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Parallel-Band Effects in Interband Optical Absorption*

WALTER A. HARRISON
Division of Applied Physics, Stanford University, Stanford, California

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Absorption edges associated with nearly parallel bands, proposed by Ehrenreich, Philipp, and Segall for aluminum, are discussed for the general case. Numerical estimates of the position, form, and strength of such edges are made for all polyvalent metals with simple structures. It is noted further that such edges provide a direct measurement of the magnitude of the orthogonalized-plane-wave form factor, or pseudopotential, for the metal.

IN interpreting the optical absorption spectrum of aluminum, Ehrenreich, Philipp, and Segall[1] noted that critical points in the relevant joint density of states occur away from symmetry points, as well as at symmetry points. Further, they found that in aluminum the effect away from the symmetry points was very large where two bands in question were nearly parallel. They noted, in fact, that such parallel bands are likely to occur in most polyvalent metals. Here we discuss these edges for the general case in a way which may illuminate their origin, as well as allowing us to make direct predictions of edges in other metals.

The electronic structure of polyvalent metals is rather well described as a free-electron band weakly perturbed by Bragg-reflection planes (Brillouin-zone planes).[2,3] The strength of the Bragg reflection may be characterized by a pseudopotential.[3] The addition of such a plane allows an additional absorption mechanism: the interaction of the electron with light, combined with a Bragg reflection. It is reasonable from this point of view to compute the additional absorption due to each plane separately. In doing this we neglect mechanisms where two Bragg reflections occur; these appear as higher order terms in the pseudopotential. The calculation itself is more conveniently done taking a band-structure point of view.

We proceed to the treatment of a single Brillouin-zone (BZ) face, using a pseudopotential approach. The electron (pseudo-) wave function near the plane is describable as a linear combination of two plane waves, $|\mathbf{k}\rangle$ and $|\mathbf{k}+\mathbf{q}\rangle$, where $\mathbf{q}$ is the lattice wave number (2π times the reciprocal lattice vector) corresponding to the reflection in question. The Hamiltonian contains diagonal terms which are the kinetic energies for the two waves and off-diagonal matrix elements of the pseudopotential connecting the two waves; we write these off-diagonal elements $W=\langle\mathbf{k}+\mathbf{k}|W|\mathbf{k}\rangle$ and can take them to be real (which does not affect the final result).

Evaluation of the energy bands involves the solution of a two-by-two Hamiltonian matrix. The results may be presented in an extended-zone scheme as shown in Fig. 1(a) or a reduced-zone scheme as in Fig. 1(b). The latter is more convenient for our purposes. We have drawn a Fermi surface intersecting (and overlapping) a zone face, a typical situation in a polyvalent metal.

In terms of Fig. 1(b), the additional optical absorption arises from vertical transitions from the lower to the upper band. The band gap is $2W$ at the zone face and the energy difference increases as we move away from the plane. Therefore the absorption edge occurs at the energy $2W$. We note that as the Fermi energy has been taken in the figure, both bands are occupied at the central point of the plane A so no absorption can occur there. However, as we move along the plane, [Fig. 1(c)] the bands remain parallel and separated by $2W$ and absorption can occur on the portion of the plane shown shaded in Fig. 1(c). Actually W, and therefore the gap, varies slowly across the plane so the bands are not precisely parallel but they are nearly so and we evaluate W in the shaded portion of the plane. The value taken at the intersection of the free-electron sphere and the plane (point B of Fig. 1) is precisely the value which we have called the orthogonalized-plane-wave (OPW) form factor[3] (times a structure factor for crystals with more than one atom per primitive cell) and we use that value to determine the absorption edge.

It is of interest also to obtain the form of the absorp-

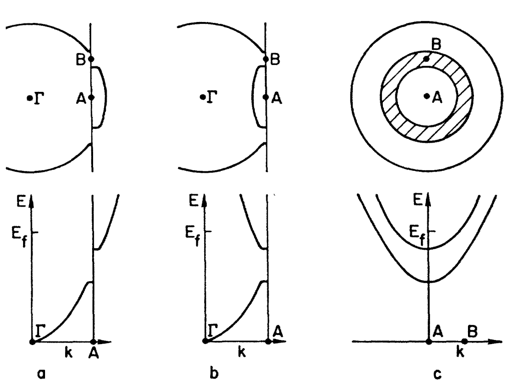

FIG. 1. Fermi surface (above) and energy bands (below) as modified by a single Brillouin-zone face. (a) The extended zone scheme; (b) the reduced-zone scheme; in both cases a section is shown which contains the lattice wave number giving rise to the face. (c) The projection of the Fermi surface on the zone face and energy bands measured in the face.

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[3] W. A. Harrison, in *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

TABLE I. Predicted parallel-band absorption edges.

Metal	Zone face	Gap (eV)	Strength $A\,(Ry^{-1/2})$
Be	(100)	0.92	0.015
	(002)	2.55	0.021
	(101)	2.26	0.105
Mg	(100)	0.17	0.005
	(002)	0.72	0.013
	(101)	0.84	0.095
Ca	(111)	0.42	0.055
	(200)	0.17	0.008
Ba	(110)	0.04	0.004
Zn	(100)	0.09	0.000
	(002)	0.36	0.002
	(101)	1.07	0.076
Cd	(100)	0.04	0.000
	(002)	0.58	0.010
	(101)	0.84	0.084
Al	(111)	0.40	0.010
	(200)	1.59	0.048
In	(111)	0.73	0.042
	(200)	0.92	0.025
	(002)	0.20	0.001
Tl	(100)	1.15	0.075
	(002)	1.52	0.036
	(101)	0.90	0.092
Pb	(111)	2.23	0.207
	(200)	0.85	0.031

tion edge. In doing this it is convenient to measure wavenumbers from the value $\mathbf{k}_0=-\mathbf{q}/2$; that is, the point A of Fig. 1. We write

$$\mathbf{k}=(1+\kappa_z/k_0)\mathbf{k}_0+\boldsymbol{\kappa}_\rho \tag{1}$$

$$\mathbf{k}+\mathbf{q}=(-1+\kappa_z/k_0)\mathbf{k}_0+\boldsymbol{\kappa}_\rho .$$

The energies in the upper and lower bands are, respectively, E_+ and E_-:

$$E_\pm=(\hbar^2/2m)(k_0^2+\kappa_z^2+\kappa_\rho^2) \pm[W^2+4((\hbar^2/2m)k_0\kappa_z)^2]^{1/2}. \tag{2}$$

We may readily compute the shaded area of Fig. 1 where absorption may occur at the zone face. It is $2\pi W/(\hbar^2/2m)$. The energy at which the absorption occurs here is $\Delta=2W$; no other absorption can occur at the plane.

As we move away from the plane, the energy gap grows as

$$\Delta=2W+\frac{4}{W}\left(\frac{\hbar^2k^2{}_0}{2m}\right)\left(\frac{\hbar^2\kappa_z^2}{2m}\right) \tag{3}$$

at small κ_z. The electrons absorbing within a given energy range $\delta\Delta$ will lie in a given $\delta\kappa_z$ range obtained by differentiating Eq. 3. The strength of this absorption will be proportional to the number of wave number states in this region which are occupied in the lower band and unoccupied in the upper band. The corresponding area at given $\delta\kappa_z$ grows only quadratically with κ_z so near the absorption edge we may take the area to be the area at the face. Similarly, the oscillator strength varies only quadratically with κ_z so we take it as constant. Therefore, $2\pi W\delta\kappa_z/(\hbar^2/2m)$ gives a measure of the strength of the absorption in the energy range $\delta\Delta$, where $\delta\Delta=(d\Delta/d\kappa_z)\delta\kappa_z$ and $d\Delta/d\kappa_z$ is obtained from Eq. 3. If we normalize the number of states to the number of electrons present, we obtain

$$\eta=\frac{2\pi W}{(\hbar^2/2m)(d\Delta/d\kappa_z)\frac{4}{3}\pi k_F{}^3}=\frac{A}{(\Delta-2W)^{1/2}} \tag{4}$$

for $\Delta>2W$; otherwise zero. Here

$$A=\frac{3}{8}\frac{(W/E_F)^{3/2}}{(\hbar^2k^2{}_0/2m)^{1/2}} \tag{5}$$

k_F and E_F are the Fermi wave number and energy. The absorption, as a function of Δ, is proportional to η and η gives the important contribution to the structure near the edge. Of course the peak will be rounded by variations in W, among other things.

To treat a given metal we need simply compute the lattice wave numbers which correspond to Bragg planes (BZ faces) intersecting the Fermi surface, a purely geometrical calculation, look up the corresponding OPW form factors, multiply by a structure factor if it is not unity, and multiply by the number of planes occurring with that lattice wave number. The most reliable form factors available to date are those obtained by Animalu and Heine[4] using the model potential of Heine and Abarenkov.[5] These have been used to give the absorption edges and strengths of absorption given in Table I.

Unfortunately, the comparison with experiment is not very conclusive. This is partly because of ambiguous experimental results and partly from uncertainty in the theoretic numbers. In aluminum the most prominent experimental peak is predicted at 1.59 eV, close to the observed 1.55.[1,6] This corresponds to the same interpretation given by Ehrenreich, Philipp, and Segall.[1] In indium we expect peaks at 0.73 and 0.92 eV; it is not clear whether these can be associated with observed structure at 0.4, 0.75, and 1.50 eV. In zinc, our predicted peak at 1.07 eV may correspond to the peak observed at 1.63 eV.[7] In cadmium we expect a strong peak at 0.84 eV, while structure appears at 1.05 to 1.23 eV and 1.90 eV.[7] In beryllium the absorption rises steadily from 0.5 eV to 5 eV,[8] which is difficult to interpret in terms of our peak at 2.26 eV.

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[6] A. P. Lenham and D. M. Treherne, Proc. Phys. Soc. (London) **85**, 167 (1965).

[7] A. P. Lenham and D. M. Treherne, Proc. Phys. Soc. (London) **83**, 1059 (1963).

[8] M. P. Givens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 313.

Except in the case of aluminum, the structure of peaks is poorly defined and it may be premature to attempt to match them with the predicted parallel-band edges. In some cases, too, observable structure might arise from symmetry points which are missed in our two-band approach. However, the approach has the virtue of giving unambiguous predictions of one or two edges in each metal in contrast to the many possible edges which may arise from symmetry points and which are obtainable only after a band calculation. The success in the cleanest experimental case, aluminum, suggests that the edges predicted may be the strongest ones. Finally, such edges bring direct contact between the optical properties and the pseudopotentials in terms of which virtually all of the properties of the crystal[3] may be studied.

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Electronic Spectrum of Crystalline Antimony*

P. J. LIN AND J. C. PHILLIPS†
Department of Physics and Institute of Metals, University of Chicago, Chicago, Illinois

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The energy levels and interband oscillator strengths of antimony have been calculated at ~90 000 points in the Brillouin zone by the pseudopotential method. The potential used was obtained with no adjustment of parameters from empirical form factors of the semiconductors grey Sn and InSb. This potential had previously been used to obtain Fermi surfaces for electrons and holes in Sb in good agreement with experiment. The present calculation agrees well with optical data of Cardona and Greenaway in the energy interval 0.5–8.0 eV with **E** polarized perpendicular to the trigonal axis. Polarization effects of order 10–20% are predicted by the calculation. The regions of the Brillouin zone contributing most strongly to the calculated structure are identified, and predictions are made concerning spin-orbit splittings of the observed peaks. Application of the analysis to As, Bi, and IV–VI semiconductors is discussed.

1. INTRODUCTION

FOR many years the electronic properties of the group-V semimetals As, Sb, and Bi have been the subject of extensive experimental investigation. Interpretation of the experiments was hampered in the past by lack of band calculations of sufficient accuracy and generality to establish the position and shape of the Fermi surfaces of electrons and holes in the Brillouin zone. Recently it has been shown that considerable progress towards interpretation of Fermi surface data can be made in Sb[1] and in As[2] by making use of empirical pseudopotentials derived from the very large amount of data available on the electronic structure of groups IV and III–V semiconductors. Thus in the case of Sb the pseudopotential form factor was obtained[1] from the known form factors of grey Sn[3] and InSb.[4] Without the introduction of any adjustable parameters the empirical form factor so derived from semiconductor spectra yielded surprisingly good quantitative agreement in the semimetals with detailed Fermi surface data obtained by cyclotron resonance[5] and de Haas–van Alphen experiments.[6]

We have been encouraged by these empirical successes to extend the calculations over a wider energy range and over the entire Brillouin zone in sufficient detail to obtain the optical spectrum in the range 0.5–15 eV. The data available in this range show only five or six broad peaks, with little fine structure evident.[7] Over the same range considerably more structure is expected in the theoretical spectrum. Thus at present we cannot hope to achieve a comprehensive and exhaustive analysis of the spectrum of Sb to the degree that was achieved in Brust's classic work on Si and Ge.[8] The present work is therefore exploratory in character. With the develop-

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[1] L. M. Falicov and P. J. Lin, Phys. Rev. **141**, 562 (1966).

[2] P. J. Lin and L. M. Falicov, Phys. Rev. **142**, 441 (1966). *Footnote added in proof.* We take this opportunity to correct an error in Ref. 1. The factor of $\frac{1}{2}$ in Eq. (2.4) should be omitted. According to Ref. 3, the correct value for $V_3(\mathrm{Sn}) = -0.20$ Ry., and using (2.4) with the factor $\frac{1}{2}$ omitted, $V_3(\mathrm{Sb}) = (-0.20-0.06)$ Ry. $= -0.26$ Ry. The value actually used was -0.27 Ry. By accident this agrees with the correct value to 0.01 Ry., which is the limit of accuracy of the method. On this scale of energies (~0.01 Ry.), agreement with the observed Fermi surface constitues the best test of the correctness of the pseudopotential.

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