schlegel, J. Math. Phys. 3, 522 (1962); T. M. Rice, J. Math. Phys. 8, 158 (1967).

[11] We note that if $v_F q \gg \omega_D$, the exact $N(0)VK(q)\to 1 - N(0)V\ln(T/T_c)$, whereas due to the assumption of a delta-function interaction in the Gor'kov theory the $K(q)$ we introduced does not have this property. Hence the true $g_n(k,\beta)$ approaches unity for large n and k, and the sum and integral in Eq. (9) are convergent. The rearrangement of terms is then valid. The rearrangement that was used here leads to convergence before the part $K(q)$ for $v_F q \geqslant \omega_D$ becomes important.

[12] We should point out that b has temperature dependence through the parameter $\alpha_0 = \hbar v_F/4\pi kT$. Hence for $\epsilon \simeq 1$, constant b is not the same as constant field B. However, because of the slowly varying nature of the magnetization curve, this adjustment is small under most circumstances.

[13] K. Maki, Physics 1, 21 (1964).

Existence of a Gap in the Electronic Density of States of a Tetrahedrally Bonded Solid of Arbitrary Structure

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Rigorous bounds for the density of electronic states are given for an idealized model of a group-IV semiconductor based on the tight-binding method. These include inner bounds which define a minimum gap in the density of states. The importance of this development lies in its independence of periodicity. It applies not only to crystalline structures made up of tetrahedral bonds but also the random tetrahedral network which recent studies have suggested for amorphous Si and Ge.

Recent experiments[1,2] have shown that amorphous Si and Ge appear to have a gap in the electronic density of states rather similar to that found in the corresponding diamond cubic crystals. This is a surprising result in view of the inevitable high degree of structural disorder, whatever the detailed structure of the amorphous phase is assumed to be. Studies of the radial distribution function[3-5] have in fact suggested a *random tetrahedral network* model for such solids. It seems that infinite networks can be constructed such that nearest neighbors are in perfect tetrahedral coordination (apart from small deviations of bond lengths and angles from ideal values) and yet the distribution of further neighbors is highly disordered. Amorphous semiconductors as prepared in the laboratory are thus considered to have such a perfectly tetrahedrally bonded structure with a distribution of voids[3] or other defects dependent on the preparation.

The occurrence of a band gap in such a system has stimulated widespread theoretical interest but most rigorous results in this area[6,7] have so far been obtained for models in which disorder is imposed on a basic *periodic* system. The relevance of such models to the amorphous semiconductor problem is at best oblique. Here we shall address ourselves to the problem as it stands without using periodicity in any way. A rather idealized tight-binding formulation of the problem will be used, but as far as the structure is concerned, we use only the assumed tetrahedral coordination of nearest neighbors, so that the results obtained apply to diamond, wurtzite, and related crystal structures and also the ideal random-network model for amorphous phases. We shall show that this model indeed entails a gap for all such structures.

We assume a Hamiltonian of the form

$$H=\sum_{i,j} V_1|\varphi_i\rangle\langle\varphi_j| + \sum_{k,l} V_2|\varphi_k\rangle\langle\varphi_l|. \tag{1}$$

The functions φ may be visualized as directed hybridized orbitals of the familiar sp^3 type. The first summation is over pairs of different orbitals i and j associated with the same atom. There are of course four per atom and they are assumed to be directed toward the nearest neighbors. The second summation is over pairs of orbitals belonging to nearest neighbors and associated with the same bond (e.g., 1, 1′ in Fig. 1). To keep things as simple as possible, we treat these orbitals as orthogonal as is commonly done in such models.

Schrödinger's equation gives

$$(H-E)\psi=0 \tag{2}$$

for an eigenstate of the Hamiltonian, assumed to be expandable in terms of φ_i. A zero density of states at E is to be deduced if either (2) has no solution or, in the limit of an infinite system, the eigenstate ψ cannot be normalized (i.e., it diverges at infinity). Let us then assume the ex-

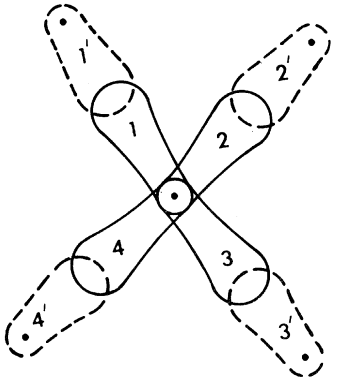

FIG. 1. The orbitals 1-4 whose coefficients in a tight binding expansion are the elements of the vector u. The coefficients of 1'-4' form the vector v.

istence of an eigenstate ψ at energy E and examine its properties. To do so we first project out that part of Eq. (1) which involves orbitals around a given atom.

Let us label 1-4 the bonds associated with a given atom (Fig. 1). The coefficients of the corresponding orbitals φ_i of that atom in the expansion of ψ may be considered as a column vector u. The coefficients of the orbitals with which they overlap form a second vector v. According to Eqs. (1) and (2),

$$\textstyle\sum_j M_{ij} u_j = -V_2 v_i, \qquad (3)$$

where

$$M_{ij}(E) = \begin{cases} -E, & i=j \\ V_1, & i \neq j \end{cases}. \qquad (4)$$

This matrix has eigenvalues

$$\lambda_1 = 3V_1 - E, \quad \lambda_2 = -V_1 - E. \qquad (5)$$

Suppose that neither eigenvalue has modulus greater than $|V_2|$,

$$\max|\lambda_i| < |V_2|. \qquad (6)$$

Then

$$|V_2|\,|v| < \{\max|\lambda_i|\}\,|u|,$$

and

$$|v| < x|u|, \qquad (7)$$

where $0<x<1$ and $|u| \equiv (\sum_i u_i^2)^{1/2}$. It remains to be shown that such a relation cannot be sustained at every site without a divergence at infinity.

Define

$$\Delta_i = |v_i|^2 - |u_i|^2. \qquad (8)$$

Such a quantity can be defined at every site and we indicate this with a site index j in parenthesis. Let $\Delta_i(j)$ be summed over some finite cluster of atoms. From Eq. (7)

$$0 > (x^2-1)\sum_j |u(j)|^2 > \sum_{i,j} \Delta_i(j). \qquad (9)$$

However, the quantities $\Delta_i(j)$ cancel in pairs associated with given bonds within the interior of the cluster; hence we obtain a result analogous to Green's theorem

$$\sum_{i,j} \Delta_i(j) = \sum_{i,j}^{\text{surface bonds}} \Delta_i(j)$$

and hence

$$\Big|\sum_{i,j} \Delta_i(j)\Big| < \sum_{j}^{\text{surface atoms}} |u(j)|^2(1+x^2). \qquad (10)$$

A surface atom is one with at least one bond not connected to an atom in the cluster. Suppose that we expand the cluster by the addition of successive layers, labeled n, such that all the surface bonds at one step are interior bonds at the next. Let the number of atoms in the cluster after n steps be $\mathfrak{N}_n$. Define the normalization function

$$S_n = \mathfrak{N}_n^{-1} \sum_{j}^{n\text{th cluster}} |u(j)|^2.$$

Then the above equations and inequalities give

$$\frac{S_{n+1}}{S_n} > \frac{\mathfrak{N}_n}{\mathfrak{N}_{n+1}} \frac{1+x^2}{2x^2}. \qquad (11)$$

It is easily shown that the layers can be added to the cluster in such a way that the ratio of $\mathfrak{N}$'s tends to unity as n tends to infinity (essentially because the ratio of surface to volume can be made to tend to zero). In that case the left-hand side of this inequality has a lower bound at infinity which is greater than unity since $0<x<1$. Therefore such a state as we are considering cannot be normalized and the condition (6) defines a range of energies such that the density of states is zero. It may be established similarly that

$$\min|\lambda_i| > |V_2| \qquad (12)$$

also defines forbidden regions of energy. Figure 2 shows all the resulting bounds on the density of states, for all values of $V_1/|V_2|$. Except for the case $|V_1/V_2| = \frac{1}{2}$ *there is always a gap in the density of states.* Is there always at least one allowed state on either side of this gap? The answer is yes, as we have demonstrated elsewhere[8] the existence of two particular states ("bonding s state," "antibonding p state," respectively) which indeed must lie on different sides of the

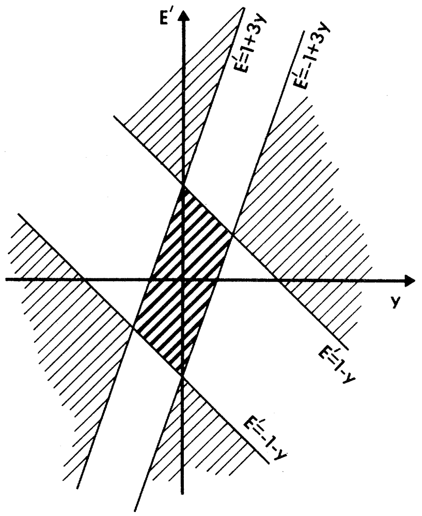

FIG. 2. Bounds on the density of states. $E'=E/|V_2|$, $y=V_1/|V_2|$. Shaded regions are forbidden, unshaded allowed. The heavily shaded region is the region to which the inequality (6) applies.

gap.

Our conclusion is that for such an idealized model (which we do not believe to be oversimplified to the point of being irrelevant to real physical systems) the existence of the gap is not dependent on periodicity of the structure. Note that the results are not compatible with the existence of localized states throughout the gap, as is often postulated, although these would presumably be introduced by defects and/or the slight deviations of bond configurations from the ideal values here assumed.

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[1] T. M. Donovan and W. E. Spicer, Phys. Rev. Lett. 21, 1572 (1968).

[2] T. M. Donovan, W. E. Spicer, and J. M. Bennett, Phys. Rev. Lett. 22, 1058 (1969).

[3] S. C. Moss and J. F. Graczyk, Phys. Rev. Lett. 23, 1167 (1969).

[4] D. E. Polk, J. Non-Cryst. Solids, 5, 365 (1971).

[5] N. J. Shevchik, Bull. Amer. Phys. Soc. 16, 347 (1971), and to be published.

[6] M. H. Cohen, J. Non-Cryst. Solids 4, 391 (1970).

[7] E. N. Economou, S. Kirkpatrick, M. H. Cohen, and T. P. Eggarter, Phys. Rev. Lett. 25, 520 (1970).

[8] D. Weaire, to be published.

Surface and Pseudosurface Modes in Ionic Crystals*

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The nature of the surface and pseudosurface modes in ionic-crystal slabs is clarified, and some apparent discrepancies among the previous studies are resolved. The first shell-model calculations of surface-mode spectra are reported; the results for NaCl are significantly different from those obtained with the rigid-ion model. A new type of long-wavelength optical surface mode has been found in the shell-model results for RbF.

Several theoretical treatments of optical surface modes in ionic crystals have appeared recently,[1-7] and it has been stated that there appear to be discrepancies among the results of these treatments.[3,5,7] In the present Letter the nature of the surface modes will be clarified, and these results reconciled.

Until the present, two methods have been used in calculations of optical surface modes in ionic crystals: The first is the continuum approximation, first used by Fuchs and Kliewer[1] for a slab with two flat surfaces, and subsequently used by Englman and Ruppin[2,3] for crystals with other geometries. The second method involves lattice-dynamical calculations for a slab-shaped crystal based on the rigid-ion model of Kellermann.[8] Such calculations were first carried out by Lucas[4] for $\vec{q}=0$, where $\vec{q}$ is the two-dimensional wave vector associated with propagation parallel to the surfaces. Subsequently Tong and Maradudin[5] carried out a calculation for values of $\vec{q}$ lying throughout the first two-dimensional Brillouin zone.

In reconciling the results of these treatments, it is necessary to recognize three limitations of the continuum approximation: First, it is valid only at large wavelengths (small $\vec{q}$) in a thick