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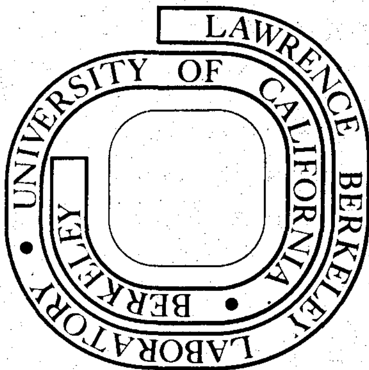

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Self-Consistent Pseudopotential Calculation for the GaAs (110) Surface*

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Abstract

The electronic structure of the GaAs (110) surface is calculated using self-consistent pseudopotentials. Charge density plots are presented for the total charge and the dangling bond surface states. A local density of states calculation for this surface is discussed and displayed. Excellent agreement with experiment is obtained for the energy spectrum of the dangling bond surface states.

We have calculated, using self-consistent pseudopotentials, the electronic structure of the (110) GaAs surface. To our knowledge, this is the first self-consistent surface calculation for a zincblende material. Although our structural model is for an unrelaxed surface, a comparison with recent experimental data exhibits excellent agreement for the energy spectrum of the dangling bond surface states. In addition to displaying the valence charge density for these states, and the total charge density, we present a local density of

states calculation. This latter function, which displays the density of states layer by layer, illustrates the relative decay into the bulk of the surface states.

The (110) surface is of natural interest in GaAs as this is the surface formed upon cleaving. Low energy electron diffraction studies[1] have indicated that this surface does not reconstruct, but retains its primitive configuration. Unfortunately, this does not rule out a non-ideal surface such as a relaxed or buckled (1 × 1) surface. Experimentally, photoemission,[2,3] partial yield photoemission,[4] energy loss spectroscopy,[5,6,7] band bending,[8] and ellipsometry[9] measurements have verfied the existence of two surface states of an apparently dangling bond nature: one occupied surface state lying approximately 0.5 eV below the valence band maximum, the other, an empty surface state, 0.8 to 1.0 eV above the valence band maximum. Although the photoemission measurement[2] responsible for the positioning of the occupied surface state has been the subject of controversy[3,6] the existence of an occupied state in this general region seems to be well accepted. The empty surface state, on the other hand, has been measured by several different methods[4,5,7,8] with agreement between the various techniques. In fact, not only is the energy placement well established for this state, but its localization and angular momentum character have also been investigated.[5] Because energy loss experiments involving excitations from the d-core levels of As show no evidence of a loss peak corresponding to the empty surface

state, it is felt that these states are localized primarily on the Ga atoms[5] (the occupied surface states then being associated primarily with As). Further, such experiments have yielded apparent selection rule effects indicating a primarily s-character for these Ga dangling-bond states.[5] The separation in energy of the Ga and As dangling bond states by an energy of the order of the bulk band gap has also been ascertained by ellipsometry measurements.[9]

The theoretical picture has lagged, regretably, behind these experimental advances. While self-consistent calculations on Si[10,11] exist in good accord with the prominent experimental features, thus far only tight binding[12,13] and "abrupt-potential" matching scheme[14] calculations have been performed on this surface. While the tight binding approach has proved quite useful,[12,13,15] it is deficient in several respects. The method is, of course, not self-consistent and thus the parameters which characterize the surface are usually obtained from bulk calculations via simplified assumptions which may not accurately reflect the actual situation at the surface. Also since the tight binding method parameterizes the surface problem by interaction parameters, wave functions are not obtained. With regard to the abrupt potential model, while such a potential is quite unphysical, useful qualitative trends can be obtained with this approach.

In any event, while such calculations have yielded dangling bond surface states in approximate agreement with

experiment, they do not agree among themselves with respect to the dispersion at the surface bands, or a precise placement for these bands.

The method which we have employed to calculate the surface electronic structure has been discussed extensively elsewhere.[11,16,17] The basic idea is to repeat a slab, or thin film, of GaAs with the (110) surface exposed to a vacuum region on both sides. If the slabs are separated by a large distance (8 interlayer distances for the case at hand), the wavefunctions are allowed to decay into this vacuum region, thus avoiding any interaction between adjoining slabs. The artificially introduced periodicity then allows the use of the well established tools in pseudopotential crystal calculations to be applied to an intrinsically non-periodic problem.

The slab thickness was chosen to be eleven layers. It has been well documented through similar calculations on metals[18] and tight binding calculations[12,13] that such a thickness allows the bulk properties of the material to be adequately reproduced, and also prohibits surfaces from opposite sides of the same slab from undergoing any appreciable interaction.

A crucial point in our calculation is that a pseudopotential for a surface atom will be quite different than that for a bulk atom. This fact is accounted for by the self-consistency process.[10,11] The self-consistency cycle is initiated by an empirical "starting" potential obtained

from bulk calculations. The valence charge density thus obtained is then used to screen a fixed ion core potential by using a Hartree screening potential derived from Poisson's equation and an exchange potential involving the cube root of the charge density.[10] The ion potential used for this calculation was modeled after the one used by Heine and Animalu.[19] The bulk spectrum derived from this ion core potential is in agreement with the main optical gaps and photoemission spectra. Our final potential was self-consistent to within 0.01 Ry. In order to assure accurately converged wavefunctions to determine the screening potential, the basis set consisted of approximately 450 plane waves; an additional 500 waves were treated in an approximate fashion by a second order perturbation technique. Because of the semiconducting nature of this surface we needed to use only a few representative points to obtain a sufficiently accurate charge density.[20] Twenty points in the two dimensional brillouin zone were used for this purpose.

In Fig. 1 the total valence charge density for the (110) surface is displayed for the two types of surface atoms. We note in both figures, as was true for the case of Si,[10,12] the presence of a channel with essentially zero charge extending from vacuum to bulk. It has been suggested[10] that impurities or interstitials could migrate along such a channel. With respect to the bonding charge we note the surface perturbation is essentially healed to its bulk configuration by the third layer. An interesting, but not

surprising, result is the localization of the dangling bond charge on the As rather than Ga atom. The stronger As potential is dominant in determining the bond shape and position, therefore, the removal of the Ga atom by the creation of a surface has relatively little effect on the bonding charge. Although the charge is localized relatively more on the As, as a whole the surface appears not to be more ionic than the bulk. By examining the bonding charge as a function of distance from the bulk to the surface, one observes an overall delocalization or weakening of the bond; however, the relative ratio of charge localized on the As with respect to Ga remains roughly the same.

In Fig. 2 the charge densities are displayed for the dangling bond surface states. The occupied surface state is localized on the As with the empty state localized on the Ga in agreement with experiment.[5] The As state is located in energy below the valence band maximum for the most part, but at the zone center it becomes quasi-degenerate with the valence band maximum. This type of energy dispersion is in agreement with the tight binding calculation of Ref. 12, but not that of Ref. 13 where the surface band minimum was found to occur at the zone center. That this band does not extend into the optical gap is of some interest, because while the precise position of this state has been questioned, it appears to be well established[3] that it does not contribute significantly to the density of states in the bulk band gap region. The width, in energy, of this state is on the

0 0 0 0 4 3 0 5 7 6 8

order of 1/2 eV again, in accord with experiment.[2] The charge density of the occupied state is of predominently p-character as can be observed from the two lobe configuration displayed in Fig. 2. This is to be contrasted with the Ga dangling bond states. Here the character is more s-like, but retains some p-character as indicated by the small lobe-like feature opposite to the charge maximum. In fact, it has been suggested, as mentioned previously, that such a trend should be observed.[5]

In Fig. 3 we present the results of a local density of states (LDOS) calculation. Previously one of the advantages of the tight binding methods relative to the pseudopotential methods was the ease in which LDOS calculations could be performed. In the tight binding case[12] we may define the local density by

$$N_i(E) = \sum_{\substack{k_{||},n \\ j}} |\langle\psi_{\underset{\sim}{k}_{||},n}|\phi^i_{\underset{\sim}{k},j}\rangle|^2 \delta[E-E_n(\underset{\sim}{k}_{||})] \quad (1)$$

where $\underset{\sim}{k}_{||}$ is the wavevector parallel to the surface, n is the band index, $\psi_{\underset{\sim}{k}_{||},n}$ is the wavefunction of the total Hamiltonian and $\phi^i_{\underset{\sim}{k}_{||},j}$ is the jth Bloch function orbital centered on an atom i. Physically this can be interpreted as the probability an electron will be at the ith site with energy, E. Such a definition can easily be modified using pseudo wavefunctions to

$$N_\Omega(E) = \sum_{\underset{\sim}{k}_{||},n} \int_\Omega |\psi_{\underset{\sim}{k}_{||},n}(\underset{\sim}{r})|^2 d^3\underset{\sim}{r} \; \delta[E-E_n(\underset{\sim}{k}_{||})] \quad (2)$$

The integral extends over the volume of interest, Ω. Thus $N_\Omega(E)$ can be interpreted as the probability an electron with energy, E, is in the region Ω.

In order to ascertain the LDOS defined by (2) as a function of distance from vacuum to bulk, we have chosen Ω to be bound by planes parallel to the surface and passing through the mid-point between layers. Thus "Layer 1" of Fig. 3 corresponds to integrating all charge within one-half an interlayer distance on both sides of the surface atoms. Five points in the irreducible zone went into the make-up of the histograms. Accordingly 220 eigenvalues went into the valence band portion of the figure.

The positions of four prominent surface states are indicated by the shaded areas in Fig. 3. These surface features have been observed previously in tight binding LDOS calculations[12] with the energy positions for these features in approximate agreement with our results. The states are centered at -9.0, -5.75, -0.5 and +1.0 eV with respect to the valence band maximum. Although our discussion thus far has been concerned with the dangling bond surface states lying near the optical gap, the low lying states at -9.0 and -5.75 eV are not without interest. These states are s-like and are localized on the As and Ga respectively. Unfortunately, both of these features lie in the general vicinity of strong bulk peaks in the density of states curves, thus it will probably be quite difficult from an experimental standpoint to separate, in an unequivocal fashion, the various contributions from surface and bulk in this region.

With regards to Fig. 3 we note the finite width of the histogram means both bulk and surface contributions can be included in the same energy interval. Nevertheless, the major features are quite clear, and the decay of the surface features can be easily discerned. In no case has the surface perturbation not decayed to less than a quarter of its value from the first to third layer in the LDOS plot. We note by the fifth layer the general features of the LDOS curve are in good agreement with the known bulk spectrum.[21] This confirms our use of only eleven layers in the repeated slab.

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References

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1. H. Lüth and G. J. Russel, Surf. Sci. 45, 329 (1974).
2. D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).
3. P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, Appl. Phys. Lett. 25, 511 (1974).
4. D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974).
5. R. Ludcke and A. Koma, Phys. Rev. Lett. 34, 817 (1975).
6. H. Froithzheim and H. Ibach, Surf. Sci. 47, 713 (1975).
7. J. E. Rowe, to be published.
8. J. M. Dinan, L. K. Galbraith, and T. E. Fischer, Surf. Sci. 26, 587 (1971).
9. R. Dorn and H. Lüth, Phys. Rev. Lett. 33, 1024 (1974).
10. J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 32, 1433 (1974).
11. M. Schlüter, J. R. Chelikowsky, S. G. Louie and M. L. Cohen, to be published.
12. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B10, 5075 (1974).
13. C. Calandra and G. Santoro, J. Phys. C. 8, L86 (1975).
14. N. Garcia, J. Solana and N. Cabrera, Solid State Comm. (in press).
15. K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 32, 1433 (1974).

0 0 0 0 4 3 0 5 7 7 0

16. M. L. Cohen, M. Schlüter, J. Chelikowsky and S. G. Louie, to be published.

17. A somewhat similar technique has been developed by G. P. Alldredge and L. Kleinman, Phys. Rev. Lett. 28, 1264 (1972).

18. G. P. Alldredge and L. Kleinman, Phys. Rev. B10, 559 (1974).

19. A. O. E. Animalu and V. Heine, Philos. Mag. 12, 249 (1965).

20. See, for example Ref. 10.

21. J. R. Chelikowsky, D. J. Chadi and M. L. Cohen, Phys. Rev. B8, 2786 (1973).

Figure Captions

Figure 1. Total valence charge density plotted in the $(1\bar{1}0)$ plane terminated on the (a) Ga atom and (b) As atom. The charge density has been normalized to one electron per unit cell volume, $\Omega_{cell} = 812\ \text{Å}^3$. The contour spacing is in units of 0.35.

Figure 2. Charge density for the (a) Ga dangling bond and (b) As dangling bond surface states in the same plane and normalization as in Fig. 1. The contour spacing is in units of 2.0.

Figure 3. Local density of states in arbitrary units as defined by Eq. (2). The total density of states was obtained by summing over all layers.

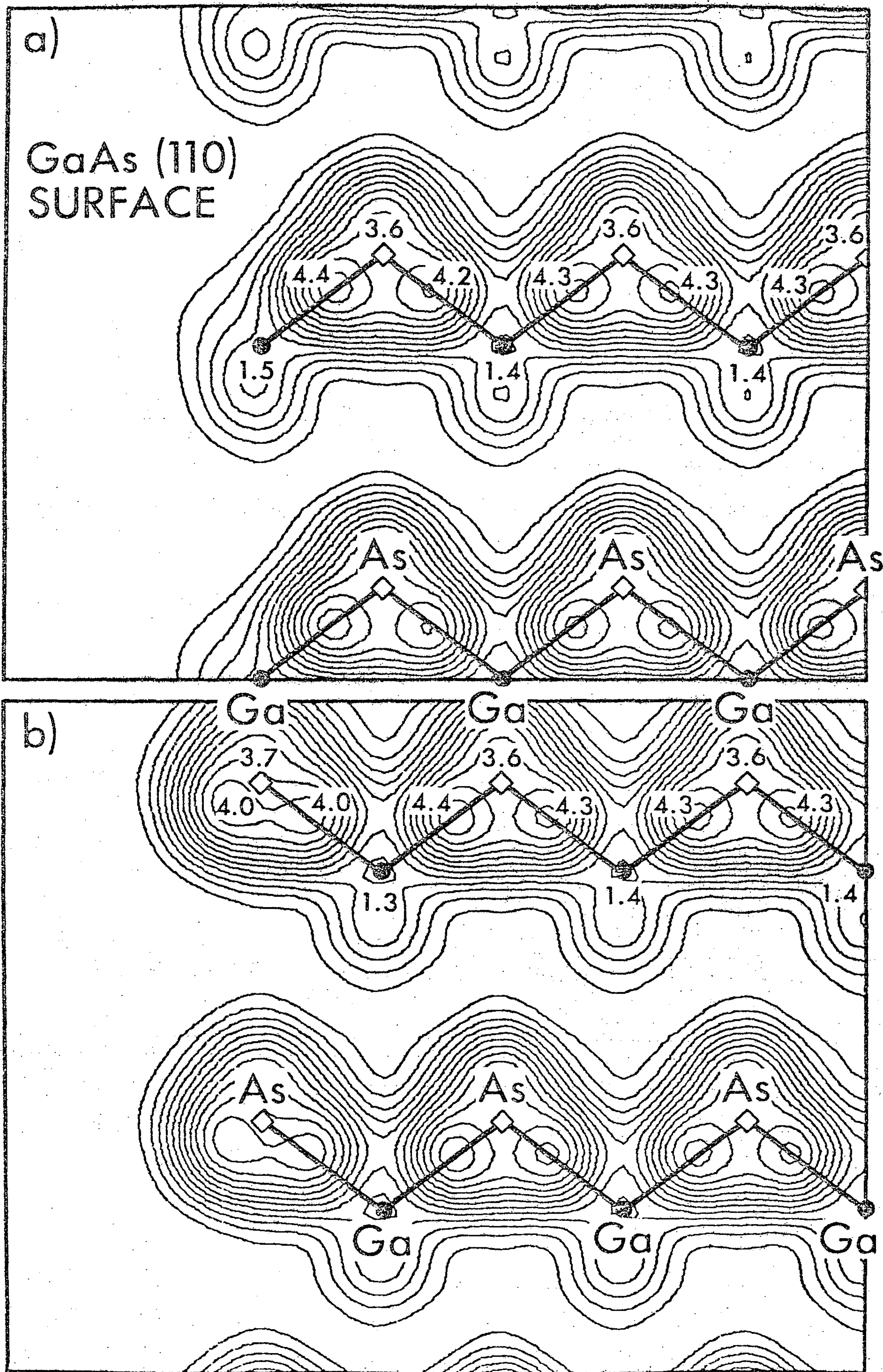

Figure 1

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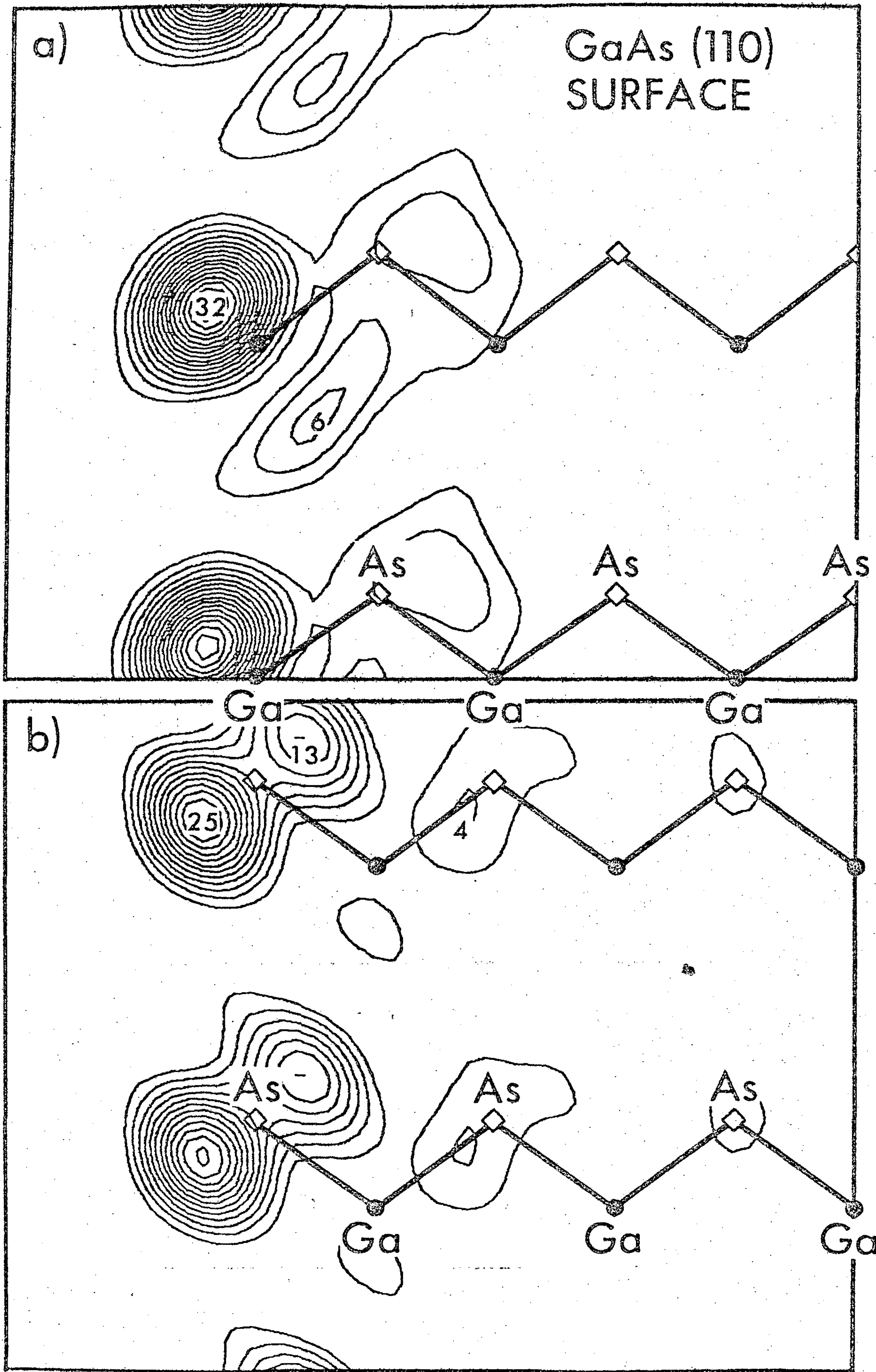

Figure 2

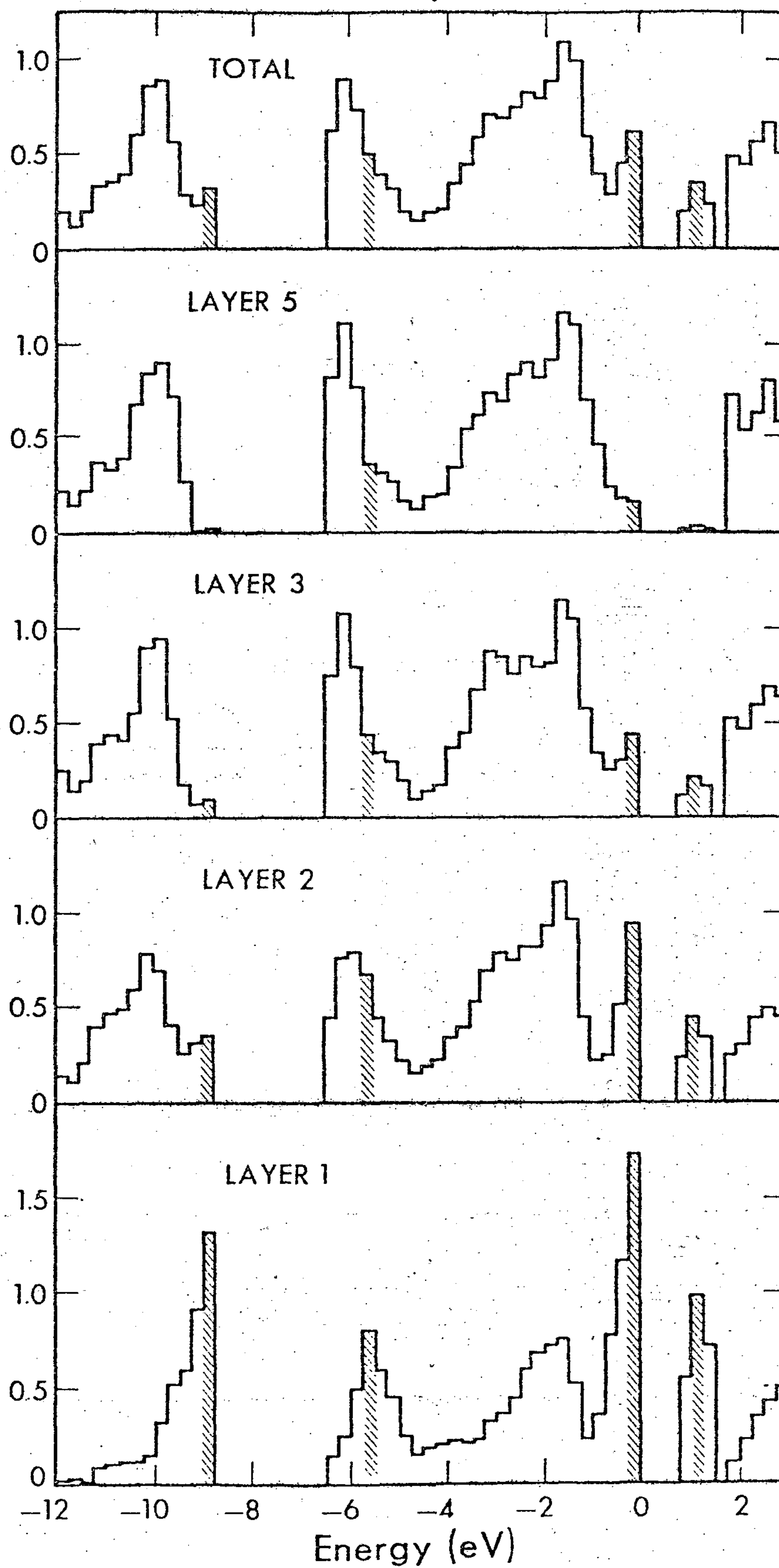

Figure 3

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