

Evaluation of Surface-State Theories

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(Received 4 November 1968)

Fundamentals of surface-state theory, such as analytic continuation and limitations of the Bloch theorem in a finite lattice, are critically discussed. For illustrative purposes, a specific and simple surface-state problem is then solved by different methods: the coefficient method, the scattering method, the determinant method, and the integral method. Many novel points of view and interconnections are introduced. The advantages and disadvantages of each method are stressed, especially with respect to more complicated problems such as three-dimensional surface states on zinc blende.

I. INTRODUCTION

ALTHOUGH theoretical interest in electronic surface states has existed since the 1930's, this interest was negligible because there was negligible technological motivation or experimental confirmation. The first major technological impetus for surface states was the advent of transistor technology during the late 1940's. Subsequent to this, further motivation has rapidly developed in a variety of solid-state technologies, such as microelectronics, electrophotography, catalysis, powders, thin films, and interfaces, where large surface-to-volume ratios emphasize the importance of surface-controlled phenomena.

In the last few years, several monographs describing the electrical properties of surfaces have appeared. Some of these monographs¹⁻³ emphasize experimental techniques and results, and include only token chapters on surface-state theory. These chapters primarily catalog the results of a few surface-state calculations and do not consider the validity or scope of computational procedures. No over-all viewpoint is given and consequently the information is fragmentary. Sometimes it is even erroneous, as will be shown later. The theoretically oriented monographs^{4,5} and individual papers, on the other hand, are specialized in that they consider one theoretical approach to the exclusion of all the others. Furthermore, it will be shown that the *fashionable* approaches are not necessarily the best.

What appears to be missing is a timely and critical appraisal of the assumptions and the various quantum-mechanical techniques that can be used for computing surface states. The purpose of this paper is to accomplish

this in a way acceptable to both experimentalists and theoreticians.

In particular, certain fundamentals, such as analytic continuation and limitations of the Bloch theorem in a finite lattice, are critically evaluated. For illustrative purposes, a specific and simple surface-state problem is then solved by four related methods: the coefficient method, the scattering method, the determinant method, and the integral method. Many novel points of view are introduced, and the advantages and disadvantages of each method are stressed, especially with respect to more complicated problems, such as three-dimensional surface states on zinc blende. The implications of bulk band structure are considered separately in Sec. V.

It is not possible, or necessary, to consider every aspect of surface-state theory in this short paper. Instead, only the highlights, in the opinion of the authors, will be emphasized. Dynamic surface-state properties (scattering, trapping, mobility, optical absorption, recombination, etc.) will not be considered here, since static surface-state properties (energies, density-of-states, band-bending, etc.) are themselves in a formative stage. For simplicity, the one-electron scheme will be used throughout, although it is probable that surface polarons and many-body interactions between surface states can occur; these complicate matters. Finally, only surface states on the *free* surface of a crystal will be treated, since interface states have similar, but more intricate, properties.

Another study⁶ of surface-state methods will appear soon. More attention will be given to the resolvent technique, the Mathieu-potential problem, the Green's-function technique, and certain semiclassical methods, such as the Madelung-potential approach and the dangling-bond approach. The approach will be encyclopedic rather than editorial. It will stress historical ac-

* Supported by the Office of Naval Research under contract No. N0014-67-A-0151-0014.

¹ A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland Publishing Co., Amsterdam, 1965).

² D. R. Frankl, *Electrical Properties of Semiconductor Surfaces* (Pergamon Press, Inc., New York, 1967).

³ F. F. Vol'kenshtein, *The Electronic Theory of Catalysis on Semiconductors* (The Macmillan Co., New York, 1963).

⁴ J. Koutecký, in *Advances in Chemical Physics*, edited by I. Prigogine (Wiley-Interscience, Inc., New York, 1965), Vol. 9, pp. 85-168. There is an extensive bibliography included.

⁵ T. B. Grimley, *Advan. Catalysis* 12, 1 (1960).

⁶ S. G. Davison and J. D. Levine, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, to be published).

curacy rather than criticism. In these respects, the new study will be complementary to the one presented here.

II. FINITE-LATTICE POTENTIAL

Any real crystal is finite. The potential representing the lattice $V(z)$ is periodic over the confined region of space occupied by the lattice, and it becomes the constant value (zero) of free space far away from the lattice. This is illustrated schematically in Fig. 1(a) by the potential profile drawn through a *particular* row of atoms of a three-dimensional binary (MX -type) lattice. To be precise, the potential in Fig. 1(a) is more nearly a pseudopotential; it is an appropriate smoothed potential which omits the Coulomb potential of the nuclei, since the valence electrons must have wave functions orthogonal to those of the core electrons. In region I, the interior of the lattice, $V(z)$ is periodic, $V(z) = V(z+na)$, where z is the one-dimensional position coordinate, a is the periodic interval of the lattice (twice the nearest-neighbor distance in the present case), and n is an integer. In the vacuum, region II, $V(z)=0$. In regions III and III', $V(z)$ describes the transition between the interior and the vacuum. Regions III and III' need not be the same, since opposite faces of a lattice may terminate in different ways, viz., the polar faces, (111) and $\bar{1}\bar{1}\bar{1}$, of zinc blende.

Clearly, if $V(z)$ is exactly specified over all space, one can, in principle, solve the Schrödinger equation rigorously for *all* the eigenfunctions and eigenvalues. These are the delocalized wave functions and eigenvalues of the "bulk" band structure (similar to that of the infinite lattice), and the localized wave functions and energies of the surface states. Since $V(z)$ is a confining potential, one automatically obtains quantization, without resorting to artificial cyclic boundary conditions frequently employed to quantize the infinite-lattice problem.

In practice, however, $V(z)$ is not well specified over all space. It can be approximated by the equivalent

infinite-lattice potential in region I and completely specified by definition in region II. But there is no knowledge of $V(z)$ in regions III and III', nor is the extent of these transitional regions generally known. The problem is even more complicated by the fact that the potential profile in Fig. 1(a) is generally different for different rows of atoms. Generally, in three dimensions, the surface potential of region III has ripples in the surface plane, because of the atomic "graininess" of the surface. That is, the locus of constant-energy points is not a plane, but is more like an egg crate. Not surprisingly, therefore, the solution of the finite-lattice problem invariably necessitates describing the surface region by some approximation.

In the earliest one-dimensional theoretical treatment,⁷ region III was replaced by a potential discontinuity separating regions I and II, a mathematically simple but approximate concept which requires only a simple boundary condition, namely, the continuity of the wave function Ψ and its gradient across the potential discontinuity. The exact point of termination is arbitrary and its effect on the surface-state energies may be obtained in certain simple cases. For a general lattice potential expanded as a Fourier series, it is convenient to terminate the lattice either at a relative maximum [Fig. 1(b)] or minimum [Fig. 1(c)] of the potential. Shockley⁸ considered termination at a maximum to be the correct one-dimensional representation of a covalent lattice. Surface states (Shockley states) appeared if there was *negligible* surface perturbation and if the bands were "crossed." Despite the figure in Shockley's paper which shows a smooth termination of the lattice, as in Fig. 1(a), his mathematics actually corresponds to the potential discontinuity shown in Fig. 1(b). This point has been overlooked.¹ [Note added in proof. Further, a more appropriate representation of a covalent lattice in one dimension would be Fig. 1(c), in accordance with the OPW calculations of Kleinman and Philips, Phys. Rev. **125**, 819 (1962). They computed a crystal-potential minimum and a valence-electron-charge-density maximum between the nearest-neighbor atoms in diamond. Accordingly, Fig. 1(b) would represent termination at the nuclei, while Fig. 1(c) would represent termination midway between nuclei.] Whether Fig. 1(b) or 1(c) is the *best* representation of the termination of a covalent crystal is *academic* because of the cleaved {111} surfaces of diamond-like lattices have *extreme* surface perturbations, since they are violently reconstructed.⁹ The reconstruction is, in fact, suggested by Fig. 1(c), where the extra half-cell at the surface would represent a chemically unsaturated or "dangling" bond. Reconstruction is practically negligible for partially ionic crystals whose surfaces are

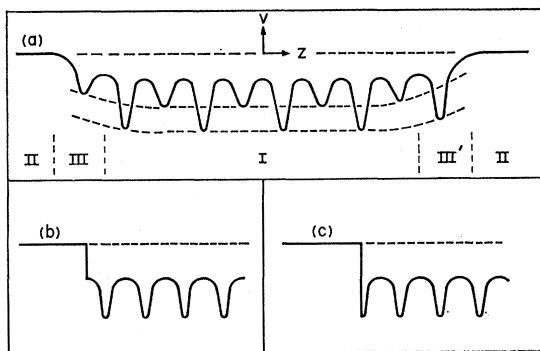


FIG. 1. Schematic 1-D crystal potentials for finite lattices, showing the nature of the termination. A binary lattice is shown in (a). A monatomic lattice is shown in (b) and (c), where the crystal termination is idealized for mathematical purposes as a step. The steps in (b) and (c) occur at the potential maximum and minimum, respectively.

⁷ I. Tamm, Z. Physik **76**, 849 (1932); Physik Z. Sowj. **1**, 733 (1932).

⁸ W. Shockley, Phys. Rev. **56**, 317 (1939).

⁹ P. W. Palmberg, J. Surface Sci. **11**, 153 (1968); J. J. Lander, *ibid.* **1**, 125 (1964).

electrostatically stabilized,¹⁰⁻¹² such as zinc blende (110), wurtzite (1120), and NaCl (100). To be precise, their surface mesh is identical with that of the bulk, according to low-energy electron diffraction (LEED).

An alternate description of the lattice termination is possible with the variety of tight-binding schemes that have appeared in the literature.¹³ Here region III may be represented by Coulomb and exchange integrals having values different from those of region I. However, to achieve quantitative computational results from these techniques, a detailed knowledge of the potential in region III is required. In Sec. IV, the various descriptions of the lattice termination are described in some detail.

III. LIMITATION OF THE BLOCH FUNCTION

A universal and powerful simplification of band-structure problems for infinite lattices is afforded by the exploitation of the symmetry properties of the lattice potential. Consequently, in attempting to solve the finite-lattice problem, symmetry properties should be invoked if they are applicable. Generally, infinite lattices display a variety of rotational symmetries, but the symmetry properly common to all infinite lattice potentials $V(\mathbf{r})$ is translational symmetry, written here in one-dimensional notation for simplicity: $V(z) = V(z+na)$. Here z is the position vector and a is an appropriate lattice constant. It then follows from Floquet's theorem¹⁴ that the solutions of the Schrödinger equation have the following forms:

$$\Psi(z+na) = e^{i n \lambda a} \Psi(z), \quad (1)$$

$$\Psi(z) = u_\lambda(z) e^{i \lambda z}, \quad u_\lambda(z+na) = u_\lambda(z)$$

where the propagation constant λ may be complex

$$\lambda = k + iK \quad (k, K \text{ real}). \quad (2)$$

It will be convenient in Sec. IV to define a dimensionless complex propagation constant

$$\theta = \lambda a = \xi + i\mu. \quad (3)$$

A second requirement, in addition to (1), imposed on Ψ by its physical interpretation according to quantum mechanics, is that Ψ must be bounded:

$$\int_{-\infty}^{\infty} \Psi^*(z) \Psi(z) dz \text{ finite.} \quad (4)$$

This constraint dictates that $K=0$, since otherwise, for an infinite lattice, $\Psi(z)$ would diverge at $+\infty$ or $-\infty$,

¹⁰ J. D. Levine and P. Mark, Phys. Rev. **144**, 751 (1966).

¹¹ J. D. Levine, Phys. Rev. **171**, 701 (1968).

¹² J. D. Levine and S. G. Davison, Phys. Rev. **174**, 911 (1968).

¹³ See, e.g., E. T. Goodwin, Proc. Cambridge Phil. Soc. **35**, 221 (1939); **35**, 232 (1939); K. Artmann, Z. Physik **131**, 244 (1952); S. G. Davison and J. Koutecký, Proc. Phys. Soc. (London) **89**, 237 (1966); and Refs. 5 and 12.

¹⁴ R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman and Hall Ltd., London, 1961), p. 133; A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), p. 22.

depending on whether K is negative or positive. Thus (1) becomes

$$\Psi(z) = u_k(z) e^{i k z}, \quad u_k(z) = u_k(z+na) \quad (5)$$

which is the well-known Bloch function. The purely imaginary exponent (k purely real) in (5) follows from (4), not from any symmetry argument.

Perhaps the most expedient approach in the derivation of surface-state wave functions of a bounded lattice would be to start with the Bloch function (5), and then to reintroduce the functions (1) by *analytic continuation* (k real $\rightarrow k$ complex) in (5). The tacit rationale for accepting the Bloch function with complex k is that it can satisfy (4) for the bounded lattice. The exponentially decaying wave function outside the lattice is matched on to an attenuated wave function (1) inside the lattice through an appropriate continuity condition chosen to represent region III. However, the justification for this procedure may *not* be Floquet's theorem or group theory since the translational symmetry condition upon which they are based is not satisfied by the bounded lattice potential. That is, near the surface, $V(z+na) \neq V(z)$. At best, the Bloch function with k complex may be introduced as an *ad hoc* assumption which may or may not yield a stationary state.

There is a novel analogy in this regard between surface states and extrinsic bulk states, such as hydrogenic donors and acceptors in Si. Analytic continuation of a Si Bloch function $\Psi = u(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}}$ with an imaginary *radial* vector $\mathbf{k} = i\mu \hat{r}$ yields $\Psi = u(\mathbf{r}) e^{-\mu r}$. This is the correct wave function for a hydrogenic donor ground state (1s) but it is not correct for the higher states, nor is it correct for nonhydrogenic impurities such as deep centers in semiconductors or *F*-centers in ionic crystals.

IV. SURFACE-STATE APPROACHES

Two basic approaches have been widely used for solving the Schrödinger equation of a finite crystal.

Suppose one could idealize the crystal termination as a potential step, as shown in Fig. 1(b). Then one could solve for the wave functions both inside and outside the crystal, and require a wave function matching condition at the potential step. This procedure has been carried out in detail for one-dimensional crystals using δ -function repulsive potentials⁷ (the so-called Kronig-Penney model), δ -function attractive potentials,¹⁵ a nearly free electron potential,¹⁶ and a sinusoidal potential,¹¹ among others. The sinusoidal potential is especially interesting because it has been terminated at an arbitrary location in the last unit cell, and the Schrödinger equation reduces to the Mathieu equation, whose properties are well known. The procedure is restrictive, however, in two ways. First, real crystals

¹⁵ T. B. Grimley and B. W. Holland, Proc. Phys. Soc. (London) **78**, 217 (1961).

¹⁶ E. T. Goodwin, Proc. Cambridge Phil. Soc. **35**, 205 (1939).

require potentials with a greater variety of harmonics than can be accommodated by simple δ wells or square wells or sinusoidal wells. Second, the matching condition becomes unwieldy in three dimensions (3D), since matching must occur at an *infinite* number of points in the unit cell of the surface plane. Even if a crystal has translational symmetry parallel to the surface, the 3-D problem cannot be reduced to a 1-D problem, by this method, because of matching difficulties. These should be more significant for localized, rather than delocalized states. Basically, the difference between a 1-D problem and a 3-D problem is that they correspond to ordinary and partial differential equations, respectively. The latter often cannot be solved in a simple way when surfaces are present. A crude approach to 3-D problems can be obtained essentially by matching the analytically continued wave functions only at a few symmetry points in the unit cell of the surface plane.¹⁷

All methods involving the step potential of Fig. 1 follow the procedure of analytic continuation of the "bulk" states and matching at the step potential. Each problem is essentially distinct, and one can draw only limited information from this line of attack. Regardless of the particular bulk-band-structure model (e.g., pseudopotential, $\mathbf{k} \cdot \mathbf{p}$, etc.), the most questionable aspect of the surface-state calculation is the lattice termination by a potential planar discontinuity. For this reason, it will not be considered further here.

A better method in terms of clarity, ease of computation, generality, and applicability to chemisorption, catalysis, etc., seems to be the so-called MO (molecular orbital) or LCAO (linear combination of atomic orbitals) or tight-binding or Hückel method.^{12,13} In this method one "digitizes" the potential in Fig. 1(a) by assigning appropriate Coulomb integrals α (diagonal elements of the Hamiltonian in a localized basis) and resonance integrals β (off-diagonal elements of the Hamiltonian in a localized basis). For example, the surface Coulomb integral α' is generally different from α ; this is generally considered a "surface perturbation." Also the surface resonance integral β' can also be different from β ; this is generally considered a "deformation." Here lies the chief conceptual advantage of the LCAO method. Rather than a potential discontinuity, the surface region is parametrized by α' and β' . Generally α and β have indices which describe the appropriate orbitals or bands involved. In this manner, the Schrödinger differential equation is transformed into a difference equation. If a crystal has translational symmetry parallel to the surface, the 3-D surface-state problem can always be reduced, by this method, to a 1-D problem.¹⁸ This feature is possible because of the finite-

mesh properties of the difference equation; it is not possible with the infinitesimal-mesh properties of the differential equation, as mentioned above. The introduction of extra orbitals or bands or interactions into the LCAO method will cause the mesh to become finer and more exact; in the limit, one would approach the infinitesimal-mesh properties of the differential equation.

In the LCAO method, the finite-lattice problem is solved by finding the solutions of

$$\mathbf{Q}\mathbf{C}=0, \quad (6)$$

where \mathbf{Q} is an $N \times N$ matrix, and \mathbf{C} is a coefficient column matrix. All appropriate bulk and surface Coulomb and resonance integrals are included in \mathbf{Q} . For the simplest problems, N is the number of atoms in the crystal. For other problems involving more than one dimension, orbital, band, atom in a unit cell, or resonance integral, (6) still applies, although N need not be the number of atoms in the crystal.

The solutions of (6) which yield energies in the forbidden gap and have wave functions damped away from the surface region are called, by definition, surface states. To obtain these solutions of (6), at least three methods have been successfully used: (a) Try to guess the forms of \mathbf{C} ; a correct guess [i.e., $e^{in\theta}$, $\sin(N-n)\theta$] will collapse $\mathbf{Q}\mathbf{C}$ into only a few recurrence equations which can be solved simultaneously. (b) Try to guess \mathbf{C} by using principles of scattering-amplitude theory. (c) Try to solve $\det|\mathbf{Q}|=0$ directly; one then ignores the \mathbf{C} matrix. (d) Try to solve an unperturbed problem $\mathbf{Q}^0\mathbf{C}^0=0$ and then consider the effect of surface perturbations by an integral method. Methods (a)-(c) require analytic continuation, while method (d) does not. In practice, method (d) involves integrals which can be performed most easily by complex integration; this feature is similar to analytic continuation. Also methods (a)-(c) are inadequate, except for the very simplest examples, while method (d) is still useful even for many-band, three-dimensional problems, with different atoms in the surface plane [i.e., zinc blende (110)].

It is instructive to solve an extremely simple surface-state problem by the four different methods above. This will demonstrate that the same answer can be obtained from different methods, and the multifold nature of surface states will be more clearly revealed. All methods are formally interrelated by appropriate transformations, however, since the results are identical.

A. Coefficient Method

In this method, one *guesses* the form of \mathbf{C} , by trying the Bloch form and analytic continuation. If this works it is undoubtedly the simplest method to use. The "guessing" aspect has *not* been emphasized by others,¹⁻⁵ although this method appears to be the most fashionable one at present.

Consider what is perhaps the simplest surface-state problem, the alkali-metal analog in 1-D. Here each alkali atom in a semi-infinite chain has an *s*-like orbital

¹⁷ H. Statz, Z. Naturforsch. 5a, 534 (1950); see also E. Antoničk, J. Phys. Chem. Solids 21, 137 (1961); V. Heine, Proc. Phys. Soc. (London) 81, 300 (1963); J. Surface Sci. 2, 1 (1964); R. O. Jones, Proc. Phys. Soc. (London) 89, 443 (1966); Phys. Rev. Letters 20, 992 (1968); D. Pugh, *ibid.* 12, 390 (1964); I. Bartoš, J. Surface Sci. 15, 94 (1969); C. M. Chaves, N. Majlis, and M. Cardona, Solid State Commun. 4, 271 (1966).

¹⁸ J. D. Levine and S. Freeman (unpublished).

$\phi(z)$ so that the wave function $\Psi(z)$ can be written as

$$\Psi(z) = \sum_{n=1}^{\infty} c_n \phi(z-n). \quad (7)$$

This is inserted into the Schrödinger equation

$$H\Psi(z) = E\Psi(z), \quad (8)$$

where H is the Hamiltonian operator and E represents the eigenvalues. One then obtains the **QC** matrix in the form (neglecting overlap)

$$\begin{pmatrix} x & 1 & & & \\ 1 & y & 1 & & \\ & 1 & y & 1 & \\ & & 1 & y & \\ & & & \ddots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \end{pmatrix} = 0, \quad (9)$$

where

$$x = (\alpha' - E)/\beta, \quad y = (\alpha - E)/\beta. \quad (10)$$

It is convenient to define

$$p = x - y = (\alpha' - \alpha)/\beta, \quad (11)$$

which is a measure of the surface perturbation. Complications due to deformations, other bands, next-nearest-neighbor interactions, etc., will be considered later. Generally β is negative (attractive interaction between atoms) so that x and y are proportional to E , not to $-E$.

To solve (9), try the simplest Bloch form

$$c_n = e^{in\theta} \quad (12)$$

as in (1) with analytic continuation $\theta = \xi + i\mu$ as in (3). This implies that E is also analytically continued, since $E = E(\theta)$.

Here the reduced zone scheme is used where $-\pi < \xi < \pi$. Also it is necessary that $\mu > 0$ to have a surface state damped into the crystal, $z > 0$. The case $\mu < 0$ must be thrown out for a semi-infinite crystal. This guess "collapses" (9) into the following set of simultaneous equations:

$$\begin{pmatrix} (x + e^{i\theta}) & & & & \\ & (y + 2 \cos \theta) & & & \\ & & (y + 2 \cos \theta) & & \\ & & & \ddots & \ddots \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \end{pmatrix} = 0. \quad (13)$$

The equations to be solved are

$$x + e^{i\theta} = 0, \quad (14)$$

$$y + 2 \cos \theta = 0, \quad (\sim N \text{ times}). \quad (15)$$

Analytical solution of (14), (15), and (11) yields

$$p = e^{-i\theta}, \quad (16)$$

$$y = -(p + p^{-1}). \quad (17)$$

For any stationary state, the energy $E(\theta)$ must be real. In this problem, then, x and y in (14), (15), and (17)

must be real. This reality condition is only satisfied for two choices of θ : $\theta = i\mu$, $\theta = \pi + i\mu$, which correspond to $p > 0$ and $p < 0$, respectively, and to the two surface states

$$y = \mp |p + p^{-1}|, \quad \mu = \ln |p|. \quad (18a)$$

If $|p| > 1$, these lie outside the allowed band $[-2 < y < 2]$. If $p > 1$, the surface state appears at the Brillouin-zone (BZ) center ($\xi = 0$) below the allowed band. If $p < -1$, the surface state appears at the BZ edge ($\xi = \pi$) above the allowed band. Thus either the $+$ or $-$ sign in (18a) applies, not both at one time. A surface state is thus found. That is, a state exists whose energy lies outside the bulk band, and whose wave function is damped away from the surface. "Virtual" surface states which exist within a bulk band have also been considered.⁶ As seen from (7) the wave function (for $\pm p$) is

$$\Psi(z) = \sum_{n=1}^{\infty} (\pm 1)^n \phi(z-n) e^{-n\mu}. \quad (18b)$$

It is a property of differential equations that a solution obtained by a trial-and-error method which satisfies all the boundary conditions is the correct solution. Thus the surface-state problem has been solved by the coefficient-guessing method. It should be noted that for $|p| < 1$, there can be no surface state since, from (16), μ is negative and the wave function blows up inside the crystal.

A graphical solution of (14) and (15) can also be performed. This has the advantage of dramatically showing the nature of the surface termination. It is similar to the graphical solution used in the ionic surface-state problem.¹² For this purpose, one must distinguish between the cases $p < -1$ or $p > 1$. Suppose p is positive. Then by (16), θ is of the form $\pi + i\mu$. It is convenient to define

$$L = e^{-\mu} \quad (0 \leq L \leq 1). \quad (19)$$

Then (15) becomes the "bulk" equation

$$y = (L + L^{-1}), \quad (20)$$

which is plotted as a curve (y versus L) in Fig. 2. Also (14) becomes the "surface" equation

$$y = -p + L, \quad (21)$$

which is plotted as a straight line in Fig. 2, taking, for example, $p = -\frac{3}{2}$. The intersection is at $y = 2\frac{1}{6}$, $L = \frac{2}{3}$, $\mu = \ln \frac{2}{3}$. An intersection always appears provided $|p| > 1$; this is the surface state. The same procedure is, of course, applicable for p positive, say, $p = \frac{3}{2}$, and the intersection in Fig. 2 would occur at $y = -2\frac{1}{6}$, $L = \frac{2}{3}$.

It is illuminating to consider the above problem in a way which emphasizes the aspect of wave function matching. This aspect is the heart of the potential-step methods as described at the beginning of Sec. IV. Thus a crude analogy can be drawn between the above method and the potential-step method. In Fig. 2, each bulk

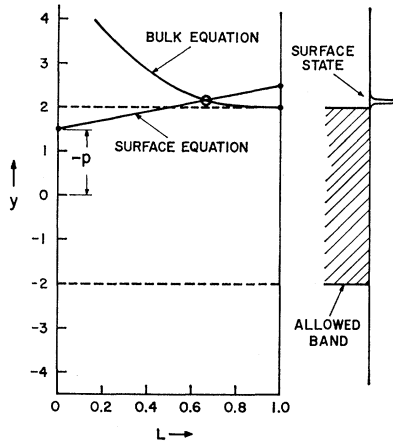


FIG. 2. Graphical solution of a simple 1-D surface-state problem. Energy y is plotted versus L , where $L = e^{-n}$, and μ is the damping constant. The surface state appears at the intersection of the bulk and surface equations.

analytically continued level is characterized by its L value. The same is true for the surface-state levels as shown in the figure. Each value of L defines the slope μ of the wave function envelope ($\mu = -\ln L$). Thus the intersection in the figure indicates a *perfect matching of the slopes* in the bulk and surface regions. At the intersection, then, there is a stationary state, which is the desired surface state. In this manner the crude analogy has been demonstrated between the above difference-equation method and the potential-step method.

In certain problems, besides the simple alkali-metal analog, the coefficient-guessing method can still be carried out. Usually better guesses than (12) have to be used. For a finite monatomic crystal, a guess of the form¹³ $c_n = \sin(N+1-n)\theta$, [$\theta = m\pi(N+1)^{-1}$; n an integer] is useful, since it contains nodes at $n=0, N+1$. For next-nearest-neighbor interactions in a monatomic crystal, a guess¹⁹ of the form $c_n = K_1 e^{i\theta_1 n} + K_2 e^{i\theta_2 n}$ is useful since it gives two damping constants, θ_1 and θ_2 , necessary for matching the boundary conditions. For 1-D diatomic crystals MX , where M and X atoms are located on odd and even sites, and where each has its own orbital ϕ_M and ϕ_X , the appropriate guess¹² is $c_n = K_1 e^{i\theta}$ for n odd and $c_n = K_2 e^{i\theta}$ for n even. For a monatomic crystal with s and p orbitals, there is also an appropriate guess¹³ of the form $c_n = K_a e^{i\theta_1 n} + K_b e^{i\theta_2 n}$, for the s orbital and $c_n = K_c e^{i\theta_1 n} + K_d e^{i\theta_2 n}$ for the p orbital.²⁰ For a crystal with surface distortion ($\beta' \neq \beta$), the coefficient method also can work. Thus suppose that in (9) the first pair of off-diagonal terms were equal to β'/β , instead of 1. Then the appropriate guess is $c_n = e^{i\theta}$ for $n=2, 3, 4, \dots$, and c_1 is chosen independent of the others. This guess gives just the right number of equa-

¹⁹ W. M. Fairbairn, *J. Surface Sci.* **9**, 439 (1968).

²⁰ Artmann (Ref. 13) made a serious error in that he hybridized wave functions which diverge at infinity *inside* the semi-infinite crystal. This error was repeated and further compounded in Ref. 1. The problem was done correctly by Goodwin (Ref. 13, p. 232), and by Koutecky (Ref. 4, p. 123).

tions and unknowns to solve uniquely for the surface states.

B. Scattering-Amplitude Method

It is possible to consider surface states by using the terminology of scattering theory. Feynman²¹ has developed a simple method for computing the states of an impurity atom located in an infinite lattice. Here the same method will be applied to the above surface-state problem. To be specific (9) will be solved using scattering amplitude terminology.

At the scattering center $n=1$, the wave-function coefficient is not immediately known, so that one can write

$$C_1 = A, \quad (22)$$

where A is to be determined. Away from the scattering center $n \geq 2$, the wave function is assumed to consist of an incident plane wave $e^{-i\theta}$ plus a reflected plane wave $\gamma e^{i\theta}$, so that

$$C_n = B(e^{-i\theta} + \gamma e^{i\theta}), \quad (23)$$

where γ is the "scattering amplitude" and B is a coefficient to be determined. In this problem there is no transmitted wave to be considered. By substituting the coefficient guesses of (22) and (23) into (9), one can eliminate A and B and solve for γ in the form

$$\gamma = -(p - e^{+i\theta}) / (p - e^{-i\theta}), \quad (24)$$

where p is defined in (11). A bound state is found when the scattering amplitude γ has a pole; that is, when $\gamma \rightarrow \infty$. The condition becomes

$$p = e^{-i\theta}, \quad (25)$$

which is identical with (16). Since p is real, it is necessary that θ be analytically continued as before and the energy obtained as in (17). Thus the surface state is found by this method.

In retrospect, the method seems almost trivial since the coefficient guess of (23) must, in the last analysis, equal the known correct guess $C_n = C_1 e^{i\theta}$. This equality exists only if $\gamma \rightarrow \infty$ (and $B \rightarrow 0$ in such a way that $\gamma B \rightarrow C_1$). Also if (23) were normalized in another way by dividing by $(1 + \gamma^2)^{1/2}$, the pole aspect would disappear. Physically, the analytic continuation accomplished at the last step of the analysis has peculiar consequences if considered in the earliest step (23). That is, for $\theta = i\mu$, the sum of incident and reflected waves in (23) becomes instead a sum of exponentially increasing and exponentially decreasing waves. One of these must be thrown out for a semi-infinite lattice; this is equivalent to the condition that $\gamma \rightarrow \infty$.

The usefulness of this interesting and suggestive method in more complicated problems is in doubt. Feynman states that it is not a straightforward matter

²¹ R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures in Physics* (Addison-Wesley Publishing Co., Inc., New York, 1965), Vol. III, Chap. 13, pp. 13.10-13.13.

to consider more than one type of scattering center; this situation occurs in three dimensions. On balance, it seems easier to use the coefficient method directly, instead of solving first for γ and then letting $\gamma \rightarrow \infty$. The scattering-amplitude method is probably most useful in applications other than bound states.

C. Determinant Method

A method which is independent of coefficient guessing is the determinant method. It can be demonstrated best when determinants are finite. For this reason it is best to construct the above surface state problem with, say, $N+1$ alkali atoms in a chain, and then to let $N \rightarrow \infty$. Consequently the determinantal equation corresponding to (9) is

$$\Delta_{N+1}(y,x) = \begin{vmatrix} x & 1 & & & \\ 1 & y & 1 & & \\ & 1 & y & 1 & \\ & & 1 & \ddots & 1 \\ & & & 1 & y \end{vmatrix} = 0. \quad (26)$$

This can be solved by expanding the first row in minors to yield

$$x\Delta_N(y) - \Delta_{N-1}(y) = 0. \quad (27)$$

For arbitrary n , $\Delta_n(y)$ can be written as²²

$$\Delta_n(y) = (-1)^n \sin(n+1)\theta / \sin\theta, \quad (28)$$

where

$$y = -2 \cos\theta. \quad (29)$$

The right-hand side of (28) is the n th Tchebycheff polynomial of the second kind of variable $\frac{1}{2}y$. For small n , (28) can easily be checked since $\Delta_1(y) = y$, $\Delta_2(y) = y^2 - 1$, $\Delta_3(y) = y^3 - 2y$, etc. Combining (27) and (28) one gets

$$x + [\sin n\theta / \sin(N+1)\theta] = 0. \quad (30)$$

For θ real, this is a transcendental equation which yields all the bulk states, each slightly perturbed $\sim N^{-1}$ due to the surface termination.¹³ For $\theta = i\mu$ and N large, one has $x + e^{-\mu} = 0$. For $\theta = \pi + i\mu$ and N large, one has $x - e^{-\mu} = 0$. In general, then, for N large

$$x + e^{i\theta} = 0. \quad (31)$$

Since (29) and (31) are identical to (15) and (14), respectively, the same surface-state results are obtained by the two methods.

The determinant method yields the energies without any assumption as to the coefficient matrix \mathbf{C} , as was to be demonstrated. To find the coefficients it is necessary to use the matrix form and work backwards.

It is curious that, besides Hoffmann,²² no other theorists have applied this type of analysis to surface-state determinations.

For more complicated problems, the determinant method becomes unwieldy. As an example, consider

the determinant obtained when a triply degenerate Γ_{15} level and a singly degenerate Γ_1 level are introduced to represent the valence-conduction band-gap region in zinc blende¹⁸: This can be written in the Hermitian form

$$\Delta_{4N} = \begin{vmatrix} \mathbf{Y}' & \mathbf{R} & & & \\ \mathbf{R}^* & \mathbf{Y} & \mathbf{R} & & \\ & \mathbf{R}^* & \mathbf{Y} & \mathbf{R} & \\ & & \mathbf{R}^* & \mathbf{Y} & \\ & & & & \mathbf{R} \\ & & & & \mathbf{R} & \mathbf{Y} \end{vmatrix} = 0, \quad (32a)$$

where \mathbf{Y} , \mathbf{Y}' , \mathbf{R} , and \mathbf{R}^* are 4×4 matrices and have the forms

$$\mathbf{Y} = \begin{vmatrix} x & \beta_1 & \beta_2 & \beta_3 \\ \beta_1^* & y & & \\ \beta_2^* & & y & \\ \beta_3^* & & & y \end{vmatrix}, \quad (32b)$$

$$\mathbf{Y}' = \begin{vmatrix} x' & \beta_1' & \beta_2' & \beta_3' \\ \beta_1'^* & y' & & \\ \beta_2'^* & & y'' & \\ \beta_3'^* & & & y''' \end{vmatrix}, \quad (32c)$$

$$\mathbf{R} = \begin{vmatrix} \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4 \\ \gamma_5 & & & \\ \gamma_6 & & & \\ \gamma_7 & & & \end{vmatrix}, \quad (32d)$$

$$\mathbf{R}^* = \begin{vmatrix} \gamma_1^* & \gamma_5^* & \gamma_6^* & \gamma_7^* \\ \gamma_2^* & & & \\ \gamma_3^* & & & \\ \gamma_4^* & & & \end{vmatrix}. \quad (32e)$$

One can solve the entire $4N \times 4N$ determinant to obtain the surface states. This is not a fruitful procedure, since only a few terms are perturbed ($x', y', y'', y''', \beta_1', \beta_2', \beta_3'$). It is possible to solve the entire $4N \times 4N$ determinant, if desired, by high-speed computer; but a better method, involving only a 4×4 determinant, is given below.

D. Integration Method

Assume that the surface perturbation extends over a region involving only Ω atoms or orbitals. It would be desirable to solve the surface-state problem with a relatively small determinant $\Omega \times \Omega$, instead of the much larger determinant $\sim N \times N$. This reduction in determinant size is accomplished at the expense of appropriate "integrations" over all N "bulk states." The integrals are conveniently carried out using complex integration; this feature causes the surface-state wave function to be a sum of a few ($\sim \Omega$) analytically continued bulk wave functions, as anticipated from the "guessing" method in Sec. IV A.

To be specific, and to define the above terms more precisely, consider the problem of a *reference* crystal which is finite, but whose surface Coulomb integrals and surface resonance integrals are otherwise unperturbed. One example of this is (32) with $\mathbf{Y}' = \mathbf{Y}$,

²² T. A. Hoffmann, Acta Phys. Acad. Sci. Hung. 2, 195 (1952), in English.

Another example is (26) with $x=y$; this will be treated in more detail later. The eigenstates of this reference problem will henceforth be called "bulk states." They form a complete and orthogonal set which can be used as the basis states for the surface-state problem. By appropriate summation (or integration if N is large), these bulk-state wave functions combine via the surface perturbations (primed integrals) to give reinforcement and cancellation. Reinforcement represents the surface state; and cancellation represents the perturbed bulk states, which now tend to avoid the surface region, since all wave functions must be orthogonal.

To demonstrate this integration method, the same alkali-metal problem will be considered below as a prototype example.

Following closely the procedure of Baldock,²³ (6) can be written for a one-band material in the form

$$(\mathbf{A}-y\mathbf{I})\mathbf{C}=\mathbf{P}\mathbf{C}, \quad (33)$$

where $\mathbf{A}=[a_{ns}]$ is a real symmetric $N \times N$ matrix, \mathbf{C} is the vector formed by the coefficients c_r , and the perturbation matrix \mathbf{P} is taken, for simplicity, to be a diagonal matrix with p_r in the r th row. Typically $p_r=(\alpha_r-\alpha)/\beta$. The perturbed energies y can be solved in terms of the normalized energies of the unmodified equations ($\mathbf{P}=\mathbf{0}$), which are assumed known. Let these be

$$y=y_j, \quad c_r=u_{rj}, \quad (34)$$

$$\sum_{r=1}^N u_{rj}^2=1 \quad (j=1, 2, \dots, N).$$

Then $\mathbf{A}=\mathbf{U}\mathbf{Y}\mathbf{U}^{-1}$, where $\mathbf{U}=[u_{rj}]$ and \mathbf{Y} is the diagonal matrix of the eigenvalues y_i . \mathbf{A} is real and symmetric, and since the u_{rj} are normalized, $\mathbf{U}^{-1}=[u_{jr}]$. Only those surface states are considered here which lie in the forbidden bands, so $y \neq y_j$. Then $(\mathbf{Y}-y\mathbf{I})^{-1}$ exists, and (33) becomes

$$\mathbf{C}=\mathbf{U}(\mathbf{Y}-y\mathbf{I})^{-1}\mathbf{U}^{-1}\mathbf{P}\mathbf{C}, \quad (35)$$

or in component form

$$c_r=\sum_{s=1}^N Z_{rs}(y)p_s c_s, \quad (36)$$

$$Z_{rs}=\sum_{j=1}^N (y_j-y)^{-1}u_{rj}u_{sj}. \quad (37)$$

Since in general only a few of the p_s are nonzero, say, $p_1, p_2, \dots, p_\Omega$, the eigenvalues y are determined from

$$\begin{vmatrix} p_1 Z_{11}-1 & p_1 Z_{12} & \dots & p_\Omega Z_{1\Omega} \\ p_1 Z_{12} & p_2 Z_{22}-1 & \dots & p_\Omega Z_{2\Omega} \\ \vdots & \vdots & \ddots & \vdots \\ p_1 Z_{1\Omega} & p_2 Z_{2\Omega} & \dots & p_\Omega Z_{\Omega\Omega}-1 \end{vmatrix} = 0. \quad (38)$$

Thus the energies of a localized perturbation can be in-

²³ G. R. Baldock, Proc. Cambridge Phil. Soc. 48, 457 (1952); see also R. D. Levine and A. T. Amos, Phys. Status Solidi 19, 587 (1967).

vestigated by using a relatively small $\Omega \times \Omega$ determinant instead of the more cumbersome $N \times N$ determinant of the $\mathbf{A}-\mathbf{P}$ Hamiltonian. The price to pay for this reduction is the summation (or integral) over all the N states, as indicated in (37). The only equations needed to solve specific surface-state problems with this method are (37) and (38). They are designed for application to one-band problems, but they can be extended to many-band problems easily.

For the alkali-metal analog problem described in (26), there is only one perturbed site $n=1$, so that $p_1=p$, but $p_2, p_3, \dots=0$. The unperturbed problem is obtained by replacing x by y in (26):

$$\begin{vmatrix} y & 1 & & & \\ 1 & y & 1 & & \\ & & 1 & y & \\ & & & \ddots & \ddots & \\ & & & & 1 & \\ & & & & & 1 & y \end{vmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_N \end{bmatrix} = 0. \quad (39)$$

The solutions of this unperturbed problem are known (and easily checked) to be

$$y_i = -2 \cos \theta_j, \quad \theta_j = j\pi/(n+1) \quad (40)$$

$$c_{nj} = [2(N+1)]^{1/2} \sin n\theta_j; \quad (j=1, 2, \dots, N).$$

Note that there are nodes at the surfaces $n=0$ and $n=N+1$. It can be shown that (38) reduces to the one-by-one determinant

$$pZ_{11}(y)-1=0, \quad (41)$$

where

$$Z_{11}(y) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{2 \sin^2 \theta}{-2 \cos \theta - y} d\theta. \quad (42)$$

The numerator is normalized in the sense that $Z_{11}=1$ for a denominator of unity. By complex integration, this integral (spectral-density function) becomes

$$Z_{11}(y) = -\frac{1}{2} [y + (y^2 - 4)^{1/2}]. \quad (43)$$

Combining (41) and (43) to eliminate $Z_{11}(y)$, one obtains

$$y = -(p + p^{-1}), \quad (44)$$

which is identical with (15). Thus the integral method yields the same results as before. This should not be surprising, since complex integration is formally similar to analytic continuation. All methods A, B, C, D are formally equivalent. The integral method, D, because of its rigor, seems more appropriate for three-dimensional problems involving real lattices.

Koster and Slater²⁴ have developed a similar method for dealing with point impurities in the crystal bulk. Their formalism is more general and complicated than Baldock's; in addition they primarily derive their results from the Wannier, rather than the Bloch, representation. Koustecký⁴ has applied the Koster-Slater method (he calls it the "resolvent method")

²⁴ G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

to a variety of surface-state problems. But all integrals used by Kouřtecký and by Koster and Slater involve the unperturbed wave functions of an *infinite or cyclic* crystal. Thus the numerator of (42) is replaced by terms of modulus unity. To get the surface states, it is necessary to include other types of integrals Z_{rs}' which *subtract* the β terms and "cleave" the surface. It seems to the authors that, for surface states, Baldock's method has certain advantages over the others. [It has been (unfortunately) neglected.] It is acknowledged that if the perturbation matrix P is nondiagonal, the problem becomes more complicated, but the matrix is still of order $\Omega \times \Omega$.

It is interesting to note that the problem of an impurity atom in an *infinite* (rather than semi-infinite) chain can easily be treated by (37) and (38). Then one has

$$Z_{11} = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{d\theta}{-2 \cos\theta - y}, \quad (45)$$

which is the same as in (42), but with a numerator of unity. Integration gives

$$Z_{11} = (y^2 - 4)^{-1/2} \quad (46)$$

and (38) yields

$$y = \pm (4 + p^2)^{1/2}. \quad (47)$$

Comparison of (47) with (44) shows that there is a threshold for localized-state formation in the semi-infinite lattice, but no threshold in the corresponding infinite lattice. Thus it is harder to bind a surface state than to bind an equivalent bulk impurity state. This same conclusion has been pointed out for extrinsic surface hydrogenic donors,²⁵ as opposed to bulk hydrogenic donors, in semiconductors. Essentially, the presence of the free surface introduces a "nodal" condition on Ψ which raises the energy. To be specific, for the surface donors, the $1s$ state is not allowed and the ground state is $2p_0$.

V. DISCUSSION

Surface-state calculations can be carried out by a number of different methods, only some of which are discussed at length above. But these will be *irrelevant* unless correspondence is made with the band structure of the real crystal prototype.

It seems much better first to describe *accurately* the bulk band structure in the vicinity of the valence-to-conduction-band gap. In fact, a band-edge (or $\mathbf{k} \cdot \mathbf{p}$ -like) method¹² and a directed-orbital LCAO method²⁶ have been used to describe surface states in that gap. For example, in a particular zinc-blende crystal such as GaAs, ZnS, or InSb, the conduction- and valence-band

edges are known²⁷ and the corresponding wave functions have symmetries Γ_1 and Γ_{15} (with no spin-orbit coupling). The band curvatures, related to the effective masses, are also known both theoretically and experimentally. It has been shown¹² that this information can adequately fix the various bulk Coulomb and resonance integrals. To help evaluate the Coulomb integrals of the *surface* atoms, use can be made of the Madelung method,¹⁰ based on simple electrostatics. In this manner comparison of theory and experiment in surface states becomes more natural,¹² and complicated integrals which define the α 's and β 's can be estimated easily.

Even this procedure is useless, unless it is established experimentally that a particular free surface of a particular crystal is unreconstructed, as theoretically assumed. As mentioned in Sec. II, zinc-blende (110) surfaces and certain others are unreconstructed, according to LEED. That is, the spots have the same location as those expected for the bulk. Second-order effects may appear such as relaxation of layers, in the normal direction, by a few percent, or sliding of the M and X sublattices with respect to each other by a few percent. But these are minor effects, compared to the reconstruction (new spots) on Si and Ge surfaces, on the (111) and ($\bar{1}\bar{1}\bar{1}$) polar faces of zinc blende, and on the (0001) and (000 $\bar{1}$) polar faces of wurtzite.

The calculations above can also be *extended* easily by unitary transformations. For example, a unitary transformation U applied to (6) yields

$$U^{-1}QU = 0. \quad (48)$$

This problem *looks* different from (6) but has exactly the same eigenvalues of all bulk and surface states. For example, suppose

$$U = \begin{bmatrix} 1 & & & & \\ & -1 & & & \\ & & 1 & & \\ & & & -1 & \\ & & & & 1 & \\ & & & & & \ddots \end{bmatrix}. \quad (49)$$

Then (48) becomes

$$\begin{bmatrix} x & -1 & & & \\ -1 & y & -1 & & \\ & -1 & y & -1 & \\ & & -1 & y & \\ & & & & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \end{bmatrix} = 0. \quad (50)$$

This corresponds to a linear chain of p orbitals, instead of s orbitals, as in (9). Essentially, the transformation causes a phase shift of π in the y -versus- ξ diagram, while leaving all energies invariant.

In conclusion, some techniques for treating surface-state problems have been described, interrelated, and

²⁵ J. D. Levine, Phys. Rev. **140**, A586 (1965); R. J. Bell, W. T. Bousman, Jr., G. M. Goldman, and D. G. Rathbun, J. Surface Sci. **7**, 293 (1967); W. E. Tefft, R. J. Bell, and H. V. Romero, Phys. Rev. (to be published).

²⁶ J. Kouřtecký and M. Tomášek, J. Surface Sci. **3**, 333 (1964).

²⁷ M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

evaluated here. The guessing method has been shown to work for very simple examples, but in general it will not work for more complicated examples [i.e., zinc blende as in (32)]. Approximations can be made, of course, by neglecting certain boundary conditions, or by matching Ψ at only one point, or by using 1-D analogs. These are only crudely representative, however, of the correct solution. After all, the surface states are extremely sensitive to the boundary conditions in the surface-termination region. A definitive and realistic computation of surface states on a 3-D crystal has not yet appeared, in the opinion of the authors. In a sense, surface-state physics is 10-15 years behind solid-state (or bulk) physics. The reason for this is the

lack of symmetry in the surface region; the free surface is a huge planar defect. At present very little is known experimentally about its topography and energy structure. Even less is known about *interface* regions [e.g., Si-SiO interface, metal-semiconductor interface, electrolyte-semiconductor interface, etc.], because LEED and other tools cannot be applied there.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the many stimulating conversations and helpful suggestions of S. Freeman of RCA and Professor S. G. Davison of the University of Waterloo, Waterloo, Ontario, Canada.

Photostimulated Thermoluminescence in Additively Colored KCl

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(Received 16 August 1968)

Thermoluminescence is observed in additively colored alkali-halide crystals following illumination at low temperature with light of wavelength in the absorption bands of the sample (F , K , and L bands) and subsequent heating. In this method one deals with only one type of carrier (electrons) and with one type of activator (negative-ion vacancies). Thus, the nature of the trap and the trapping mechanism can be studied under circumstances which avoid the complications intrinsic to the thermoluminescence of x - or γ -irradiated samples. At least two types of traps are present besides the F' in KCl in the temperature range 55-300°K. Hence the quantum yield of the $\bar{F} \rightarrow F'$ optical conversion is less than 2. No traps were found associated with fresh dislocations. Two different mechanisms of trap filling have been observed, one through the conduction band, and another through tunneling from the lower excited state of the F center to a neighboring trap.

1. INTRODUCTION

IN alkali-halide crystals, thermoluminescence is usually studied in samples which have been irradiated with ionizing radiation (x, γ, e^-). The emission glow curves which result when the sample is subsequently heated are often subject to ambiguous interpretations, in spite of the efforts to correlate the glow peaks to the intensity changes of given absorption bands, EPR spectra, etc. This is due to the fact that one deals with many unknown parameters at the same time, e.g., traps, carriers, activators, and killers. In the literature, one can still find unsolved questions on basic points, such as the nature of the carrier involved. A useful simplification is obtained when a crystal previously irradiated at a relatively high temperature with x or γ rays, in order to obtain color centers and activators, is stimulated at a lower temperature with monochromatic light.¹⁻⁶ Even in this case, however, the nature and the

concentration of activators remain largely unknown, because the crystal contains different kinds of color centers and the high-energy radiation may introduce a variety of traps whose properties mask the effect of the intrinsic traps and of the traps due to known color centers.

We propose here an experiment which provides the simplest way to study the thermoluminescence process in alkali-halide crystals, thereby avoiding all the complications intrinsic to x - or γ -irradiated samples. Let us take an additively colored crystal, properly quenched so that only F centers are present. The sample is cooled in darkness down to a temperature T_0 and then illuminated with monochromatic light of wavelength λ_s , corresponding to a wavelength in the absorption bands due to the F centers (F , K , or L bands); a fraction of the electrons excited by the illumination leaves the negative-ion vacancies and is captured by the traps of the crystal. During the subsequent heating, the

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⁴ R. Fieschi and P. Scaramelli, *Phys. Rev.* **145**, 622 (1966).

⁵ P. Scaramelli, *Nuovo Cimento* **45B**, 199 (1967).

⁶ P. R. Crippa, C. Paracchini, and J. Felszerfalvi, *J. Phys. Soc. Japan* **24**, 92 (1968).