# Electronic structure of natural self-organized PbS-Bi$_2$S$_3$ twinning superlattices

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The electronic structure of naturally occuring self-organized twinning superlattices based on PbS-Bi$_2$S$_3$ alloy is calculated and discussed. It is found that these structures have many features common to the conventional ''man-made'' superlattices, which, together with their stability against interdiffusion and interface roughness problems, makes them very attractive for further theoretical and experimental research, and possible applications. [S0163-1829(97)08715-8]

Semiconductor superlattices, normally comprising the modulation of the crystal composition and/or the doping along the structure, have traditionally been made by sophisticated methods such as molecular beam epitaxy (MBE) or metal-organic chemical-vapor deposition. Recently, however, some research effort has been devoted to the ''self-organized'' growth of superlattices. This is clearly an attractive route, where the superlattices would, in effect, fabricate themselves. Spontaneous short period (CuPt-type) ordering is encountered in some semiconductor alloys, InGaP$_2$ and AlInP$_2$ for instance,[1] with the period twice that of the bulk material. The corresponding electronic structure is different from that of a random alloy, but, due to the short period, is far from having the desired appearance of narrow minibands with anisotropic two-dimensional (2D) carrier gasses, characteristic of superlattices. Longer period spontaneous ordering in semiconductor alloys may appear in surface layers,[2] resulting in surface superlattices with the periodicity of $\sim 200$ Å. Another recent discovery is the sinusoidal composition modulation with the periodicity $\sim 18-32$ Å, that appears in the strained system ZnSe-ZnTe when grown on a misaligned substrate.[3]

Yet another example of self-organization in semiconductors is polytypism. The phenomenon, known long before the development of the field of superlattices, was considered in the present context much more recently.[4] Appearing mainly in SiC and ZnS, among the semiconducting materials, polytypism may provide a rather long-period modulation of the structure, based on a different principle than that in conventional superlattices: in such cases the zinc-blende and wurtzite phases of the same material are interlaced. Yet, with the formation energies of various polytypes being very close to each other, it is presently rather difficult to grow the superlattice with precisely required period.

In this paper we consider another class of self-organized superlattice structures. These have also been known for some time and occur in natural minerals, though never considered as potentially useful semiconductor superlattices. This class is based on the phenomenon of ''chemical'' twinning as found in alloys of PbS and Bi$_2$S$_3$.

Twinning, i.e., the reversal of atomic stacking sequence along some axis, is a commonly occuring phenomenon in a number of crystals, including many semiconductors. We have recently proposed that it may also be used as a building principle for superlattices.[5] In cases of zinc-blende-type crystals the (111) plane is the most common twinning plane, because such a twin has a very low formation energy as the nearest-neighbor atomic distances and bond angles remain unchanged. The same is approximately true for twins in rocksalt-type semiconductors. Although the crystal structure and the material composition are identical on both sides of the twin boundary, the wave function symmetry mismatch due to the opposite orientation giving rise to considerable electron scattering at the periodically distributed interfaces. Indeed, calculations for Si- or Ge-based,[5] and for PbS-based[6] superlattices indicate a prominent miniband structure. Unfortunately, except for a rather irregular twinning ''superlattice'' that appears in free-standing GaAs quantum wires,[7] none of these structures have been realized so far: only a single high-quality twin interface has been fabricated.[8]

Twinning of a somewhat different type is the building principle of another kind of twinning superlattices, which occur spontaneously in alloys of semiconductors lead sulfide and bismuth sulfide. The existence of special compositions of PbS-Bi$_2$S$_3$ which form superlattice-type structures in mixed lead-bismuth sulfide ore minerals has been known for quite some time. These have been extensively studied from the crystal chemistry viewpoint.[9–12] Minerals with the (ideal) compositions $3\times$PbS-Bi$_2$S$_3$ and $6\times$PbS-Bi$_2$S$_3$ are named lillianite and heyrovskyte, respectively. These two are the only known compositions making stable superlattice structures. Although the mineral samples contain a minor (in the few % range) amount of impurities, the overall structure remains unaffected. These natural superlattices have also been grown in laboratory,[13,14] by either melt crystallization or by vapor phase epitaxy (not MBE). Other examples of twinning superlattices are based on PbS-Bi$_2$S$_3$-Ag$_2$S and PbS-Bi$_2$S$_3$-Cu$_2$S, some existing as natural minerals and others being synthesized in the laboratory.[12] These are less thoroughly investigated than lillianite and heyrovskyte, and here we concentrate on the latter structures. While the crystal chemistry of these structures has been studied rather extensively, there seem to be no studies, either theoretical or experimental, of their electronic or optical properties. Nor have these structures ever been considered as possible *semiconductor superlattices*.

A quite simplified explanation of the formation of superstructures in PbS-Bi$_2$S$_3$ alloys would be the following. In the crystallization process the atoms prefer to occupy the positions corresponding to the rocksalt (i.e., PbS-like) struc-
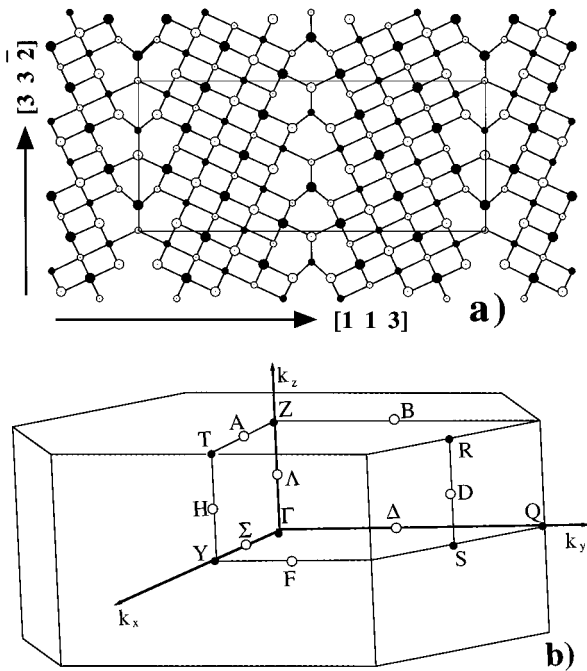
FIG. 1. (a) The side view of the idealized structure of the (9,9) superlattice (heyrovskyte) unit cell. Empty and solid circles denote the sulphur and metal atoms, respectively, on a particular $(1\bar{1}0)$ plane (large circles) or on the first neighboring $(1\bar{1}0)$ plane (small circles). The direction or plane notation corresponds to the cubic system of the underlying ''bulk slabs.'' The thin rectangle outlines the unit cell; (b) The first Brillouin zone of the base centered orthorhombic unit cell of (6,6) and (9,9) superlattices, with the irreducible part indicated.

ture, which, however, requires an equal number of metal and nonmetal atoms in the composition. There is thus a ''shortage'' of metal atoms in the alloy. Instead of forming a rocksalt-type structure with a large number of vacancies, the crystal finds a more favorable way out—to make a superlattice structure with (113) as the twinning plane so that some metal atoms are ''shared'' between nonmetal atoms. The frequency of twinning plane occurrence depends on the alloy composition and is such that the shortage of metal atoms is exactly compensated for. The idealized structure of a heyrovskyte $Pb_{12}Bi_4S_{18}$ unit cell is displayed in Fig. 1(a). It clearly includes slabs of bulk rocksaltlike material, rotated in respect to each other by $180^\circ$ about the [1 1 3] axis, joined at the (113) twinning planes, both labeled with respect to the cubic unit cell of the underlying material. The ''shared'' metal atom comes exactly at the twin boundary, so that the full structure is not much distorted. Viewed as superlattices, the two structures may be labeled in terms of the ratio of the width of two half-periods and the width of the underlying rocksalt elementary cell in the [1 1 3] direction. They may thus be labeled as $(n,m)$ twinning superlattices, with $n=m=6$ and $n=m=9$ for lillianite and heyrovskyte, respectively.

The unit cell of both superlattices is base-centered orthorhombic, with the two sides of the base measuring ideally $a/\sqrt{2}$ along $[1\bar{1}0]$ and $a\sqrt{22}/2$ along $[33\bar{2}]$, with $a$ denoting the cubic lattice constant. The third side measures $(n+m)a/\sqrt{11}$ along the [113] direction. The ratio of mea-

sured unit-cell dimensions[10,11,14] deviates very slightly (within 1%) from the idealized value. The lillianite unit-cell measurements (in Å) are $4.112\times13.522\times20.608$, and those of heyrovskyte $4.132\times13.697\times31.355$, with the corresponding effective cubic lattice constants of 5.759 and 5.820 Å, respectively. In real structures some amount of atomic relaxation takes place, mostly close to twinning interfaces. The relaxed atomic coordinates, as well as ordering of metal atoms from layer to layer, have been quite precisely measured for both lillianite[10] and heyrovskyte.[11] In lillianite it was found that the interface metal atoms are Pb only, and all other layers have a 50-50 % mixture of Pb and Bi. In heyrovskyte the interface metal atoms are Pb, two layers next to it contain Pb-Bi (50-50 %), and the three layers in the middle only Pb atoms. For either phase no significant atomic ordering in the (113) plane was measured. None of these effects perturb the symmetry of the unit cell. The first Brillouin zone corresponding to the base-centered orthorhombic unit cell[15] is displayed in Fig. 1(b).

In the band structure calculations we employed the supercell method, using the nonlocal empirical pseudopotential approach. The form functions for S and Pb atoms are constructed from graphical data in Ref. 16, and for Bi from the expressions given in Ref. 17. For convenience, all these (in the case of Bi, the local part only) were fitted to the standard form $V(q)=a_1(q^2-a_2)/\{\exp[a_3(q^2-a_4)]+1\}$, where $a_{1-4}=$ (0.208, 2.967, 2.041, 2.720) for S, (0.256, 2.171, 1.343, 1.829) for Pb, and (0.818, 3.831, 0.505, $-3.468$) for Bi. The nonlocal part for Bi was taken from Ref. 17. In the absence of precise knowledge about distribution of metal atom species on the (113) plane, we employed the virtual crystal approximation for atomic positions with a mixture of Pb and Bi. The plane wave basis was chosen, with the kinetic energy cutoff set at 5.1 Ryd, corresponding to 747 and 1165 plane waves at the zone center for (6,6) and (9,9) superlattices, respectively. To keep the size of the problem reasonable, the spin-orbit coupling was neglected, though it is generally important in heavy elements compounds. However, in rocksalt bulk PbS the spin-orbit coupling affects the main band gap by $\sim$ 0.1 eV while leaving the valence and conduction bands doubly degenerate (some remote bands are much more affected). Since a significant part of the structure is rocksaltlike, we expect the error introduced not to exceed the reliability limits of the method and the values of parameters used, the latter not being readjusted to this specific system due to the lack of any experimental data. In any case, due to the approximation already made, there is hardly any point in including the spin-orbit coupling in the calculations.

The band structure was calculated at a number of **k** points along a few symmetry directions in the Brillouin zone. The highest filled and the lowest unfilled bands were found to be well separated throughout it, indicating that these structures are semiconductors. The top of the highest filled (valence) band in (6,6) superlattice was found at a point $k=0.5(2\pi/a)$ away from $\Gamma$ along the $\Delta$ line, and the bottom of the lowest empty (conduction) band at the $Y$ point. This indirect band gap of 0.97 eV is, however, only marginally lower from the direct gap of 1.07 eV at the $Y$ point. For the (9,9) superlattice extrema of both bands are at the $Y$ point, and the band gap is direct, amounting to 0.69 eV. The calculated band gaps are intermediate to the values for bulk PbS
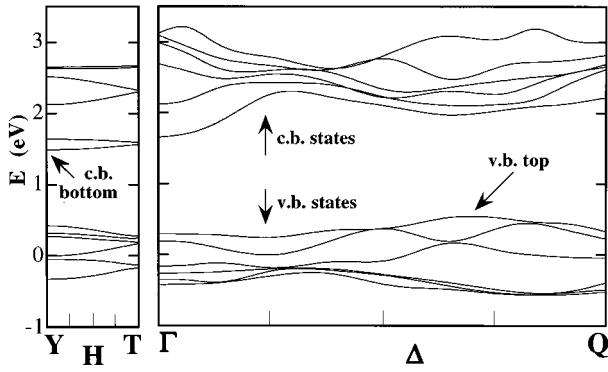
FIG. 2. The dispersion of the six highest valence and six lowest conduction minibands in the (6,6) superlattice along some characteristic directions. The $H$ line is along the superlattice "growth direction" [113]. The zero of energy is arbitrarily chosen.

and $Bi_2S_3$ (i.e., 0.30 and 1.38 eV, respectively). That the band gap of the (9,9) superlattice is lower than that of (6,6) is in accordance with what one would expect based on the content of PbS and the period length (which, within the superlattice terminology, respectively, give the "bulk" and "quantization" contributions to the total band gap). In Fig. 2 we give the dispersion of six valence and six conduction bands (i.e., minibands) for the (6,6) superlattice along the $H$ line, which coincides with the superlattice "growth direction" [1 1 3], and along the $\Delta$ line. The corresponding data for the (9,9) superlattice along the $H$ and $\Sigma$ lines are given in Fig. 3. Low dispersion in the superlattice growth direction and presence of minigaps, typical for 2D systems, are more prominent in the (9,9) case. These effects are due to both the symmetry mismatch of the two half-periods[5,6] and the non-bulk-like interface regions which constitute significant "barriers" to electron transmission.

In Fig. 4 (left) we give the calculated total charge density on the $(1\bar{1}0)$ plane of the (9,9) supercell. The bonding picture is consistent with the ionic model, with a significant degree of covalency, indicating the strength of the material. The atoms at the interface retain the sixfold coordination but with distorted bond angles, which is evident in Fig. 4 (right) for the (113) interface plane.

The wave functions corresponding to various minibands in these structures are more complicated than in many other semiconductor superlattices. In Fig. 5 we give the (113) plane averaged charge densities for the three highest valence
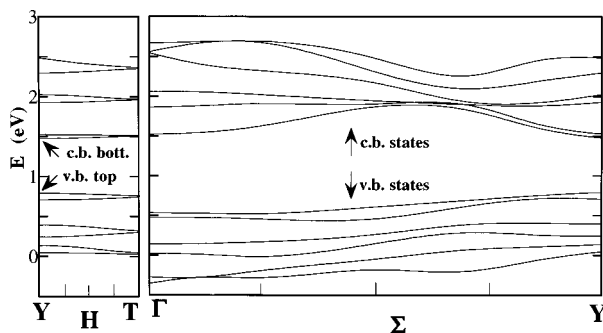


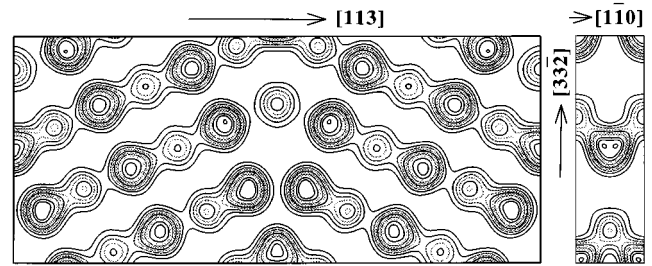FIG. 4. The total charge density on the $(1\bar{1}0)$ plane passing through the base-center sulphur atoms of the (9,9) supercell (left), and on the (113) plane at the interface (right). High density regions correspond to S and lower density ones to Pb-Bi atoms.

and three lowest conduction minibands at the $Y$ point, as they vary along the (9,9) superlattice axis. The presence of nodes of the charge density at the interface for some of the bands indicates the strength of the scattering.

In conclusion, we calculated the band structure of natural, self-organized twinning superlattices based on PbS-$Bi_2S_3$ alloys, and found that they are semiconductors and have 2D characteristics, just as the conventional superlattices do. In view of their relatively easy fabrication it is hoped that this will attract further theoretical and experimental research on their properties and applications. The fact that only two stable phases exist in the PbS-$Bi_2S_3$ system does limit the versatility of these structures but, on the other hand, this could be considered as a distinct advantage. The micrographs in Ref. 13 reveal that the interfaces are perfectly flat. Also, interdiffusion was observed to take place only in samples quenched from the melt.[13] While polytype superlattices and (111) twinning superlattices could also be free of interface roughness problems, the stability of the superlattice period may not always be guaranteed. On the other hand, the (113) chemical twinning superlattices, by the very nature of their formation, are expected to be very stable structures. Some amount of fine tuning of the band structure may be achieved through appropriate isovalent substitutions, e.g., replacing
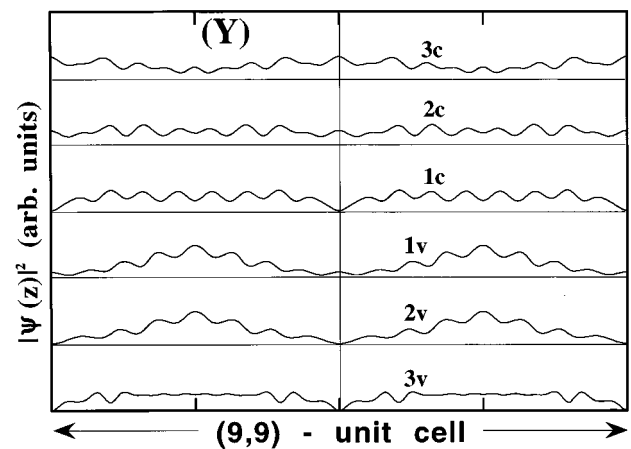


FIG. 3. Same as in Fig. 2, but for the (9,9) superlattice.



FIG. 5. Planar averaged charge density along the (9,9) superlattice growth direction [1 1 3] for the three highest valence and three lowest conduction band states at the $Y$ point.

some of sulphur by (Se, Te), or some of Bi by Sb, etc., as occurs in the composition of natural minerals of this type.[12,14] This kind of tunability does have limits, however, because highly or fully substituted crystals may have a different and more complex structure than the twinning superlattices. Nonisovalent impurities, also occuring in minerals, constitute their natural dopants, leading to the possibility of artificial doping of grown crystals.

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