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Authors

Chadi, D.J.
Cohen, Marvin L.

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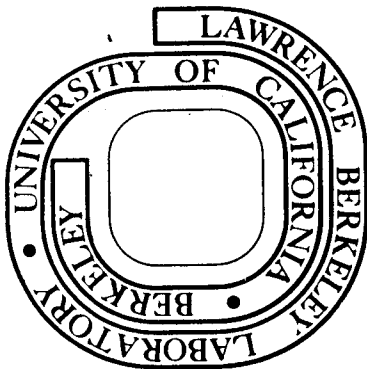
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Intrinsic (111) Surface States of Ge, GaAs and ZnSe*

D. J. Chadi and Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division,

Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

The intrinsic (111) surface states of Ge, GaAs and ZnSe are studied using the tight-binding method. The local density of states of atoms on different layers are calculated and the various types of surface states are discussed. The effects of relaxation on the surface states are examined for Ge.

I. Introduction

The tight-binding (TB) method is very useful in providing a practical and relatively simple way of studying the electronic surface states of semiconductors. By using a small number of interaction parameters it is possible to obtain good results for both bulk¹ and surface states of diamond² and zincblende type³ compounds. We have previously¹ obtained the (TB) parameters appropriate for Ge, GaAs and ZnSe and have discussed³ briefly the results of our calculations on the (111) surface states of Ge and GaAs. Similar calculations on the (110) surface of diamond and zincblende semiconductors

have also been done⁴ recently. In this paper we wish to describe in more detail the (111) surface states of Ge, GaAs and ZnSe. Surface reconstruction is not considered in our calculation, however, the effects of surface relaxation are studied for Ge. The local density of states (LDS) for surface atoms and atoms close to the surface layer are calculated. The character and degree of localization of the charge density associated with the various surface states are also calculated.

This paper is organized in the following way. In Section II we briefly discuss some aspects of the calculation and give the interaction parameters we have used. The surface states of Ge with and without relaxation effects are studied in Sec. III. The (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of GaAs and ZnSe are discussed in Section IV.

II. Calculation

The calculation of surface states by the TB method for group IV materials has been discussed by Hirabayashi⁵ and we have extended the method to zincblende compounds. In the calculation of surface states we have taken a system consisting of a finite number, N , of atomic layers. To distinguish surface states from bulk states without ambiguity we have taken $N = 16$. For GaAs or ZnSe the atomic layers are composed only of one type of atom which alternate between the Ga-type and As-type atoms.

The interaction parameters for Ge, GaAs and ZnSe were determined¹ by fitting the bulk valence bands. Fig. 1 shows the directed orbitals on two adjacent tetrahedra in a diamond or zincblende crystal with the orbital 1 being along the (111) direction. Denoting the Hamiltonian matrix elements between orbitals i and j by $(i|j)$ we have taken the following interactions (in eV) into account for Ge:

$$\begin{aligned}\gamma_1 &= (1|1) = 0. & \gamma_2 &= (1|2) = -2.10 \\ \gamma_3 &= (1|8) = -5.46, & \gamma_4 &= (2|8) = -0.07 \\ \gamma_5 &= (2|5) = -0.45, & \gamma_6 &= (2|7) = 0.60.\end{aligned}$$

For GaAs (ZnSe), assuming the orbitals 1-4 and 5-8 refer to As(Se)_{and} Ga(Zn) respectively, we have used the following parameters (in eV)

$$\begin{aligned}\alpha_1 &= (1|1) = -1.36(-2.14), & \beta_1 &= (8|8) = 2.25(5.57) \\ \alpha_2 &= (1|2) = -1.55(-2.26), & \beta_2 &= (7|8) = -2.35(-1.93) \\ \alpha_3 &= \beta_3 = (1|8) = -4.4(-4.12) \\ \alpha_4 &= (2|8) = -0.92(-0.51) \\ \alpha_4 &= \beta_4 = (1|5) = -0.03(-0.32) \\ \alpha_5 &= (2|5) = -0.28(-0.23) \\ \alpha_6 &= (2|7) = 0.66(0.62)\end{aligned}$$

To simulate the effects of surface relaxation for Ge we have assumed that the surface layer moves inward⁶ by 0.3 Å and we have changed the interatomic interaction parameters at the surface according to⁷

$$H_{ij} = H_{ij}^0 \exp(\beta \Delta R)$$

where H_{ij}^0 is the matrix elements given above and ΔR is the

change in the nearest-neighbor distance. This approximation works well in the case of Si.² We have used $\beta = 10.4/a$ where a is the cubic lattice constant. The intra-atomic interaction parameter γ_2 was also changed (as in Ref. 8) to account for the change in the s-p character of the orbitals resulting from relaxation.

We have calculated the local density of states $N_\ell(E)$ of atoms on different layers for Ge, GaAs and ZnSe. To do this the expression

$$N_\ell(E) = \sum_i \sum_{\underline{k},n} \delta(E - E_n(\underline{k})) |\langle \psi_{\underline{k},n} | \phi_i \rangle|^2$$

was used where $\psi_{\underline{k},n}$ is the total wavefunction corresponding to the n th eigenvalue, and the sum i is over the orbitals of the atoms on a particular layer. All the densities of states curves discussed in the next section have been normalized to the bulk (or crystalline) density of states to facilitate comparison between them.

III. Results

A. Ge: Unrelaxed Surface

In Fig. 2 we show the total density of states of 16 layers together with the LDS of the surface layer. Figures 3 and 4 show the LDS of a layer just below the surface (denoted by $(\text{Ge})_2$) and the LDS of atoms four layers below the surface $(\text{Ge})_5$. The total density of states of 16 layers (Fig. 2) is very similar to the bulk (or crystalline) density of states shown in Fig. 4, except for structure arising from

the two surfaces. In particular the structures S_1 and T_1 are associated with localized surface states and can be seen to become weaker as we go away from the surface. The peak denoted S_1 is seen in energy loss spectroscopy; it has an integrated weight equal to one electron per surface atom. It has a width of about 1 eV and lies 0.4 eV above the top of the bulk valence bands E_v . Over 70% of the charge density associated with this peak is localized in the first two layers at the surface: 52% at the surface layer and 20% on the layer below. The Fermi energy E_F lies about 0.6 eV above E_v inside the S_1 peak. The energy E_s in Fig. 1 gives the energy at which the integrated LDS of surface atoms equals the number of surface atoms (so that the surface is neutral); it is less than 0.1 eV away from E_F in the unrelaxed surface configuration.

The contribution to the S_1 peak comes mainly from the dangling bond states and also from the back-bonding states of the atoms on the layer below the surface. As seen in Figs. 2-4 these states become progressively weaker as we go away from the surface and virtually disappears within four to five layers below the surface.

The T_1 peak in Fig. 2 corresponds to back-bonding surface states. Only certain wavevectors in the region near the point K (corner of the hexagonal Brillouin zone) contribute to this peak. At K the charge density associated with T_1 has a concentration of 80% on the surface layer.

The average contribution over the Brillouin zone is however much smaller and the integrated weight of the structure is equivalent to 0.25 electrons per surface atom.

The structures R_1 and R_2 (Fig. 2) are resonant states also associated with back-bonding states. The wavefunctions associated with these states have a charge density of about 0.15 electrons per atom at the surface layer. The D_1 structure (Fig. 2) is not associated with any surface states but apparently results from the use of a finite number of layers; the states involved have a small dispersion throughout the Brillouin zone.

The Figs. 2-4 show that the LDS of atoms on the surface layer and on layers near the surface are remarkably similar to the total density of states (of 16 layers) or to the bulk density of states (except, of course, for the presence of surface structure). Most of the small step-like structures evident in these Figs. result from the use of a finite number of planes in the calculations and they gradually disappear as more planes are used. We have smoothed out the step-like structures and the noise in the densities of states by using Gaussian functions 0.15 eV wide at half-maximum.

The structures we have obtained for the (111) surface of Ge are very similar to those for a (110) surface⁴ except for the T_1 peak which is absent for the (110) surface. The existence of the T_1 structure is however very sensitive to the value of the structure factor describing the relative positions of the atoms on the surface.

B. Ge: Relaxed Surface

The effect of surface relaxation on the LDS of the atoms on the surface layer is shown in Fig. 5. As can be seen relaxation results in the appearance of new surface states denoted by S_2 and S_3 and a weakening of the S_1 and T_1 states. There is a broadening of about 0.4 eV in the top valence bands for states near the surface.

The energy E_s which corresponds to the neutrality level for the surface layer is 2.0 eV below E_F . This shift in E_s (relative to the unrelaxed case) would result in an excess charge density of 0.07 electrons per surface atom but this is unlikely since band bending near the surface would cause a redistribution of the surface charge.

The integrated weight of the S_1 peak in the total density of states (Fig. 5) is still equivalent to one electron per surface atom. But the charge density associated with this peak is not strongly concentrated on the surface layer but extends over the first four layers at the surface.

The S_2 and S_3 surface states result from surface relaxation and correspond to back-bonding orbitals of the first two atomic layers. At the K point of the zone the charge associated with the S_2 structure is completely localized on the first two layers. The localization is however much smaller (about 10%) for most of the other points in the zone. The S_3 structure has a weight of 0.35

electrons per surface atom over an energy range of about 3 eV. The T_1 structure is strongly damped by relaxation and this may explain why it has not been observed experimentally. A comparison of Figs. 2-5 shows that relaxation effects are very important in the description of surface states. Although we have treated surface relaxation only approximately here the results give an indication of the type of changes that occur as a result of relaxation.

C. GaAs and ZnSe

The (111) surface is not a cleavage plane for zincblende crystals, however it has recently become possible to prepare such surfaces by Ar^+ bombardment and annealing under ultra high vacuum conditions¹⁰⁻¹² and photoemission^{10,11} energy loss¹² and experiments have been done on GaAs and GaP samples. The (111) surfaces are polar, i.e., the layers alternate between Ga-type and As-type atoms.

In Figures 6-10 we show the results of our calculations on a system consisting of 16 layers. The notation used in these figures is as follows. The various layers are numbered consecutively so that $[Ga]_1$ refers to the gallium and $(As)_1$ to the arsenic surface layers respectively. Layers near the Ga surface are denoted by brackets and those near the As surface by parenthesis. Thus $[As]_2$ refers to the arsenic layer just below the Ga surface layer and $(Ga)_2$ to the gallium layer next to the As surface layer. A similar procedure is also used for identifying the Zn and Se layers in ZnSe.

Let us now examine the detailed structure in the densities of states. A comparison of Figs. 6 and 9 shows the structures in GaAs and ZnSe to be very similar. The only differences between the two are in the width of the surface peaks and the degree of charge localization in each peak. We will discuss these in detail later in this paper. For the moment we will give a general description of the surface states and concentrate on GaAs.

Figure 6a shows the LDS of the gallium surface layer ($[\text{Ga}]_1$), the LDS of the arsenic layer below it ($[\text{As}]_2$), together with the total density of states for 16 layers. The LDS of the As surface layer, $(\text{As})_1$ and the gallium layer next to it, $(\text{Ga})_2$ are shown in Fig. 6b. The structure A_0 corresponds to the first conduction band in the zincblende phase (see also Fig. 8). The peaks A_1, \dots, A_4 are however associated with the various surface states. The peaks A_1 corresponds to a mixture of dangling bond Ga states together with back-bonding As states. The peak A_2 however is almost totally an As dangling bond state. It is interesting to note that nearly all the contribution to the A_1 (A_2) peak comes from atoms near the Ga (As) surface layer. There is, for example, practically no contribution to the A_2 (As-dangling bond state) from As atoms near the Ga surface layer; only As atoms near the As surface contribute to this peak.

The A_3 structure corresponds to Ga surface states which overlap with the bulk valence bands. These surface states

are associated with Ga back-bonding orbitals. Gallium atoms on both the Ga-rich and As-rich sides contribute to the A_3 peak. The localization of the charge density at the surface layer is less for this state than for the A_1 and A_2 peaks. Our calculation also shows As surface states overlapping with bulk bands at -3 eV, near the region that corresponds to the Σ_1^{min} edge for the zincblende case. (The zero of energy in Figs. 6-10 has been chosen at the top of the bulk valence bands. This also happens to be (see Fig. 8) the energy for the top As (Se) surface states.) The A_4 structure corresponds to As back-bonding states and the major contribution to it comes from the As surface layer. There is no contribution to A_4 arising from As or Ga atoms near the Ga rich surface.

We will now examine the character and degree of localization of the various peaks in GaAs and ZnSe. The A_1 structure in GaAs (ZnSe) has an integrated weight of one electron per Ga (Zn) surface atom and the Fermi energy lies in the middle of this peak. The Ga (Zn) dangling orbitals contribute 0.32 (0.55) electrons to the whole peak while the As (Se) back-bonding states next to the surface layer contribute 0.47 (0.33) electrons. About 80% of charge density associated with A_1 is therefore seen to be localized within the first two surface layers with a stronger localization in the case of the more ionic ZnSe.

The integrated weight of the A_2 structure is one electron per As (Se) surface atom. The As (Se) dangling bond orbitals

contribute 0.71 (0.82) electrons to this structure. The Ga (Zn) atoms next to the surface layer make no contribution to this peak but other As (Se) layers near the surface make smaller contributions to A_2 as can be seen from Figs. 6-10.

In the A_3 structure surface states begin near the edge of the band and extend over an energy range of about 1 eV. The localization at the surface of the states associated with A_3 are on the average smaller than those for A_1 and A_2 . The A_3 peak is very interesting in that Ga (Zn) and As (Se) atoms near both the Ga (Zn) rich and As (Se) rich surfaces contribute to it as can be seen from Figs. 6 and 9. The major contribution in GaAs is from Ga back-bonding orbitals located at the Ga surface layer or on Ga atoms on the layer below the As surface. The contribution of As back-bonding orbitals on both the Ga and As side of the surface is about half as large as that coming from the Ga orbitals. In ZnSe the Zn and Se atoms contribute almost equally to the A_3 structure.

The As (Se) back-bonding orbitals on both the As (Se) surface and on atoms next to the Ga (Zn) surface layer also give rise to surface states which are very similar to A_3 . These states occur at -3 (-2) eV in GaAs (ZnSe) for wave-vectors near K.

The A_4 states are very strongly localized on the As (Se) surface atoms. Figure 5 shows the A_4 structure to have a very small overlap with the bulk states. The integrated

weight of A_4 is equivalent to 1 electron per As (Se) surface atom. The As (Se) back-bonding surface orbitals contribute about 0.36 (0.78) electrons and the Ga back-bonding orbitals next to the As surface atoms contribute 0.11 (0.10) electrons.

References

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1. D. J. Chadi and M. L. Cohen (to be published).
 2. K. C. Pandey and J. C. Phillips, Phys. Rev. Letters 32, 1433 (1974).
 3. D. J. Chadi and M. L. Cohen, Solid State Comm. (in press).
 4. J. D. Joannopoulos and M. L. Cohen (to be published).
 5. K. Hirabayashi, J. Phys. Soc. Japan 27, 1475 (1969).
 6. For Si the surface layer has been estimated to move inward by 0.33 A: J. A. Appelbaum and D. R. Hamann, Phys. Rev. Letters 31, 106 (1973).
 7. This form has been found to work well for Si (see Ref. 2).
 8. K. C. Pandey and J. C. Phillips, Solid State Comm. 14, 439 (1974).
 9. J. E. Rowe and H. Ibach, Phys. Rev. Letters 31, 102 (1973); 32, 421 (1974).
 10. W. Ranke and K. Jacobi, Solid State Comm. 13, 705 (1973).
 11. K. Jacobi and W. Ranke, Proc. of the 12th Int. Conf. on the Physics of Semiconductors, Stuttgart (1974) (to be published).
 12. R. Ludeke and L. Esaki (to be published).

Figure Captions

- Figure 1. Directed orbitals on two adjacent tetrahedra in a diamond or zincblende semiconductor. The (111) plane is normal to the bonds 1,8. The possible interactions between these orbitals are discussed in Sec. II.
- Figure 2. Total density of states (solid line) of Ge for a system consisting of 16 layers. The local density of states (dashed line) of surface atoms has been normalized to the total density of states for a better comparison between the two.
- Figure 3. Local density of states (LDS) of Ge atoms on the layer below the surface. Surface states are labelled in Fig. 2.
- Figure 4. Local density of states of Ge atoms four layers below the surface (solid line) and the bulk (or crystalline) density of states (dashed line).
- Figure 5. Total density of states (solid line) of Ge for a system consisting of 16 layers and for a relaxed surface. The local density of states of surface atoms is also shown.
- Figure 6. Total density of states (solid line) of GaAs for a system of sixteen layers (a) and (b). The local densities of states (LDS) of Ga surface atoms denoted by $[Ga]_1$ and the LDS of the As layer $[As]_2$ next to the $[Ga]_1$ are also shown in (a). The corresponding LDS for the As surface are shown in (b).

Figure 7. The LDS of Ga atoms $[\text{Ga}]_5$ on a plane four layers below the $[\text{Ga}]_1$ surface (solid line) and the LDS of $[\text{As}]_6$ atoms five layers below the surface (dashed line) are shown in (a). The corresponding features for atoms below the As surface are shown in (b).

Figure 8. The total density of states of GaAs for a system consisting of 16 layers (solid line) as compared to the bulk crystalline density of states calculated using the same interaction parameters. The dotted zincblende curve refers to the bulk.

Figure 9. The LDS of $[\text{Zn}]_1$, $(\text{As})_1$ surface atoms and the LDS of $[\text{Se}]_2$ and $(\text{Zn})_2$ atoms next to the surface layers. See also caption for Fig. 6.

Figure 10. See caption for Fig. 7.

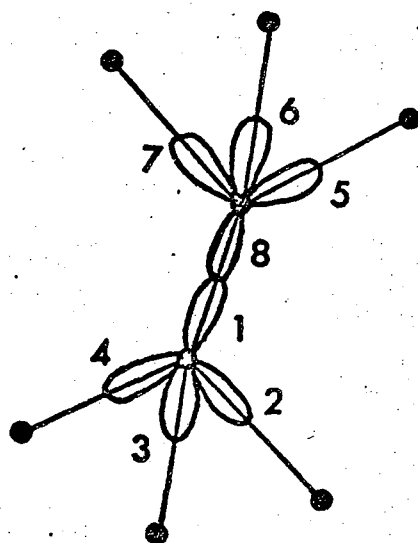


Figure 1

DENSITY OF STATES (arbitrary units)

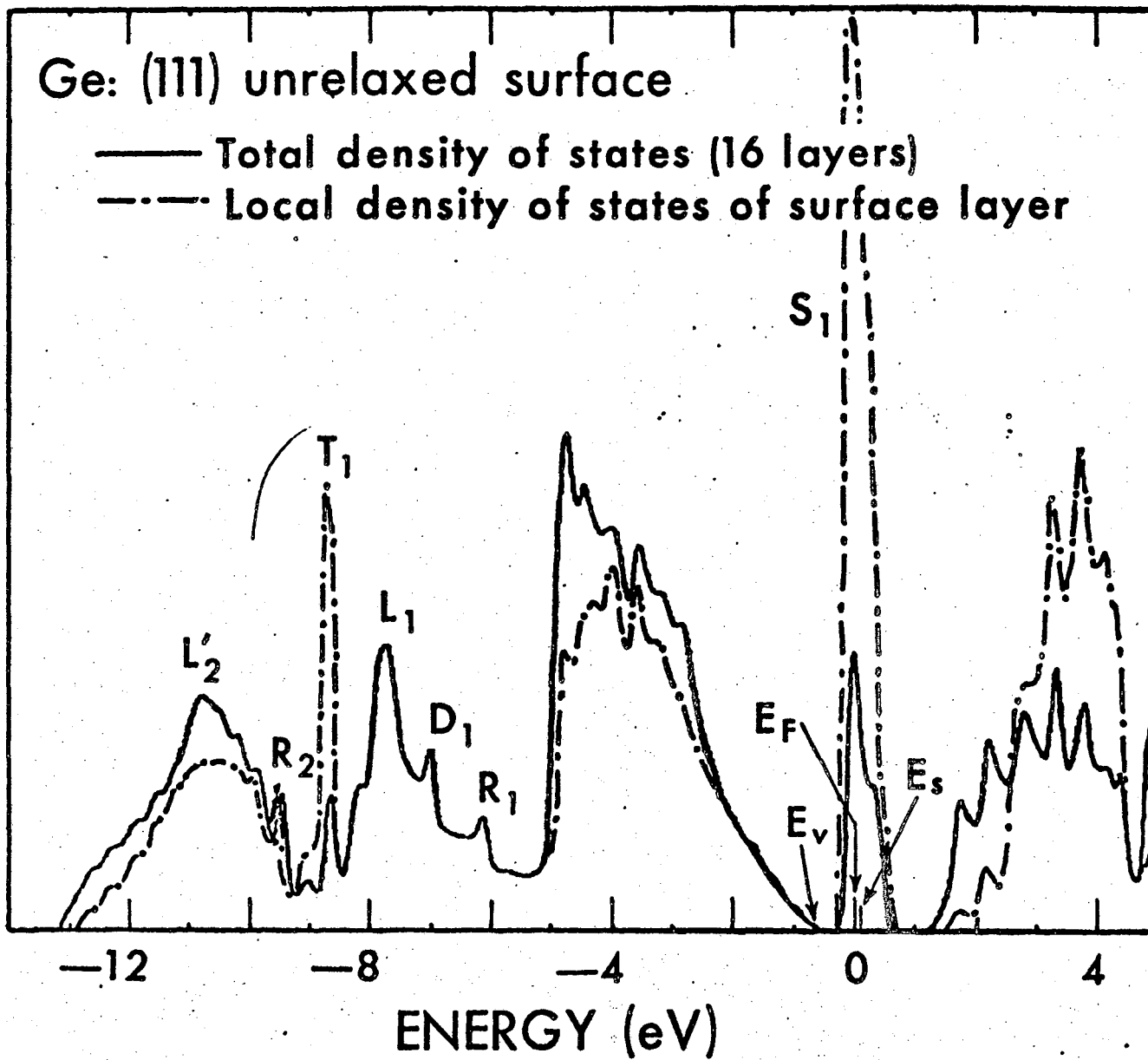


Figure 2

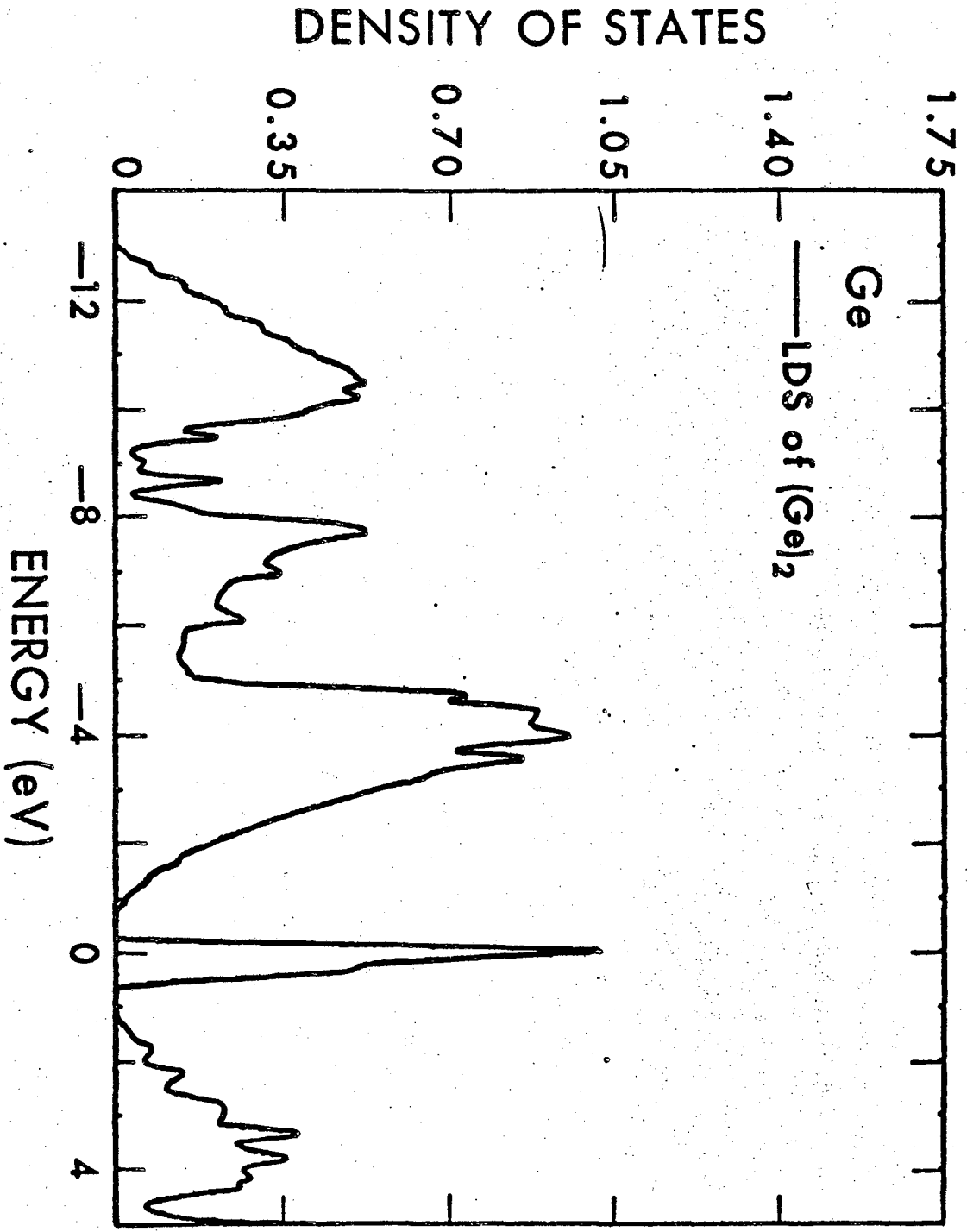


Figure 3

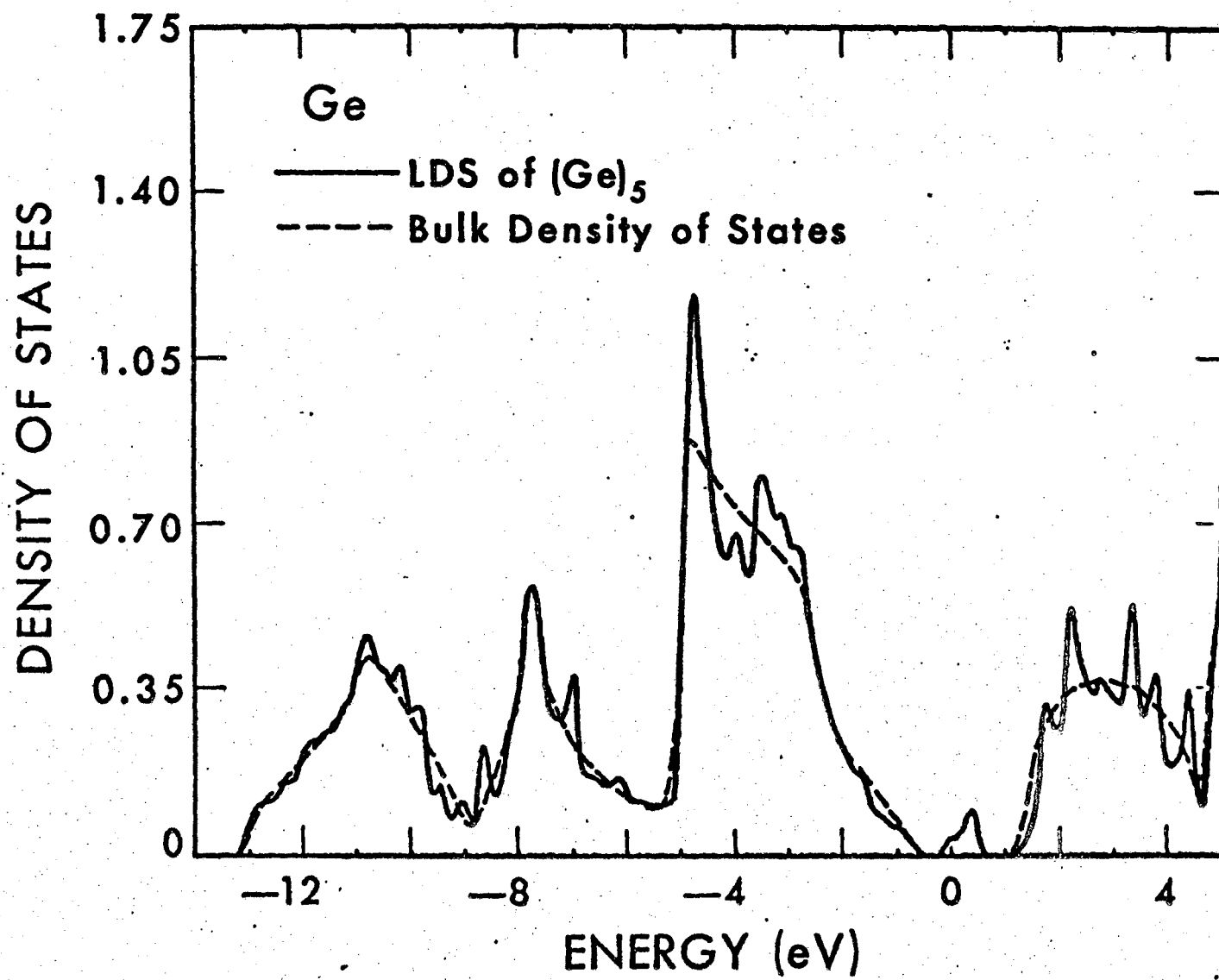


Figure 4

DENSITY OF STATES (arbitrary units)

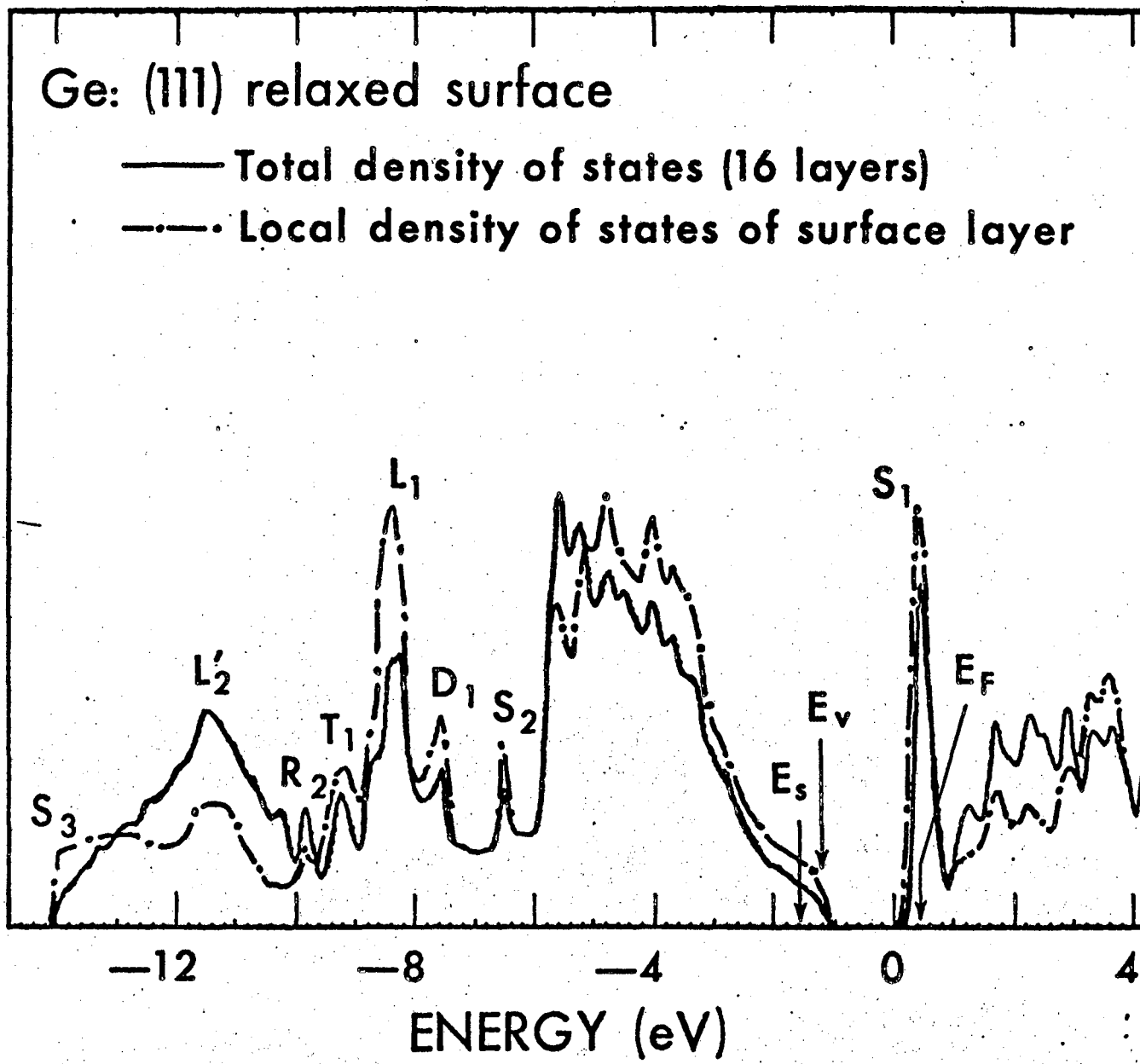


Figure 5

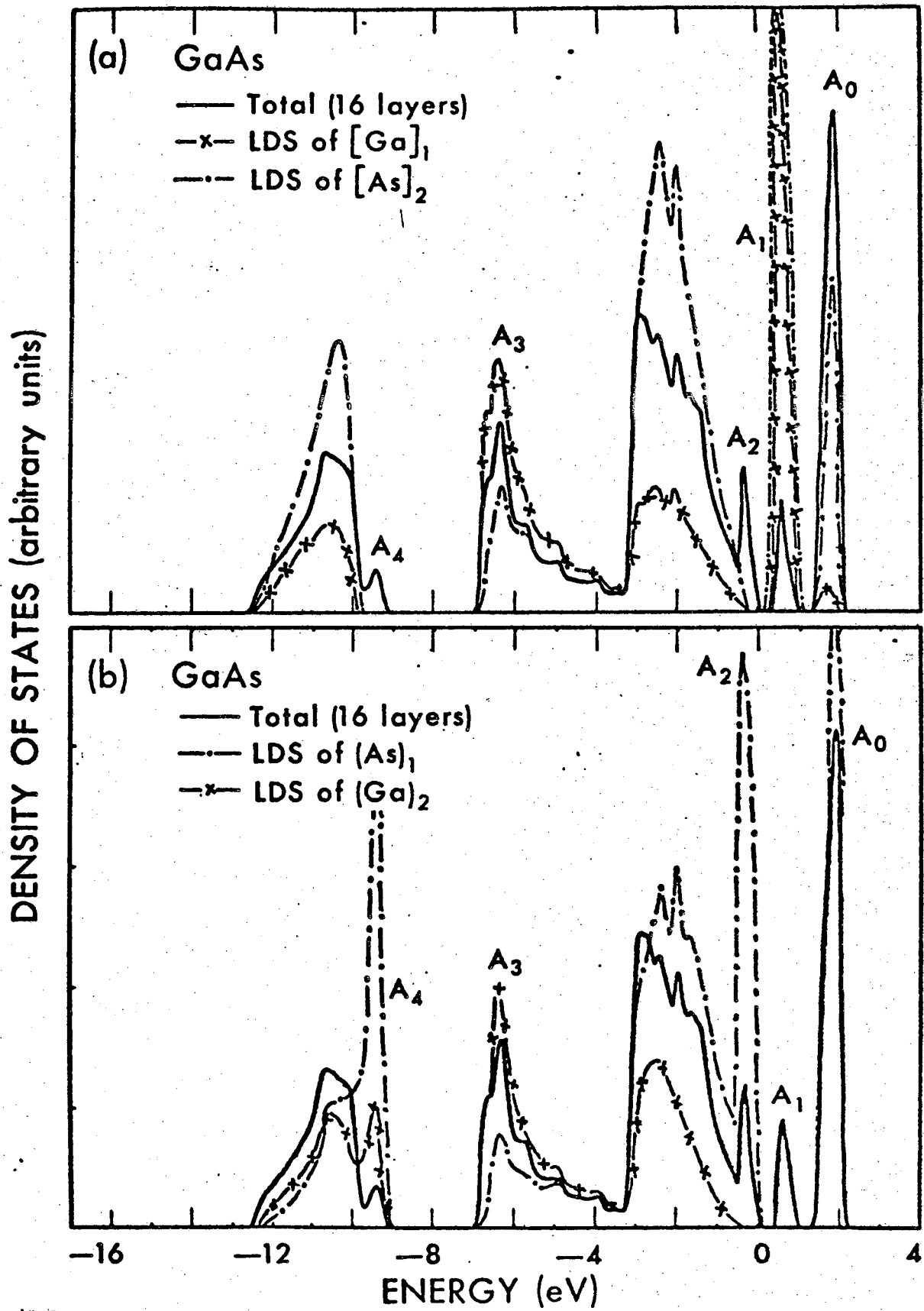


Figure 6

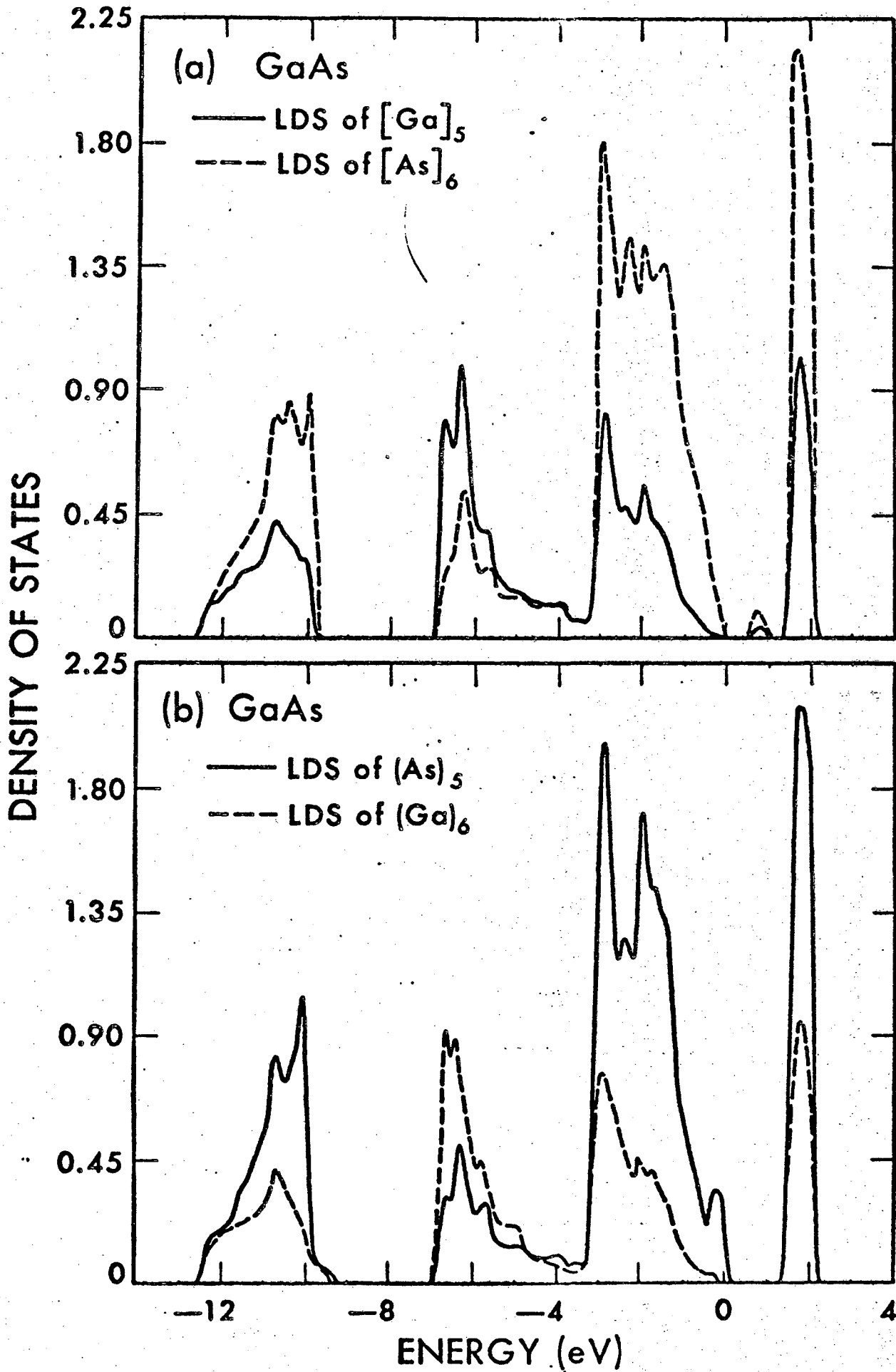


Figure 7

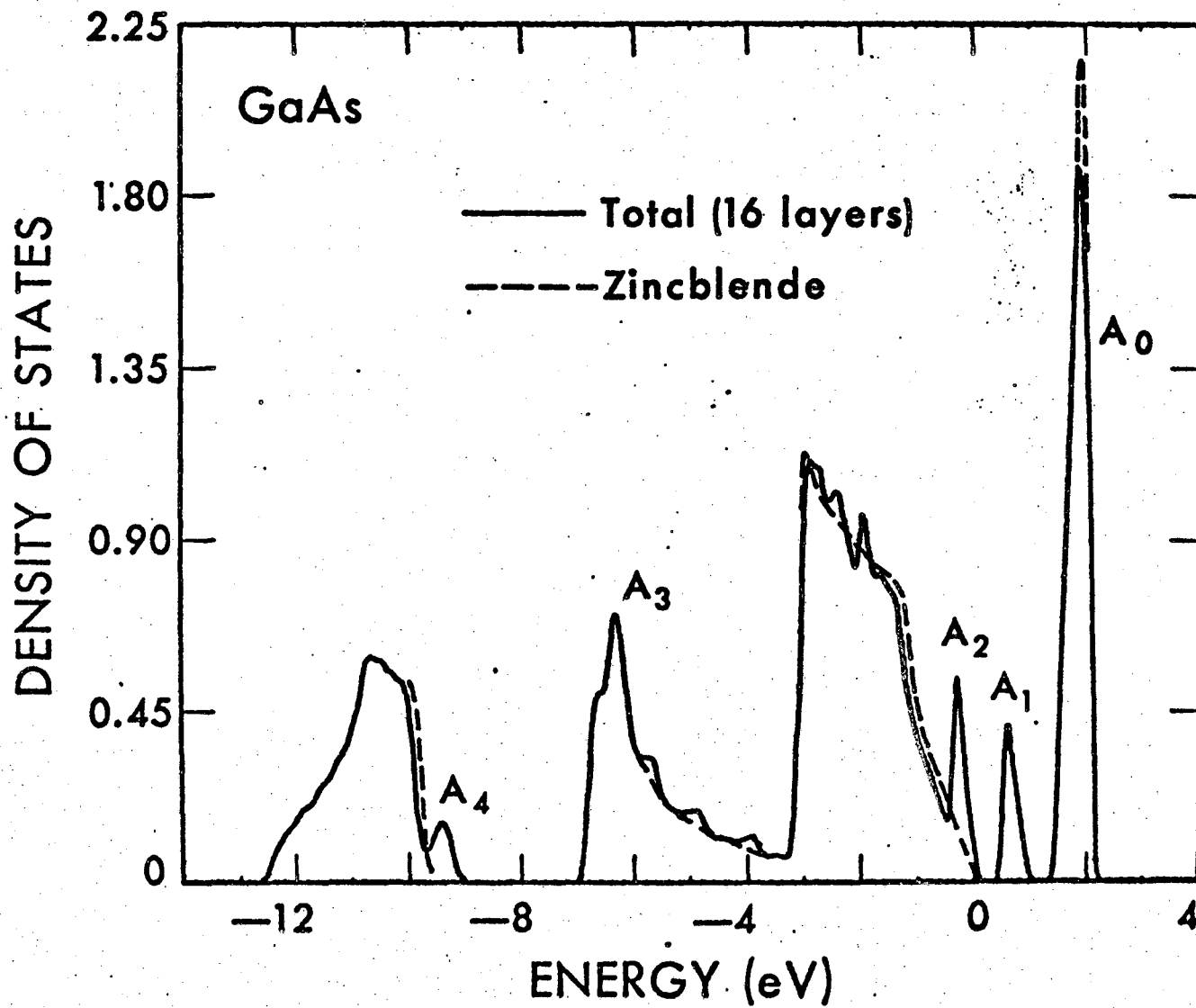


Figure 8

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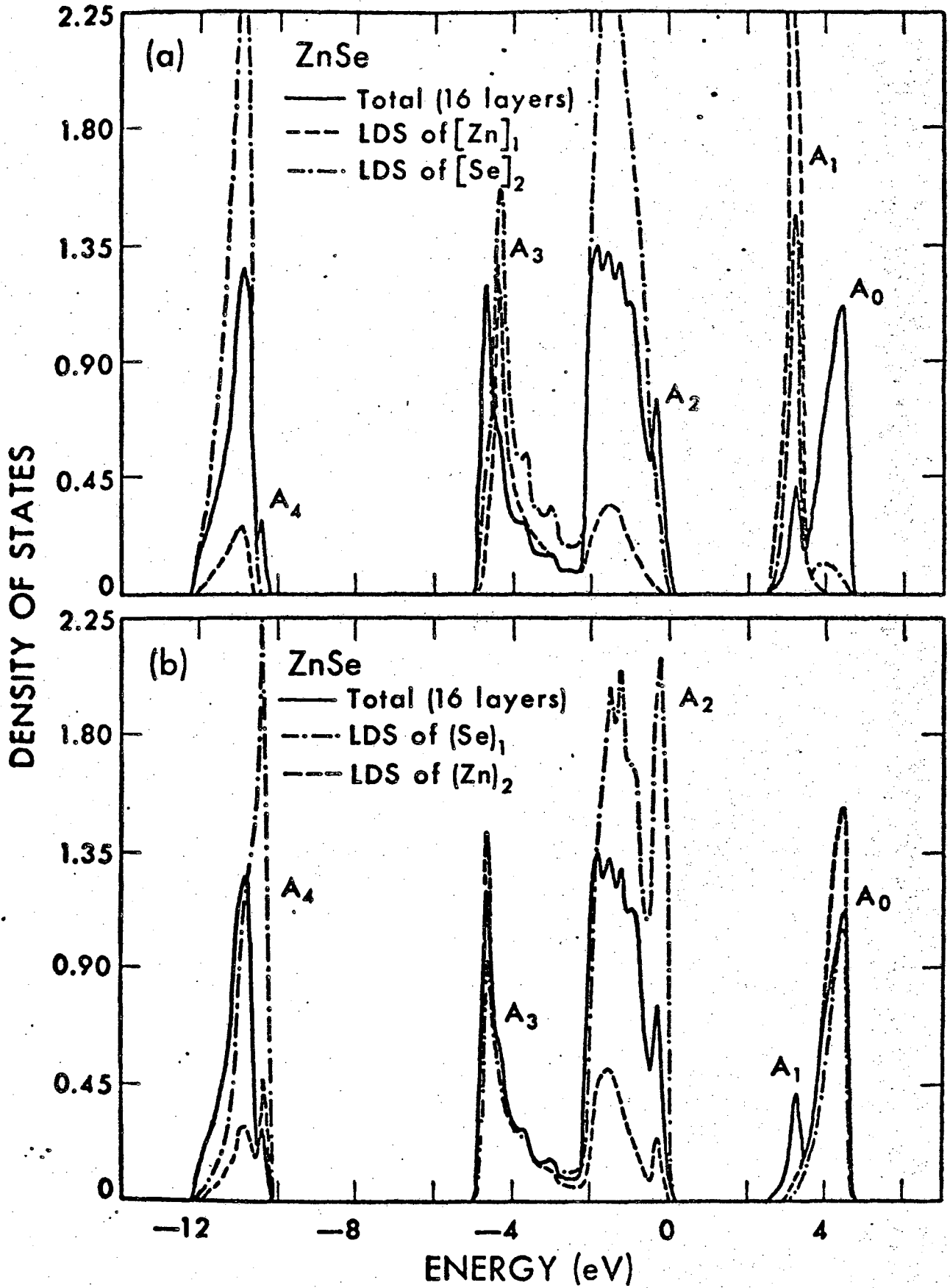


Figure 9

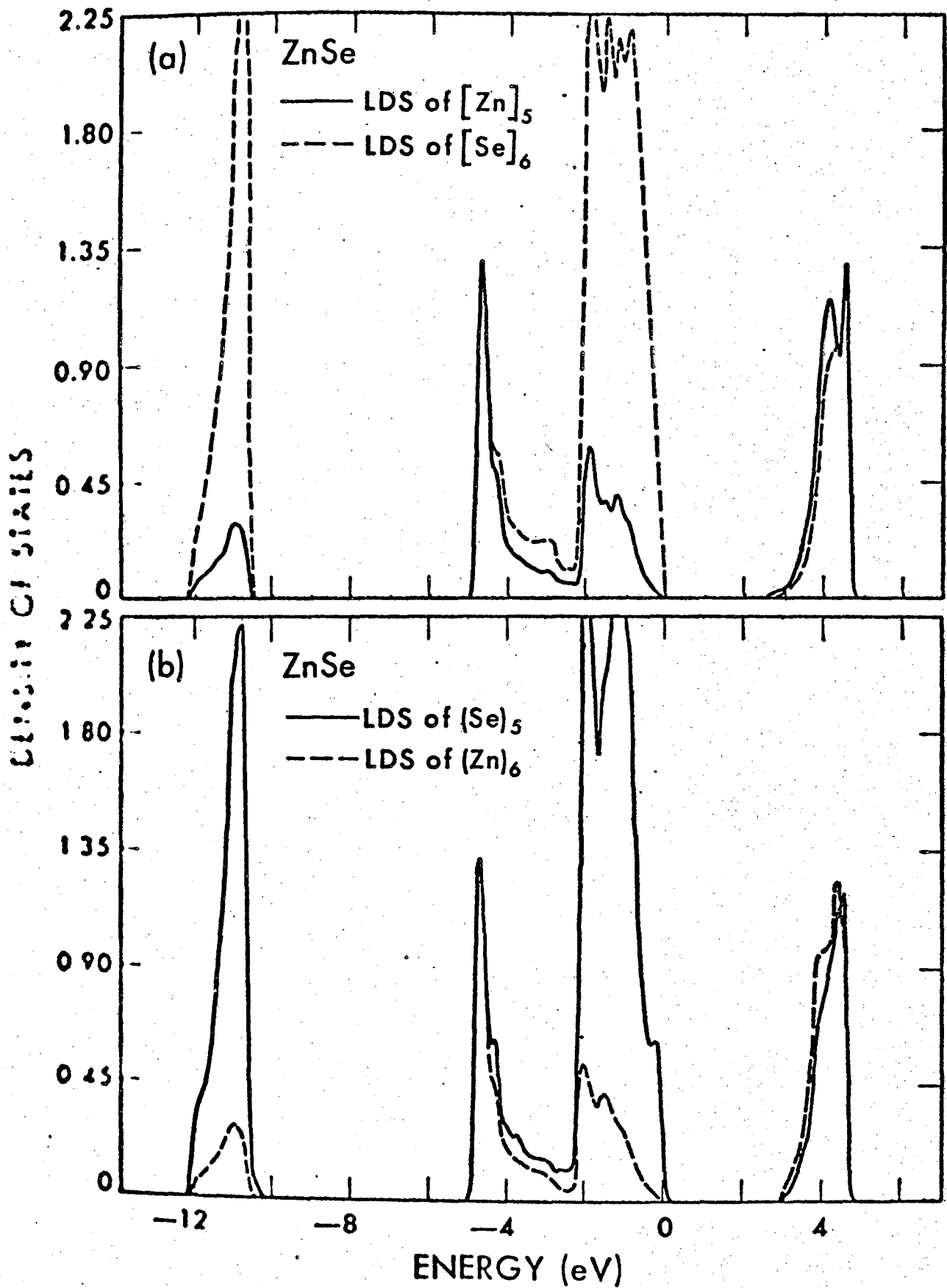


Figure 10

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720