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=d. In this respect, it might be interesting to see if Al-AlO<sub>x</sub>-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  $\Delta p = (2\pi/2)$  $d\eta\hbar$ . 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

The authors are indebted to G. W. Lehman

for valuable discussions, and to R. R. Hargrove for preparing the diodes studied.

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## BAND STRUCTURE AND OPTICAL PROPERTIES OF DIAMOND\*

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Recently several authors<sup>1-4</sup> 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)<sup>5,6</sup> which has been used<sup>5-8</sup> 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<sup>9,10</sup> arising from tetrahedral bonding. This tetrahedral distribution of charge accounts for the presence of the otherwise forbidden (222) reflection in x-ray data.<sup>11,12</sup>

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.<sup>13</sup> In Table I we list the principal energy gaps of this band structure and the corresponding experimental values. The location of the conductionband 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.

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,<sup>14</sup> a density of states or  $\epsilon_2$  calculation may be necessary to fix this energy difference more precisely.

The structure in the 16- to 17-eV range was previously assigned<sup>3,1</sup> 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<sup>1,2,4</sup> 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.

Table I. Theoretical and experimental values for the location of the conduction band minimum and the principal band gaps of diamond. Except for the  $\Gamma_{25'}$ - $\Delta_1$  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) <sup>a</sup>	Experiment (eV) <sup>a</sup>
$\begin{array}{c} \Delta_{\rm minimum} \\ \Gamma_{25'} - \Delta_1 \\ \Gamma_{25'} - \Gamma_{15} \\ X_4 - X_1 \\ L_{3'} - L_1 \\ \Gamma_{25'} - \Gamma_{12} \end{array}$	(0.77, 0, 0) 5.4 7.3 12.9 10.9 16.5	$(0.76 \pm .02, 0, 0)^{b}$ 5.48 <sup>C</sup> 7.3 <sup>d</sup> , e 12.3-12.6 <sup>f</sup> , d, e 9.5-10.5 <sup>d</sup> , e 16-17 <sup>f</sup> , e

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<sup>d</sup>Ref. 2.

e<sub>Ref. 4</sub>.

<sup>f</sup>Ref. 1.

We assign the first direct threshold to  $\Gamma_{\rm 25'}\text{--}$  $\Gamma_{15}$  and put this edge at 7.3 eV. Some measurements<sup>15</sup> 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.<sup>3</sup> We presume that further study of this region is warranted. At present we cannot predict the form of the  $\Gamma_{25'}$ - $\Gamma_{15}$  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  $\Gamma_{25'}$ - $\Gamma_{15}$  edge ~7.3 eV restricts the size and shape of the proposed exciton. The  $\Gamma_{\rm 25'}\text{--}$  $\Gamma_{15}$  edge cannot be raised without moving the  $\Delta_1$  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.<sup>16</sup> If this constraint is relaxed and  $\Delta_1$  is moved out beyond (0.80, 0, 0), only then can the  $\Gamma_{25'}$ - $\Gamma_{15}$  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 c	hange	of the	principal	energy	gaps in	
eV for a cha	ange i	n form	factor	c  of  +0.01	Rv.		

	<i>V</i> <sub>111</sub>	$V_{220}$	V <sub>311</sub>	${V}_{222}$
$\Gamma_{25'} - \Gamma_{15}$	-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<sup>17</sup> band calculations, but it was not obvious a <u>priori</u> that the EPM method would be successful for diamond. The success of this method presumably relies on the applicability of the Phillips cancellation theorem.<sup>18</sup> However, the absence of p core states means that the kinetic energy of the valence p electrons is not cancelled.<sup>19</sup> 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 pwave function, and therefore complete cancellation is not imperative for these states.

One of us (MLC) benefitted from conversations with Dr. Frank Herman and Professor J. C. Phillips.

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## 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<sup>1</sup> stated as

$$J_{S} = \frac{4\pi e m (kT)^{2}}{h^{3}} e^{-(\varphi_{0} - \Delta \varphi)/kT}.$$
 (1)

In this expression  $\varphi_0$  is the work function, and the Schottky term is given by

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

where  $\epsilon$  is the dielectric constant, and  $F_C$  the

field strength immediately in front of the cathode. It has recently been pointed out by Simmons<sup>2</sup> 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

$$J = ne\,\mu F\,,\tag{3}$$

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