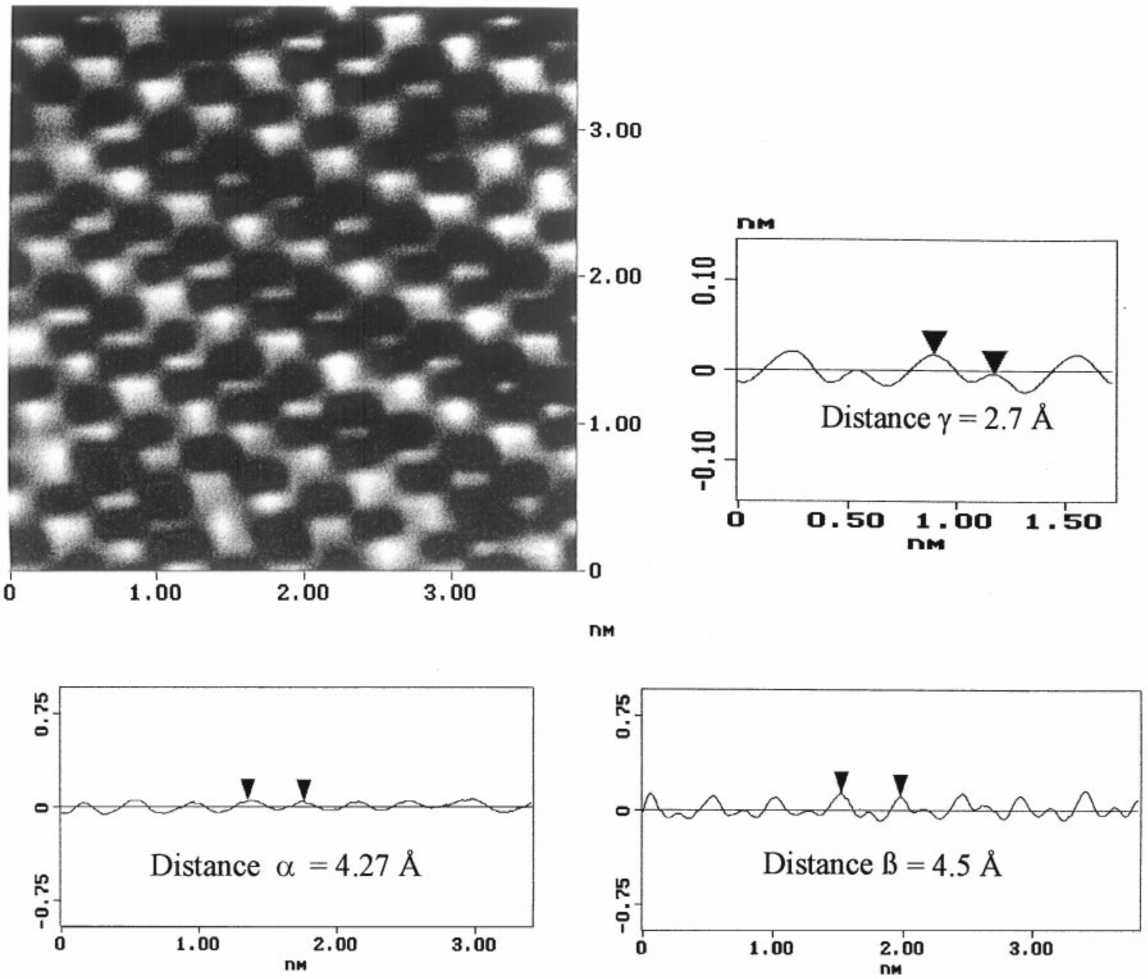

FIG. 2. AFM, FFT filtered and amplified, topographic image obtained from a 400 × 400 Å 30 Hz scan, and height profiles along the α, β, and γ directions.

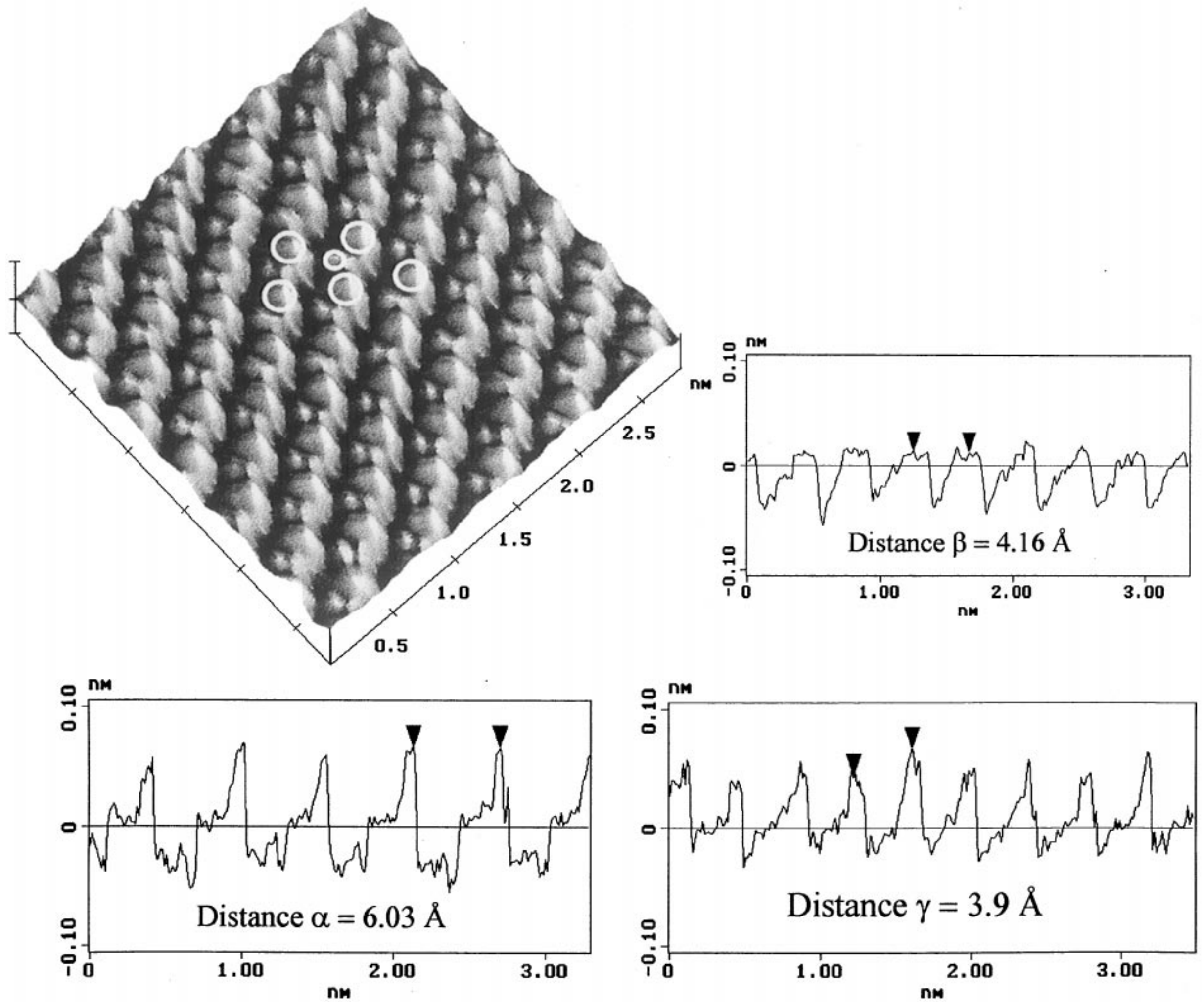

FIG. 3. AFM, FFT filtered topographic image obtained from a 35 × 35 Å, 128 Hz scan, and height profiles along the α, β, and γ directions.

plane is a (101) plane. It is worth noting the height difference between alternate rows of Se atoms along the γ direction in the real structure. This is barely perceptible in the height profile along the γ direction (Fig. 3), where, however, Se atoms tend to lie in the same plane. This finding, and the small differences between the observed and the calculated distances, may be associated to surface relaxation induced by the tip.

ACKNOWLEDGMENTS

This work was supported by Spain's Ministerio de Educación y Cultura (CICYT Project PB95-0561) and the Junta de Andalucía (Group FQM-175).

REFERENCES

1. S. N. Magonov and M.-H. Whangbo, "Surface Analysis with STM and AFM." VCH, Weinheim, 1996.
2. C. Wang, L. Dotson, M. McKelvy, and W. Glaunsinger, *J. Phys. Chem.* **99,** 8216 (1995).
3. A. R. H. F. Ettema, Ph.D. Thesis, University of Groningen, The Netherlands, 1993.
4. A. R. H. F. Ettema, C. Haas, P. Moriarty, and C. Hughes, *Surf. Sci.* **287/288,** 1106 (1993).
5. H. Martinez, C. Auriel, M. Loudet, and G. Pfister-Guillouzo, *Appl. Surf. Sci.* **103,** 149 (1996).
6. L. Hernán, J. Morales, L. Sánchez, and J. Santos, *J. Electrochem. Soc.* **146,** 657 (1999).
7. H. Martinez, C. Auriel, D. Gonbeau, M. Loudet, and G. Pfister-Guillouzo, *Appl. Surf. Sci.* **125,** 259 (1998).
8. S. Kim, S. Park, I. C. Jeon, C. Kim, C. Pyun, and K. A. Yee, *J. Phys. Chem. Solids* **58,** 659 (1997).
9. H. Bengel, H.-J. Cantow, S. N. Magonov, L. Monconduit, M. Evain, W. Liang, and M.-H. Whangbo, *Adv. Mater.* **6**(9), 649 (1994).
10. JCPDS-ICDD card no. 32-1382.
11. A. F. Wells, "Structural Inorganic Chemistry," 4th ed., p. 936. Oxford University Press, London, 1975.
12. R. Dovesi, V. R. Saunders, and C. Roetti, "Crystal92: An ab-initio Hartree-Fock LCAO Program for Periodic Systems." University of Turin, Italy, 1994.