PHYSICAL REVIEW B VOLUME 17, NUMBER 12 15 JUNE 1978

# Pseudocharge densities and the (110) surface of GaAs

D. J. Miller and D. Haneman
*School of Physics, University of New South Wales, Sydney, Australia 2033*
(Received 4 May 1977)

Pseudocharge densities on (110) GaAs obtained by self-consistent pseudopotential methods are compared with atomic charge densities and experimental information. Considerable disagreement is found and possible reasons are considered. It is concluded that current pseudocharge densities may not provide an accurate representation of the charge density at the surface.

The surface band structures of various solids have been elucidated in the past few years by self-consistent calculations based on pseudopotential methods.[1] This approach has made a very significant contribution to the understanding of surfaces. The results of the calculations have usually included the corresponding pseudocharge densities from which conclusions have sometimes been drawn about the real electron charge densities at the surfaces.[1-3] The extent to which pseudocharge densities correspond to real charge densities has been discussed for some bulk calculations,[4,5] but hardly at all for surface calculations. It is suggested here that the surface pseudocharge densities may be less reliable than their bulk counterparts. In view of the large number of pseudo-charge-density (PCD) diagrams for surfaces,[1-3] it seems appropriate to examine the status of surface PCD.

First, we consider the PCD for the (normally unfilled) broken Ga orbital on the ideal (110) surface,[2] and reconstructed (110) surface,[3] of GaAs. The reconstructed case corresponds to a relaxation of the Ga atom into the (111) plane of its three As neighbors, leading to planar bonding between the Ga and As atoms. From a consideration of the bonding in the two configurations, one would expect the hybridization of the Ga orbital to change considerably. In the ideal case, there is tetrahedral bonding between the Ga and its three As neighbors, and so the broken Ga orbital is expected to be $sp^3$-like. In the reconstructed case, the bonding is planar and the broken orbital is expected to be $p$-like.

Turning to the pseudopotential calculation, in both cases the PCD consists of two unequal lobes on either side of the Ga atom. For the ideal geometry, the largest lobe is exterior to the crystal and, from a consideration of the two lobes, the PCD is described by the authors[2] as $s$-like with some $p$ character. For the reconstructed geometry, the largest lobe is interior to the crystal and the PCD is described by the authors as $p$-like.

The PCD is often classified according to atomic nomenclature in this way. Therefore, it is instructive to compare the PCD along its symmetry axis with the charge density from an atomic $sp^n$ hybridized Ga orbital. The charge density of the latter is $|\psi_{Ga}(r)|^2$, where

$$\psi_{Ga}(r) = (1/2\sqrt{\pi})[\alpha R_{4s}(r) + \beta\sqrt{3}\cos\theta R_{4p}(r)],$$

where $\theta$ is the polar angle with respect to the symmetry axis of the orbital and the radial wave functions $R_{4s}(r)$ and $R_{4p}(r)$ were obtained from Clementi and Roetti.[6] The degree of $p$ hybridization of the orbital is given by $\beta^2$ $(=1-\alpha^2)$. The heights of the PCD lobes in Fig. 1 were adjusted to fit the atomic charge density. Thus the PCD is plotted in arbitrary units.

In order to choose the value of $\beta$ which best fits the PCD, the criterion was adopted of matching the ratio of the heights of the outermost lobes (on either side of the nucleus) of the atomic charge density and of the PCD. The ratio of the heights

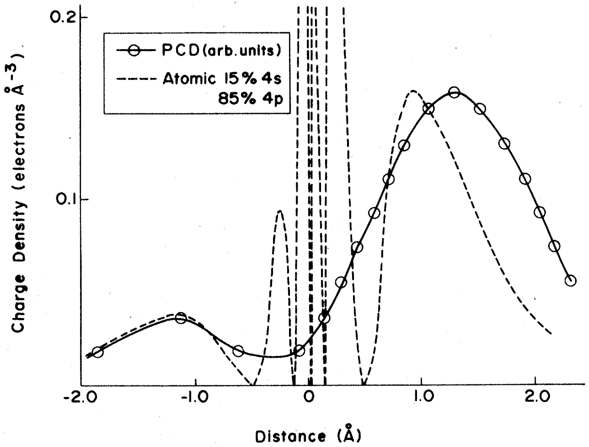

FIG. 1. Charge density for 15% 4$s$ and 85% 4$p$ hybridized Ga atomic wave function compared with the pseudocharge density (PCD) calculated for the empty Ga orbital on the reconstructed (110) GaAs surface. The points marked as circles have been read from the contours in Fig. 3 of Ref. 3, their magnitudes adjusted to fit the atomic charge density and joined by a smooth curve.

of the PCD lobes has been used previously to estimate, in a qualitative way, the *sp* hybridization of PCD.[7] The relevant ratio is 7.25 for a Ga $sp^3$ hybrid (75% *p*) and 1.0 for pure *p*. In Fig. 1, the PCD ratio is 4.25 which can be fitted, as shown, by taking $\beta^2 = 0.85$. This means a *p* content of 85% for the reconstructed case. For the ideal configuration, the ratio of the lobes [from Fig. 5(a) of Ref. 2] is 5.3 and a similar analysis leads to 81% *p* content. Note that the direction of the orbital is reversed in the two cases.

Thus the expected change in the Ga orbital from 75% *p* content (ideal case, tetrahedral bonding) to 100% *p* content (reconstructed case, planar bonding) is not reflected in the PCD which only shows a change from 81% to 85% *p* content. Also the position of the major lobe is reversed. It may be the case, however, that the PCD is the better representation of the real charge density. The following experimental and theoretical[8,9] results cast doubt on this possibility.

An electron paramagnetic resonance (EPR) spectrum is obtained[10-12] from $O^-_2$ ions reversibly adsorbed on clean GaAs surfaces at about 100 K. From an analysis[11,12] of the hyperfine structure in the spectrum, the broken Ga orbital on the GaAs (110) surface was found to be 97% *p*-like. As noted above, a *p*-like Ga orbital implies near planar ($sp^2$-like) bonding between the Ga and its three As neighbors. Thus, on the basis of this EPR result, it was originally proposed[10] that the Ga atom moves towards or into the (111) plane defined by its three As neighbors. Recently it was found[13] that low-energy-electron-diffraction (LEED) results could be explained by such a reconstruction. This structure, on a bond-orbital interpretation, predicts a *p*-like orbital on the Ga atom, which agrees precisely with what was found by EPR.

It may be argued that the EPR results, which refer to an $O^-_2$ covered surface, are not applicable to the clean reconstructed surface. In this connection we note that since $O^-_2$ ions are desorbed at about 130 K and reform on reexposure to $O_2$ at lower temperatures, the geometry of the GaAs surface would not be changed appreciably by the presence of the $O_2$. The coverage of the $O^-_2$ ions is a few percent of a monolayer and they therefore cannot be associated with defects which are of appreciably lower concentration. It should also be noted that the EPR results are sensitive to the charge density near the nucleus. It is conceivable that the apparent hybridization of the wave function alters in the regions further from the nucleus so as to agree with the PCD result. This strained hypothetical situation would, however, still not be in agreement with the bond-orbital picture.

Before proceeding, some comment may need to be made about the use of atomic wave functions to describe electron states in solids and at surfaces. For the particular case of the GaAs (110) surface, it has recently been found[9] that atomic dipole selection rules apply to electron transitions from core to empty surface states. This is further experimental evidence that atomic orbitals can be used to describe surface wave functions. More direct evidence about the adequacy of atomic charge densities is available from x-ray measurements in the bulk. For example, for InSb the charge density of normal atomic wave functions is in overall good agreement along the symmetry axis with the best estimate of the bulk charge density (see Fig. 9 of Ref. 8). The agreement of the latter with PCD based on a local pseudopotential (as used for surface calculations) is significantly worse.[8] However, it is found that better agreement is obtained if the PCD is calculated using a nonlocal form of the pseudopotential.[8]

Other results show that PCD calculated from nonlocal pseudopotentials is in better agreement with the x-ray results than PCD calculated from local pseudopotentials. For example, PCD calculated for bulk Si using a *local* pseudopotential suggest incorrectly that the valence charge density is elongated perpendicular to the Si-Si bond direction.[4] In that respect, calculation using a *nonlocal* pseudopotential[4] are in agreement with experiment which indicates that the valence charge is elongated parallel to the bond direction. Unfortunately, PCD calculated for surfaces has been based on local pseudopotentials.

As well as the use of a local pseudopotential, another problem associated with surface PCD may be the lower translational symmetry present at the surface. To investigate this possibility, consider the PCD calculation[14] for a diatomic Si molecule, $Si_2$, where there is no translational symmetry. (Except for that artificially imposed by the calculation technique.[14]) Figure 2(a) is a schematic diagram of the PCD said to represent[14] the bonding $\pi$ orbital of $Si_2$. In fact, this charge density is different from that expected for that molecular orbital. Figure 2(b) shows a schematic representation of the charge density when the bonding $\pi$ orbital of $Si_2$ is represented by a linear combination of Si atomic *p* wave functions (from Ref. 6). We have calculated the charge density based on a linear combination of atomic orbitals for several first-row homonuclear diatomic molecules. The results are in excellent qualitative agreement with the charge density[15] based on wave functions[16] which are thought to be very close to the restricted Hartree-Fock solution to the relevant molecules.

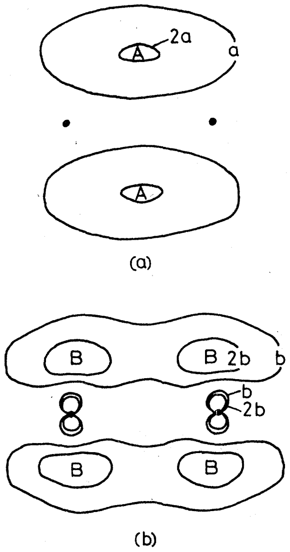

FIG. 2. (a) Schematic representation of two pseudocharge density contours of the bonding $\pi$ orbital of $Si_2$ (taken from the $\pi_p$ orbital of Fig. 2 of Ref. 14). The maxima of the pseudocharge density are marked $A$. (b) Schematic representation of two contours of the charge density of the bonding $\pi$ orbital of $Si_2$ calculated from a linear combination of atomic $p$ wave functions. The maxima of the charge density are marked $B$. The magnitude of the contours in (a) and (b) is not the same since the comparison is meant to be qualitative. The internuclear distance is 2.25 Å in both cases.

Leaving aside quantitative comparisons, it is apparent from Fig. 2 that the maxima of the PCD are not in the correct position relative to the nuclei in $Si_2$. This apparently has not be realized previously.[14] It is worthwhile noting that PCD in good agreement with valence-charge density from an *ab initio* calculation has been obtained[17] for molecules by the use of a nonlocal pseudopotential and an atomic orbital basis set. However, the $Si_2$ molecular calculation featured only a local pseudopotential and used plane-wave basis functions. The same pseudopotential model was used for the GaAs and other surface calculations. Therefore, those calculations must be viewed with some suspicion in the absence of independent supporting evidence. In particular, conclusions drawn[3] from the position of the major PCD lobe, on the reconstructed GaAs (110) surface, may not be reliable.

In conclusion, the purpose of the present article is to suggest that the PCD, particularly with a local approximation, may not be a realistic representation of the charge density at the surface. In an effort to check the reliability of PCD, comparison was made with experiment for the GaAs (110) surface. That comparison suggested that the distribution of PCD about the Ga surface atom is incorrect. The reasons for the possible shortcomings of surface PCD to date may be the use of a local pseudopotential and the lower translational symmetry at the surface. These comments do not necessarily imply that energies calculated by the self-consistent pseudopotential method are incorrect. It is a feature of this method that energies are obtained more reliably than wave functions.

## ACKNOWLEDGMENT

This work was supported by the Australian Research Grants Committee.

---

[1] J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976), and references therein.

[2] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 13, 826 (1976).

[3] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).

[4] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 10, 5095 (1974).

[5] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 36, 229 (1976).

[6] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[7] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973).

[8] D. H. Bilderback and R. Collela, Phys. Rev. B 13, 2479 (1976).

[9] R. S. Bauer, D. J. Chadi, J. C. McMenamin, and R. Z. Bachrach, in *Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surfaces*, edited by R. Dobrozemsky *et al.* (Berger, Horn, 1977), Vol. III, p. A2699.

[10] D. J. Miller and D. Haneman, Phys. Rev. B 3, 2918 (1971).

[11] G. H. Stauss and J. J. Krebs, Phys. Lett. A 50, 49 (1974).

[12] D. J. Miller and D. Haneman, Phys. Lett. A 60, 355 (1977).

[13] A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 36, 1058 (1976).

[14] M. L. Cohen, M. Schlüter, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. B 12, 5575 (1975).

[15] A. C. Wahl, Science 151, 961 (1966).

[16] P. E. Cade and A. C. Wahl, At. Data Nucl. Data Tables 13, 339 (1974).

[17] R. N. Dixon and J. M. V. Hugo, Mol. Phys. 29, 953 (1975).