Band Structure and Optical Properties of Diamond

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$= d$. In this respect, it might be interesting to see if Al-AlO_x-Ag/In/Ag diodes (with relatively thin silver films) produce significantly sharper structure in analogy to multiple-beam interferometers, i.e., two silver mirrors rather than one. The present model proposes e-e (or h-h) composite states into which electrons (or holes) tunnel preferentially because such states satisfy a macroscopic quantum condition of the "beat" or envelope" momentum $\Delta p = (2\pi/d)\eta\hbar$. This point of view seems to differ significantly from the physical picture underlying the McMillan-Anderson calculation, although both yield the same energy spectrum. There appears to be some reason to believe that simultaneous solutions of the three-dimensional Gor'kov equations (lamina of thickness d) may lead to a régime qualitatively similar to the one discussed.[9]

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[1]W. J. Tomasch, Phys. Rev. Letters 16, 16 (1966).

[2]W. J. Tomasch, Phys. Rev. Letters 15, 672 (1965).

[3]W. L. McMillan and P. W. Anderson, Phys. Rev. Letters 16, 85 (1966).

[4]The fact that the single atypical structural feature exhibited by the thinner In films of Ref. 1 could be incorporated into the main series by plotting $\epsilon_\eta(\eta)$ was first pointed out in Ref. 3.

[5]J. R. Schrieffer, Rev. Mod. Phys. 36, 200 (1964).

[6]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[7]P. N. Dheer, Proc. Roy. Soc. (London) A260, 333 (1961).

[8]Although the choice of nodes at the surface has a certain appeal, this condition is not mandatory. Alternative boundary conditions can produce the same spectrum.

[9]T. Wolfram and G. W. Lehman, to be published.

BAND STRUCTURE AND OPTICAL PROPERTIES OF DIAMOND*

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Recently several authors[1-4] have discussed new measurements of the optical properties of diamond, and they have raised many questions about the measurements and about the theoretical interpretation of the data. To answer a few of these questions, we present in this Letter a calculation of the electronic band structure of diamond. The band structure was calculated by means of the empirical pseudopotential method (EPM)[5,6] which has been used[5-8] successfully to interpret the optical properties of a large number of semiconductors and insulators. The analysis of the resulting diamond band structure yields some new interpretation of the structure in the optical reflectivity. Within the scope of this interpretation, the calculated band gaps agree with experiment to within ~0.01 Ry near the fundamental band gap and to within ~0.05 Ry over a range of 1.0 Ry.

The EPM involves choosing pseudopotential form factors which give band structures consistent with the experimental measurements. These form factors are first constrained to give a few of the principal band gaps in agreement with experiment and then used to determine the electronic band structure at many points in the Brillouin zone. The pseudopotential form factors V_K used for diamond are (in Rydbergs) $V_{111} = -0.811$, $V_{220} = 0.337$, $V_{311} = 0.132$, and $V_{222} = 0.041$. The V_{222} form factor, which is identically zero for a linear superposition of spherical atomic potentials, is included here to account for the distribution of valence charge[9,10] arising from tetrahedral bonding. This tetrahedral distribution of charge accounts for the presence of the otherwise forbidden (222) reflection in x-ray data.[11,12]

The band structure of diamond appears in Fig. 1. The calculation of the energy bands is convergent to ~0.003 Ry. The lattice constant was taken to be 3.57 Å.[13] In Table I we list the principal energy gaps of this band structure and the corresponding experimental values. The location of the conduction-band minimum is also included in Table I. The error in the experimental energies at which the peaks occur in the optical constants is large both because of the inherent broadness of the

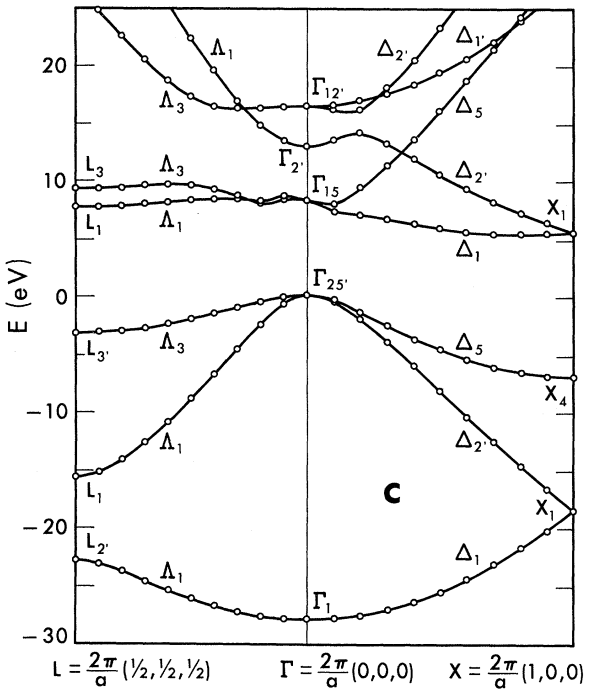

FIG. 1. The electronic band structure of diamond.

Table I. Theoretical and experimental values for the location of the conduction band minimum and the principal band gaps of diamond. Except for the $\Gamma_{25'}$-Δ_1 gap which was determined using absorption measurements, all experimental splittings were obtained only from plots of the imaginary part of the frequency dependent dielectric function.

	Theory (eV)[a]	Experiment (eV)[a]
Δminimum	(0.77, 0, 0)	(0.76 ± .02, 0, 0)[b]
$\Gamma_{25'}$-Δ_1	5.4	5.48[c]
$\Gamma_{25'}$-Γ_{15}	7.3	7.3[d,e]
X_4-X_1	12.9	12.3-12.6[f,d,e]
$L_{3'}$-L_1	10.9	9.5-10.5[d,e]
$\Gamma_{25'}$-Γ_{12}	16.5	16-17[f,e]

[a]Except for Δminimum.
[b]P. J. Dean, E. C. Lightowlers, and D. R. Wright, Phys. Rev. 140, A352 (1965).
[c]C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) A277, 312 (1964); C. D. Clark, J. Phys. Chem. Solids 8, 481 (1959).
[d]Ref. 2.
[e]Ref. 4.
[f]Ref. 1.

structure and because of the broadness and shifts introduced by the Kramers-Kronig transformations of the data. The agreement between theory and experiment is very good, especially when one notes that the gaps are large and the errors in these gaps are a small percentage of the total splitting.

The most prominent peak in the reflectivity spectrum is associated, as in other semiconductors and insulators having the diamond structure, with the X_4-X_1 transition. The theoretical X_4-X_1 splitting appears to be 0.3-0.6 eV too large. Since this transition may itself constitute only a nominal part of the optical structure around this peak, as in Si,[14] a density of states or ϵ_2 calculation may be necessary to fix this energy difference more precisely.

The structure in the 16- to 17-eV range was previously assigned[3,1] to the L point in the zone. As is shown in Fig. 1, the L splittings are lower in energy and the only ostensible candidate for this transition is $\Gamma_{25'}$-$\Gamma_{12'}$; we tentatively make this assignment. The $L_{3'}$-L_1 transition is assumed to give rise to the hump-like structure in the experimental spectrum[1,2,4] at 9.5-10.5 eV. The $L_{3'}$-L_3 transition, which lies higher in energy, is most likely masked by the X_4-X_1 peak.

We assign the first direct threshold to $\Gamma_{25'}$-Γ_{15} and put this edge at 7.3 eV. Some measurements[15] have revealed that the structure near this threshold appears to be very sensitive to temperature, and this sensitivity has stimulated interpretation of the optical structure in terms of hybrid excitons.[3] We presume that further study of this region is warranted. At present we cannot predict the form of the $\Gamma_{25'}$-Γ_{15} peak or its temperature dependence since there are several critical points in this region which may give rise to optical fine structure and these critical points are very sensitive to the choice of form factors. In addition, our calculation is not sufficiently accurate to confirm the existence of hybrid excitons, but our assignment of the $\Gamma_{25'}$-Γ_{15} edge ~7.3 eV restricts the size and shape of the proposed exciton. The $\Gamma_{25'}$-Γ_{15} edge cannot be raised without moving the Δ_1 minimum closer to the X point unless the X_4-X_1 splitting is made larger than 13 eV. We have forced the conduction-band minimum to agree with the value obtained by Dean et al.[16] If this constraint is relaxed and Δ_1 is moved out beyond (0.80, 0, 0), only then can the $\Gamma_{25'}$-Γ_{15} gap be increased beyond 8 eV for a fixed X_4-X_1 splitting. The dependence of the principal gaps on the values of the form factors is

Table II. The change of the principal energy gaps in eV for a change in form factor of +0.01 Ry.

	V_{111}	V_{220}	V_{311}	V_{222}
$\Gamma_{25'}-\Gamma_{15}$	−0.116	−0.052	0.222	−0.265
$\Gamma_{25'}-\Gamma_{12'}$	−0.132	−0.162	−0.190	−0.154
X_4-X_1	−0.094	0.018	0.176	−0.102
$\Gamma_{25'}-X_1$	−0.154	−0.012	0.274	−0.206
$L_{3'}-L_1$	−0.018	0.192	0.258	−0.152

given in Table II.

The simplicity of the $(1s)^2$ cores of carbon have inspired orthogonalized plane-wave[17] band calculations, but it was not obvious a priori that the EPM method would be successful for diamond. The success of this method presumably relies on the applicability of the Phillips cancellation theorem.[18] However, the absence of p core states means that the kinetic energy of the valence p electrons is not cancelled.[19] The apparent success of the EPM method for diamond probably arises from the fact that the valence p states have small probability of being in the core because of the form of the p wave function, and therefore complete cancellation is not imperative for these states.

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[1]W. C. Walker and J. Osantowski, Phys. Rev. 134, A153 (1964).
[2]H. R. Philipp and E. A. Taft, Phys. Rev. 136, A1445 (1964); 127, 159 (1962).
[3]J. C. Phillips, Phys. Rev. 139, A1291 (1965).
[4]D. M. Roessler, thesis, University of London, 1966 (unpublished).
[5]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
[6]J. C. Phillips, Phys. Rev. 112, 685 (1958); D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962); D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters 9, 389 (1962); D. Brust, Phys. Rev. 134, A1337 (1964).
[7]T. K. Bergstresser, M. L. Cohen, and E. W. Williams, Phys. Rev. Letters 15, 662 (1965).
[8]M. L. Cohen and J. C. Phillips, Phys. Rev. 139, A912 (1965).
[9]L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).
[10]K. H. Bennemann, Phys. Rev. 133, A1045 (1964).
[11]M. Renninger, Z. Krist. 97, 107 (1937).
[12]M. Renninger, Acta Cryst. 8, 606 (1955).
[13]R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, New York, 1963).
[14]E. O. Kane, to be published.
[15]C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) A277, 312 (1964); C. D. Clark, J. Phys. Chem. Solids 8, 481 (1959).
[16]P. J. Dean, E. C. Lightowlers, and D. R. Wright, Phys. Rev. 140, A352 (1965).
[17]F. Herman, Phys. Rev. 93, 1214 (1954); Proceedings of the International Conference on the Physics of Semiconductors, Paris (Dunod, Paris, 1964), p. 3.
[18]P. W. Anderson, Concepts in Solids (W. A. Benjamin, Inc., New York, 1963), p. 66.
[19]L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959).

RICHARDSON-SCHOTTKY EFFECT IN INSULATORS*

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The Richardson-Schottky formula for thermionic emission from a metallic cathode into the conduction band of an insulator is frequently[1] stated as

$$J_S = \frac{4\pi e m (kT)^2}{h^3} e^{-(\varphi_0 - \Delta\varphi)/kT}. \quad (1)$$

In this expression φ_0 is the work function, and the Schottky term is given by

$$\Delta\varphi = (e^3 F_c/\epsilon)^{1/2}, \quad (2)$$

where ϵ is the dielectric constant, and F_C the field strength immediately in front of the cathode. It has recently been pointed out by Simmons[2] that this expression is invalid when the mobility of the electrons in the dielectric is low, for if one determines the density of current carriers in the insulator, n, from the relationship

$$J = ne\mu F, \quad (3)$$

one may then find that n becomes so large that back-diffusion from the dielectric to the metal will occur. Unfortunately Simmons's discus-

ERRATA

BAND STRUCTURE AND OPTICAL PROPERTIES OF DIAMOND. W. Saslow, T. K. Bergstresser, and Marvin L. Cohen [Phys. Rev. Letters 16, 354 (1966)].

Three points in Fig. 1 were drafted 1 eV too high. They are the Γ_{15} point in the conduction band, and the two adjacent points along the Λ line. A correct picture of the band structure is given in Fig. 1 of Luis R. Saravia and D. Brust, Phys. Rev. 170, 683 (1968).

RECENT ρ-PRODUCTION EXPERIMENTS AND THE PREDICTIONS OF CHIRAL SYMMETRY. D. A. Geffen and T. Walsh [Phys. Rev. Letters 20, 1536 (1968)].

The following additions in proof to Refs. 1 and 3 were inadvertently omitted. Reference 1: See also J. Schwinger, Phys. Rev. 167, 1546 (1968), for a similar analysis of the Novosibirsk data. Reference 3: R. Arnowitt, M. H. Friedman, and P. Nath, Phys. Rev. Letters 19, 1085 (1967).

It is worth mentioning that the latter authors were the first to note in print the possibility of a virtual ρ-mass dependence of the $\rho\pi\pi$ vertex following from an effective Lagrangian.

TEST OF THE $\Delta S = \Delta Q$ RULE IN LEPTONIC DECAYS OF NEUTRAL K MESONS. Bryan R. Webber, Frank T. Solmitz, Frank S. Crawford, Jr., and Margaret Alston-Garnjost [Phys. Rev. Letters 21, 498 (1968)].

In the abstract, "$\mathrm{Im}(x) = -0.88 \pm 0.08$" should be replaced by "$\mathrm{Im}(x) = -0.08 \pm 0.08$."

In the fourth line of the second column of p. 498, "four-constant" should be "four-constraint."

The second sentence after Eq. (7) should read, "They are also insensitive to our choice for $|\delta|$."