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Pseudopotential Valence Charge Densities in Homopolar and Heteropolar Semiconductors*

James R. Chelikowsky† and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Recent x-ray data on InSb allows an assessment of the valence charge density provided by pseudopotential calculations. These calculations based upon detailed information on the valence-band electronic density of states, as expected, yield significantly improved structure factors as compared to pseudopotnetial calculations based solely on reflectivity data.

In a recent Letter, Bilderback and Colella[1] (BC) investigated the valence charge density in InSb through a series of accurate x-ray measurements of quasi-forbidden structure factors. A comparison of these measurements was made by BC with the results of five theoretical models for the valence charge density. Included among the models considered was a pseudopotential-calculated valence charge density. The pseudopotential-model result as calculated by BC was found to be unimproved as compared to the result obtained by a simple superposition of free atoms in the lattice. This comparison would suggest the unfavorable conclusion that a superposition of free atoms, which contains no solid-state effects, would yield a result comparable to the pseudopotential charge density.

The unfavorable comparison occurs as a consequence of employing an inaccurate pseudopotential. While early pseudopotential work, upon which the BC calculation is based, was able to describe adequately the reflectivity data, it has been demonstrated that this work cannot produce a satisfactory configuration for the valence-band structure and, thus, the valence charge density. This situation was described, in part, in a recent Letter[2] by the present authors. In that Letter, we noted that a comparison between recent x-ray work on Si and a pseudopotential charge-density calculation had ascertained that the pseudocharge density yielded a correct bonding-charge maximum, but not a correct bond shape,[3] and that such a discrepancy could be alleviated by a nonlocal pseudopotential.[2] In particular, it is necessary to consider nonlocal pseudopotentials based

on accurate experimental information concerning the valence-bonding states.[4]

The valence-band structure can be related to the valence-charge localization and ionicity.[5] Therefore, detailed information on the valence-band electronic density of states, such as provided by photoemission,[6,7] can provide an invaluable guide to obtaining an accurate band structure (and specifically an accurate valence charge density).

No detailed information on the occupied states was included in the pseudopotential used in the BC calculation. The pseudopotential parameters in their calculation were fixed by a comparison to reflectivity data alone. These data have proven insufficient to obtain an accurate valence-band structure as they specify data only on direct band gaps and not on indirect transitions as required for determining an accurate valence-band configuration.[4] Since an accurate electronic density of states is not obtained by the local pseudopotential employed by BC, it is not surprising that the resulting charge density is not accurate.

Recently, by means of nonlocal pseudopotentials,[8] accurate valence-band electronic densities of states have been obtained for several zinc-blende semiconductors. The parameters required for these pseudopotentials involve valence-band density of states data[6,7]; however, the parameters were *not* adjusted to any valence-charge-density data. Nevertheless a comparison of the charge density for InSb shows a dramatic improvement over the local pseudopotential calculation as displayed in Fig. 1 and Table I.

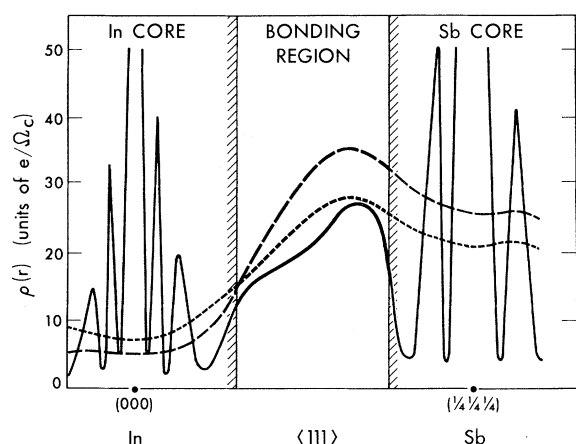In Fig. 1 the results of three theoretical calcu-

FIG. 1. The valence charge density for InSb as cal-
culated from a tetrahedrally distorted spherical-atom
model (solid line) (Refs. 1 and 9), a local pseudopoten-
tial (long-dashed line) (Ref. 10), and a nonlocal pseudo-
potential (short-dashed line) (Ref. 8).

lations for the valence charge density along the
bonding direction are presented. The tetrahedral-
ly distorted spherical-atom model as calculated
by BC yields highly accurate structure factors,
and is, presumably, close to the true charge den-
sity. This model involves two parameters which
were fitted to the experimental structure factors.[1]
Also displayed are local- and nonlocal-pseudopo-
tential charge densities. The nonlocal result
gives a bond maximum in good agreement in both
magnitude and position as compared to BC's re-
sult; however, the local-pseudopotential result,
while agreeing with the bond-maximum position,
is in discrepancy by over 30% for the bond mag-
nitude as compared to the BC model.

It should be stressed that it is *not* proper to
compare the pseudocharge density in the core re-
gions to the actual charge densities. The core
regions have been excluded from consideration

in the construction of the pseudopotential, and
the oscillatory nature of the wave functions has
been removed.[11] It is, however, important for
the pseudopotential to describe accurately the
charge density in the "bonding" region as shown
on Fig. 1.

In Table I we compare the experimentally de-
termined structure factors to the theoretical re-
sults of a local pseudopotential, nonlocal pseudo-
potential, and those from a superposition of free
atoms. Core contributions for the pseudopoten-
tial calculations were evaluated by using Hatree-
Fock wave functions.[12]

A measure for the quality of the fit between the
theoretical and experimental structure factors
used in Ref. 1 is

$$R = \sum_i |F_i^{exp} - F_i^{calc}| / \sum_i |F_i^{exp}|.$$

We obtain $R = 0.1$ for both the spherical-atom and
local-pseudopotential calculated structure fac-
tors. The nonlocal pseudopotential gives $R = 0.04$
and is clearly an improvement over the spherical-
atom or local-pseudopotential results. We have
not compared the pseudopotential results to the
higher coefficients of the structure factors (i.e.,
$h^2 + k^2 + l^2 > 20$) as done by BC. These factors
correspond to short-wavelength fluctuations of
the valence charge density in the core region.

The main deficiency of the local-pseudopoten-
tial results, as indicated in Fig. 1, is its over-
estimation of the ionicity of the crystal. This is
reflected in the (222) and ($\bar{2}\bar{2}\bar{2}$) structure factors
of Table I. The local-pseudopotential-calculated
valence-band electronic density of states also in-
dicates a result which is too ionic.[4]

In conclusion the agreement between our calcu-
lated charge densities and x-ray experimental
data is now confirmed for both a homopolar[2,3]
and a heteropolar semiconductor. This agree-
ment suggests that nonlocal-pseudopotential re-

TABLE I. Theoretical structure factors for InSb at 300°K compared to exper-
iment.

| hkl | Theory | | | Experiment[a] |
	Spherical[a] atom	Local pseudopotential[a]	Nonlocal pseudopotential	
200	6.77	7.86	6.96	7.20
222	6.54	9.63	8.41	7.79
$\bar{2}\bar{2}\bar{2}$	6.54	7.23	6.93	7.19
420	7.65	8.76	8.48	8.24

[a]See Ref. 1.

sults, fixed by valence-band density of states data, can be expected to yield accurate information concerning the valence charge densities.

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Field Dependence of the Onsager Phase Factor

Whittak Huang
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

and

P. L. Taylor
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106, * and Department of Physics ₁and Institute of Theoretical Science, University of Oregon, Eugene, Oregon 97403
(Received 15 September 1975)

The apparent discrepancy between the theoretical prediction of the Onsager phase factor σ and its experimental measurement using the de Haas–van Alphen effect in Cd is resolved by showing σ to be field dependent.

The interpretation of the de Haas–van Alphen effect has been hindered in recent years by an apparent discrepancy between the experimental results and theoretical predictions of the Onsager constant σ. Onsager's semiclassical theory[1] shows that in the presence of a uniform magnetic field $\vec{B}$ the area $\vec{a}(\epsilon)$ in wave-number space of an allowed orbit of energy ϵ is given by

$$\vec{a}(\epsilon) = (n + \sigma)(2\pi e/\hbar c)\vec{B}$$

with n an integer and σ an unspecified constant. An exact high-field calculation[2] of σ for a model of the lens orbit in Cd with $\vec{B}$ in the basal plane had predicted a value of $\frac{3}{4}$, while the precise experiments of Coleridge and Templeton[3] unambiguously gave a value of $\frac{1}{2}$. The present paper resolves this apparent discrepancy by showing σ to be a function of the strength of the applied field and to change smoothly from $\frac{1}{2}$ to $\frac{3}{4}$ as the field

reaches the strength at which magnetic breakdown can occur.

In Ref. 2 the lattice potential was treated as a perturbation of a system of independent electrons moving in a uniform applied field directed along the z axis. The effect of this perturbation was to split the degenerate free-electron levels into bands and to shift the centers of these bands in such a way as to introduce new periodicities in the density of states. With the lattice potential a periodic function of only x (and not y or z) a clustering of levels was observed around energies such that in the absence of motion in the z direction

$$\vec{a}_l(\epsilon) = (n' + \tfrac{3}{4})(2\pi e/\hbar c)\vec{B},$$

where n' is an integer and $\vec{a}_l(\epsilon)$ is the area of a semiclassical "lens" orbit, formed by the intersection of the Brillouin-zone boundary with the

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