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<sup>24</sup>If in fact the assertion of Kenkre and Dresden (Refs. 22, 23) were correct, it would have been of paramount importance in the theory of electrical conductivity in solids, since it would have bypassed the often difficult task of solving the integral transport equation figuring in all earlier theories. They also emphasized that their formal expression for  $\sigma(0)$ , equivalent to our Eq. (10), can be used without invoking the technique of the " $\lambda^2 t$  limit" of van Hove, in contrast to other formal expressions (Ref. 2) for the conductivity which necessitate the use of the " $\lambda^2 t$  limit" technique. As our discussion shows, this claim is wrong.

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## Layer Method for Band Structure of Layer Compounds

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We present a method of calculating the band structure of layer compounds that combines the transmission and reflection matrices from individual atomic layers. The computing time increases linearly with the number  $p$  of layers in the repeat unit, compared with  $p^3$  for other methods, thus rendering the method suitable for layer compounds with complicated stacking sequences. Results for  $\text{MoS}_2$  are described.

The method presented here is based on the layer-scattering method originally developed for low-energy electron diffraction.<sup>1-4</sup> We believe that it is particularly well suited for the calculation of the band structure of the layer compounds such as the transition-metal dichalcogenides. The latter compounds have recently attracted much experimental interest.<sup>5</sup>

The usual methods of calculating band structure [augmented plane wave (APW), Korringa-Kohn-Rostoker, etc.] when applied to crystals, especially anisotropic crystals having so many atoms per unit cell, are cumbersome to the point that calculations are possible only for points of high symmetry. Calculations made so far have mainly employed semiempirical methods because of these difficulties, though recently Mattheiss<sup>6</sup> has

made first-principles calculations using the APW method at symmetry points, with a tight-binding scheme interpolating between the points.

All the various structures of the layered transition-metal dichalcogenides can be broken down into layers containing only one type of atom. The complexity is generated by the stacking together of layers. It is the large unit-cell dimension normal to the layers that necessitates the large number of Fourier components required to describe the wave functions. Parallel to the layers only a modest number of Fourier components are required. It would seem logical to employ a two-dimensional Fourier expansion of the wave function parallel to the layers, the  $z$  variation being represented in real space.

The treatment given here follows Pendry.<sup>3</sup> The

crystal is described as an array of atomic layers stacked on top of one another, each with two-dimensional translational symmetry parallel to the  $x$ - $y$  plane. We shall imagine that between consecutive layers there is a region of constant potential  $V_0$  (which can, if desired, be shrunk to zero

width).

For a given energy  $E$  and component of the Bloch wave vector  $\vec{k}$  parallel to the planes, the Bloch waves are expanded in a Fourier series of the two-dimensional reciprocal lattice of the basic layers. Between the  $i$ th and  $(i+1)$ th planes the Bloch wave  $\psi_i$  is given by Eq. (13) of Pendry<sup>3</sup>:

$$\psi_i = \sum_{\vec{g}} [u_{\vec{g}}^+ \exp(i\vec{K}_g^+ \cdot \vec{r}) + u_{\vec{g}}^- \exp(i\vec{K}_g^- \cdot \vec{r})], \quad (1)$$

where

$$\begin{aligned} \vec{K}_g^\pm &= (k_x + g_x, k_y + g_y, \pm [E - V_0 - (k_x + g_x)^2 - (k_y + g_y)^2]^{1/2}), \quad E - V_0 > (k_x + g_x)^2 + (k_y + g_y)^2, \\ &= (k_x + g_x, k_y + g_y, \pm i[(k_x + g_x)^2 + (k_y + g_y)^2 - E + V_0]^{1/2}), \quad E - V_0 < (k_x + g_x)^2 + (k_y + g_y)^2, \end{aligned} \quad (2)$$

and  $k_x, k_y$  are the  $x, y$  components of  $\vec{k}$ . Atomic units are used, with energies in rydbergs.

We have made use of the translational symmetry of the layers to require that our wave function has Bloch-wave properties parallel to the layers, with wave vector  $\vec{k}$ . If the layers are stacked together repeating every  $p$  layers, we also place the requirement of a Bloch condition in the  $z$  direction:

$$\psi_{i+p} = \exp(i\vec{k} \cdot \vec{d}_z + i\vec{k}_\parallel \cdot \vec{d}_\parallel) \psi_i, \quad (3)$$

where  $\vec{d}$  is the displacement of each identical set of  $p$  layers relative to the previous one. Or, in terms of the plane-wave amplitudes,

$$u_{i+p}^+ = \exp(i\vec{k} \cdot \vec{d}) u_i^+, \quad (4)$$

$$u_{i+p}^- = \exp(i\vec{k} \cdot \vec{d}) u_i^-, \quad (5)$$

where  $u_i^\pm$  denotes the whole column matrix  $u_{\vec{g}}^\pm$ .

If the transmission and reflection coefficients  $Q$  of the repeat unit consisting of  $p$  layers are known,

$$u_{i+p}^+ = Q^I u_i^+ + Q^{II} u_{i+p}^-, \quad (6)$$

$$u_i^- = Q^{III} u_i^+ + Q^{IV} u_{i+p}^-, \quad (7)$$

these equations lead<sup>1,2,3</sup> to an eigenvalue problem for the Bloch waves and Bloch wave vector  $\vec{k}$ :

$$\begin{aligned} \begin{bmatrix} Q^I & Q^{II} \\ -(Q^{IV})^{-1} Q^{III} Q^I & (Q^{IV})^{-1} (I - Q^{III} Q^{II}) \end{bmatrix} \begin{bmatrix} u_i^+ \\ u_{i+p}^- \end{bmatrix} \\ = e^{i\vec{k} \cdot \vec{d}} \begin{bmatrix} u_i^+ \\ u_{i+p}^- \end{bmatrix}, \end{aligned} \quad (8)$$

where the notation of Pendry<sup>3</sup> has been followed. This equation is used to find  $k_z$  having fixed  $E$  and  $\vec{k}_\parallel$ .

The dimensions of the matrix to be diagonalized are  $2n \times 2n$ , where  $n$  is the number of two-dimen-

sional Fourier components used, typically  $n=9$ . Increasing complexity of structure in the stacking of layers leaves  $n$  unaffected, and calculating the band structure once the  $Q$ 's are determined remains a modest computational problem even for layer compounds. Herein lies the power of the method.

The crux lies in calculating the  $Q$ 's. Kambe<sup>1c</sup> has given a method of calculating reflection and transmission matrices for an isolated layer of atoms. Layers can be built up into more complex units by adding one layer at a time, multiplying by its reflection and transmission matrices. Each successive addition of a layer involves the same amount of computation and so the time to combine  $p$  atomic layers into the repeat unit of the crystal is proportional to  $p$ . In an APW calculation the number of three-dimensional Fourier components is proportional to  $p$ , but the machine time required to diagonalize the Hamiltonian matrix is proportional to  $p^3$ . Similarly, times for Korringa-Kohn-Rostoker methods scale as  $p^3$ . Hence, layer methods are increasingly useful as the complexity of the crystal increases.

With the same formalism we can establish the two-dimensional band structure of an isolated atomic layer or isolated triple-layer "sandwich" such as S-Mo-S. The relevant  $Q$  matrices can be used to determine how an incident wave is reflected and transmitted by such a layer. If the latter has a bound state for this wave we shall have a pole of the reflection and transmission matrices. A bound state of the isolated sandwich is what is meant by the two-dimensional band structure. The poles of, e. g.,

$$\det[Q^{III}(E\vec{k}_\parallel)] \quad (9)$$

thus give the two-dimensional band structure.

This means that we are able to calculate the two-dimensional band structure as a subsidiary result when calculating the three-dimensional case.

Calculations begin with the Kambe<sup>1c</sup> treatment of scattering by individual layers of atoms. This requires the phase shifts of atoms, and we must now describe how we obtained these. We used the conventional assumptions<sup>7</sup> that the charge density in the solid is to be had by allowing the charge of spherically symmetrical atoms to overlap; Herman-Skillman<sup>8</sup> atomic wave functions were used to find this charge.

Only the spherically symmetric component of the charge density about any given atom was considered; and the potential was constructed for an electrostatic component, found by solving Poisson's equation, and an exchange and correlation<sup>1d</sup> component, for which we adopted the  $X\alpha$  approximation with  $\alpha = 1$ :

$$V_x = -6[3\rho(\vec{r})/8\pi]^{1/3} \text{ Ry.} \quad (10)$$

We also tried using the recommended best atomic values for  $\alpha$ .<sup>9</sup> However, we found that this procedure gave band structures slightly less satisfactory than with  $\alpha = 1$ .

Muffin-tin spheres were drawn about the atoms. Outside the spheres, but within the S-Mo-S sandwiches, the potential was approximated as a constant equal to an average potential in this region. Between sandwiches, where the lower charge density can be expected to give a less attractive potential, another average was taken, which allows the potential to be rather more realistic than the simplest muffin-tin approximation.

Convergence of the calculation was investigated, and required phase shifts up to  $l = 2$ , while in the Fourier expansion, thirteen terms were used within a layer and seven between layers (the large interlayer spacing reduces the importance of the strongly decaying higher Fourier components). Computation times on an IBM 370/165 were 0.4 sec to evaluate all scattering by individual layers, 1.5 sec to assemble the layers into sandwiches and the two sandwiches into a repeat unit, and a further 0.2 sec to solve the eigenvalue equation (8).

We have calculated the three-dimensional band structure of  $2H$  and  $3R$   $\text{MoS}_2$  and the two-dimensional band structure of  $\text{MoS}_2$ . The calculated bands along  $\Gamma K M T A$  in the Brillouin zone<sup>10</sup> are shown in Fig. 1 for the  $2H$  structure. The other band structures mentioned and more extensive results for the  $2H$  structure will appear in a full paper, together with comparison with exper-

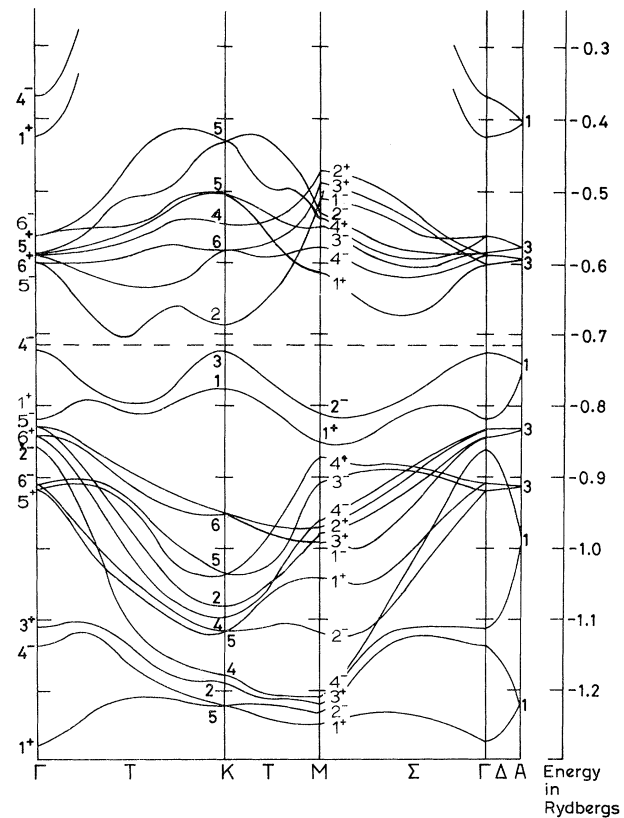


FIG. 1. Energy bands for  $2H$   $\text{MoS}_2$  relative to the vacuum level.

iment and other calculations. Suffice it to say here that broadly the ordering and nature of the bands agrees with the model of Wilson and Yoffe,<sup>11</sup> earlier semiempirical tight-binding calculations,<sup>10,12</sup> and recent first-principles calculations,<sup>6,13</sup> while differing in the magnitudes of some band gaps.

As regards the indirect gap between valence and conduction bands, our value of  $\frac{1}{4}$  eV agrees with Yoffe's<sup>5</sup> 0.3 eV from transport properties, while Mattheiss's<sup>6</sup> calculated 1 eV agrees better with the indication of about 1.2 eV from photoemission.<sup>14</sup> Which experimental value is correct for the bulk is at present uncertain, but in photoemission the relevant electrons probably originate in the first sandwich layer and thus reflect perhaps more the two-dimensional band structure which has a larger gap.<sup>15</sup> In any case, there are uncertainties about how the exchange and correlation hole changes between the full valence bands and empty conduction bands.<sup>16</sup> More significant, therefore, may be our finding that the so-called  $d(z^2)$  band just below the Fermi level (from  $-0.72$  to  $-0.85$  Ry in Fig. 1) overlaps the lower  $p$  va-

TABLE I. Features in the optical spectrum.

Feature	Observed (Ref. 17) (eV)	Calculated (eV)	Levels
$A, B^a$	2.01	1.9	$\Gamma_4^- \rightarrow \Gamma_5^+$
$C$	2.76	3.0	$K_3 \rightarrow L_5$
$D$	3.17	3.5	$K_6 \rightarrow K_4$
$\alpha, \beta^a$	3.81	3.6	$\Gamma_6^+ \rightarrow \Gamma_5^-$
$E$	4.59	4.6	$M_1^+ \rightarrow M_2^-$
$F$	4.86	4.9	$M_2^- \rightarrow M_4^+$

<sup>a</sup>Spin-orbit splitting.

lence bands a little, in agreement with experiment<sup>14</sup> and Kasowski,<sup>13</sup> whereas Mattheiss<sup>6</sup> finds a gap. The differences between the three calculations presumably arise from some difference in the treatment of the interstitial potential, since the setting up of the potential in other respects was the same. In Table I we list the calculated energy gap which we assign to various features in the observed<sup>17</sup> optical spectrum. In particular, we agree with Mattheiss over the vexing question of the  $A, B$  excitons in assigning them to the  $d-d$  transition  $\Gamma_4^-$  to  $\Gamma_5^+$ . All in all, the accuracy is as can be expected from such calculations, and a fuller test of the theory awaits the calculation of matrix elements and densities of states.

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## Interaction of High-Energy Phonons with Conduction Electrons in Small-Gap Semiconductors

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We consider phonon-electron interactions in highly doped III-V and II-VI semiconducting compounds, including nonparabolicity of the conduction band and the spin-orbit interaction. Absorption coefficients are calculated for monochromatic phonons produced by superconducting Sn and Al tunnel junctions, and we predict the possibility of observing directly an interaction of conduction electrons with slow and fast transverse modes, and phonon-induced spin-flip transitions.

Special properties of conduction electrons in small-gap semiconductors introduce new elements into their interaction with acoustic phonons. The involved character of the conduction

band and a large spin-orbit energy give rise to an interaction of electrons with transverse phonon modes and to spin-flip processes. The same features affect the electron transport properties