

summarize by saying that the core polarization effect does not seem to affect significantly the agreement between our theoretical and experimental values of P_f ; however, this conclusion cannot be extended to other quantum defect calculations. Further investigation of this point would appear to be very desirable.

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Theory of Electron-Phonon Interactions

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The theory of the interaction of electrons and acoustic phonons in nonpolar crystals has been formulated in terms of a new set of basis states, whose wave functions are essentially Bloch functions that deform with the lattice. The major part of the interaction may then be calculated in terms of the strain tensor rather than the displacement of the lattice. A result of the theory is a generalization of the deformation potential theorem.

I. INTRODUCTION

IN considering the mobility of electrons in nonpolar semiconductors, Bardeen and Shockley¹ introduced a new approach to electron-phonon coupling. They showed that in certain simple semiconductors the electron-phonon interaction can be accounted for by replacing the interaction term in the Hamiltonian by $D\nabla \cdot \mathbf{u}$, where \mathbf{u} is the displacement of the lattice due to the thermal vibrations. The constant D is the deformation potential. It is defined by setting the change in the electron energies in a homogeneously strained crystal equal to $D\nabla \cdot \mathbf{u}$; hence D can be determined from experiments independent of the electron-phonon interaction.²⁻⁵ This idea has already proved very fruitful and has been extended to include arbitrary strains and more complicated semiconductors.⁵

It was the feeling that the deformation potential approach affords a basis for a much more comprehensive theory of electron-phonon interactions (within the framework of the one-electron model) that motivated the present research. Moreover, it was felt that if one could find a means of expanding the Hamiltonian in a power series in the strains, instead of the lattice displacements (as is done in the standard theory⁴), the deformation potential theorem in its most general form would follow immediately.

We find that we are able to carry through this

program when we express the Hamiltonian in terms of a new representation.⁶ The basis states of this new representation [orthogonalized deformed Bloch (ODB) functions] are essentially Bloch functions that deform with the lattice. These states have the convenient property that the matrix elements of the pertinent operators with respect to the ODB states can be expressed as matrix elements of closely related operators with respect to the Bloch states (Sec. III). In Sec. IV we show that the Hamiltonian in the ODB representation can be expanded in a power series in the strains and the lattice velocity, and that the resulting first-order coupling terms, $E^I + E^{II}$, admit of a simple physical interpretation. E^I is the dominant term and can be written as a deformation potential operator (whose diagonal matrix elements are shown in Sec. V to be just the deformation potentials) times the strain. It leads directly to a generalized deformation potential theorem (Sec. VII) which refers to the coupling between the ODB rather than the Bloch states. However, in Sec. VI we show that, to the first approximation, the transition rates between the Bloch or between the ODB states may be used interchangeably in the Boltzmann equation.

E^{II} is shown in Sec. VII to be a small term associated with the fact that a moving lattice tends to drag the electrons with it.

II. THE BLOCH REPRESENTATION

The Hamiltonian for a nonpolar crystal with one electron in the conduction band, in the one-electron

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¹ J. Bardeen and W. Shockley, *Phys. Rev.* **80**, 72 (1950).

² G. Weinrich, T. M. Sanders, and H. G. White, *Phys. Rev.* **114**, 33 (1959).

³ J. R. Drabble, *J. Electronics and Control* **5**, 362 (1958).

⁴ F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

⁵ W. P. Dumke, *Phys. Rev.* **101**, 531 (1956); and C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).

⁶ George Whitfield, *Phys. Rev. Letters* **2**, 204 (1959). Equations (7) and (8) of this reference are incorrect; see Sec. VII A-1 of this paper.

approximation is

$$H = E + H_{eL}; \quad (1)$$

where

$$E = H_e + H_L,$$

and

$$H_e = \frac{p_\alpha p_\alpha}{2m} + V_0(\mathbf{x}), \quad (2)$$

$$H_L = \frac{P_{f,s} P_{-f,s}}{2M} + \frac{1}{2} M \omega^2(\mathbf{f}, s) q_{f,s} q_{-f,s}, \quad (3)$$

$$H_{eL} = V(\mathbf{x}, q) - V_0(\mathbf{x}). \quad (4)$$

In the above, repeated indices are to be summed on; \mathbf{x} is the position vector of the extra electron, and q stands for all the normal coordinates of the lattice $q_{f,s}$, each with vibration frequency $\omega(\mathbf{f}, s)$. Although we will refer in this paper to a crystal with one atom per unit cell, we expect that the results will also apply to the long-wavelength acoustic mode scattering in a crystal with more than one atom per unit cell. At appropriate places below we will point out some limitations of this extension. The electron and ion core masses are, respectively, m and M ; the effective potential seen by the extra electron is $V(\mathbf{x}, q)$ and $V_0(\mathbf{x}) \equiv V(\mathbf{x}, 0)$. The displacement of the ν th ion core from its mean position, \mathbf{R}_ν^0 , is given by

$$\mathbf{u}_\nu = \sum_{f,s} q_{f,s} \mathbf{v}(\mathbf{f}, s) \exp(i\mathbf{R}_\nu^0 \cdot \mathbf{f}), \quad (5)$$

$$q_{f,s} = \sum_\nu \mathbf{u}_\nu \cdot \mathbf{v}^*(\mathbf{f}, s) \exp(-i\mathbf{R}_\nu^0 \cdot \mathbf{f}),$$

where \mathbf{f} is the wave vector and s refers to the polarization of the lattice mode.

The lattice points \mathbf{R}_ν^0 are given by

$$\mathbf{R}_\nu^0 = \nu_1 \mathbf{a}_1 + \nu_2 \mathbf{a}_2 + \nu_3 \mathbf{a}_3, \quad (6)$$

where the ν 's are integers and for simplicity we assume that the \mathbf{a}_i are mutually perpendicular. In this formulation the \mathbf{u}_ν satisfy the periodic boundary conditions

$$\mathbf{u}_\nu = \mathbf{u}_{\nu+M}, \quad (7)$$

where M refers to the triplet of large integers M_i ($i=1, 2, 3$).

The usual theory⁴ of electron-phonon interactions treats H_{eL} as a perturbation on the system:

$$E \varphi_l(\mathbf{x}, q) = E_l \varphi_l(\mathbf{x}, q), \quad (8)$$

$$E_l = \epsilon_n(\mathbf{k}) + \sum_{f,s} [N(\mathbf{f}, s) + \frac{1}{2}] \hbar \omega(\mathbf{f}, s), \quad (9)$$

$$\varphi_l(\mathbf{x}, q) = \psi_{n\mathbf{k}}(\mathbf{x}) \chi_{\{N(\mathbf{f}, s)\}}(q). \quad (10)$$

$\{N(\mathbf{f}, s)\}$ refers to the entire set of phonon occupation numbers $N(\mathbf{f}, s)$, and the lattice eigenfunction χ satisfies

$$H_L \chi_{\{N(\mathbf{f}, s)\}}(q) = \left[\sum_{f,s} [N(\mathbf{f}, s) + \frac{1}{2}] \hbar \omega(\mathbf{f}, s) \right] \chi_{\{N(\mathbf{f}, s)\}}(q).$$

$\psi_{n\mathbf{k}}(\mathbf{x}) = \exp(i\mathbf{k} \cdot \mathbf{x}) w_{n\mathbf{k}}(\mathbf{x})$ [where $w_{n\mathbf{k}}(\mathbf{x})$ has the periodicity of the lattice] is the Bloch function of wave vector \mathbf{k} and band index n , satisfying

$$H_e \psi_{n\mathbf{k}}(\mathbf{x}) = \epsilon_n(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{x}).$$

$\psi_{n\mathbf{k}}(\mathbf{x})$ satisfies periodic boundary conditions with the same period as \mathbf{u}_ν , namely

$$\psi_{n\mathbf{k}}(\mathbf{x}) = \psi_{n\mathbf{k}}(\mathbf{x} + \mathbf{L}_i), \quad (11)$$

where $\mathbf{L}_i = M_i \mathbf{a}_i$.

We chose the $\psi_{n\mathbf{k}}(\mathbf{x})$ to be normalized in the rectangular parallelepiped \mathcal{V} defined by the three vectors \mathbf{L}_i . We note that due to the periodic boundary conditions the $\psi_{n\mathbf{k}}$ are also normalized in any (possibly irregularly shaped) region whose bounding surfaces are separated by the \mathbf{L}_i .

We will refer to the $\varphi_l(\mathbf{x}, q)$ as the basis functions of the Bloch representation.

In the standard theories of electron-phonon interaction H_{eL} is treated in one of two models and then expanded in a power series in \mathbf{u} . The deformable-ion (D.I.) model⁷ assumes that

$$V(\mathbf{x}, q) = V_0(\mathbf{x} - \mathbf{u}(\mathbf{x})), \quad (12)$$

where

$$\mathbf{u}(\mathbf{x}) \equiv \sum_{f,s} q_{f,s} \mathbf{v}(\mathbf{f}, s) e^{i\mathbf{f} \cdot \mathbf{x}}. \quad (13)$$

Then the first order in \mathbf{u} we have

$$H_{eL}^{\text{DI}} = -\mathbf{u}(\mathbf{x}) \cdot \nabla V_0(\mathbf{x}). \quad (14)$$

The rigid-ion (R.I.) model⁸ assumes that

$$V(\mathbf{x}, q) = \sum_\nu v(\mathbf{x} - \mathbf{R}_\nu^0 - \mathbf{u}_\nu), \quad (15)$$

where v is some atomic-like potential.⁹ Then to the first order in \mathbf{u}_ν we have

$$H_{eL}^{\text{RI}} = -\sum_\nu \mathbf{u}_\nu \cdot \nabla v(\mathbf{x} - \mathbf{R}_\nu^0). \quad (16)$$

The matrix elements of H_{eL} are then given by an integral involving the periodic parts of the Bloch functions and either $\nabla v(\mathbf{x})$ or $\nabla V_0(\mathbf{x})$, times the matrix elements of $q_{f,s}$ which are given below.

$$q_{f,s} = \left(\frac{\hbar}{2NM\omega(\mathbf{f}, s)} \right)^{\frac{1}{2}} (\alpha_{f,s} + \alpha_{-f,s}^\dagger),$$

where

$$[\alpha_{f,s}, \alpha_{f',s'}^\dagger] = \delta_{f,f'} \delta_{s,s'},$$

and

$$\langle N(\mathbf{f}, s) - 1 | \alpha_{f,s} | N(\mathbf{f}, s) \rangle = [N(\mathbf{f}, s)]^{\frac{1}{2}},$$

⁷ A. Sommerfeld and H. Bethe, *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2; F. Bloch, *Z. Physik* **59**, 208 (1930).

⁸ L. Nordheim, *Ann. Physik* **9**, 607 (1931); and W. V. Houston, *Phys. Rev.* **88**, 1321 (1952).

⁹ The assumption (15) corresponds to rigidly displacing ion cores only when v is spherically symmetric or when only longitudinal modes are considered. This is because (15) shifts only the center of the ion cores, but does not change their orientation. A more involved assumption could be made to include all cases, but for simplicity we will assume that v is spherically symmetric, when we are discussing the rigid-ion model.

and

$$\langle N(\mathbf{f},s)+1 | \alpha_{\mathbf{f},s}^\dagger | N(\mathbf{f},s) \rangle = [N(\mathbf{f},s)+1]^\frac{1}{2}.$$

III. THE ODB REPRESENTATION

In this section we will introduce the orthogonalized deformed Bloch (ODB) functions and discuss some of their general properties. We have not chosen these states because they are "better" than the Bloch states in the sense that the transition rates between them caused by the lattice vibrations are appreciably smaller than the corresponding transition rates between Bloch states. In fact, in Appendix C we show that in certain special cases the two transition rates are equal.¹⁰ It is rather for their formal properties that we use them; chiefly that the largest part of their transition rates can be expressed directly in terms of the strains rather than the displacement of the lattice and that they permit the use of a much less limiting assumption for the form of the crystal potential in a vibrating crystal.

The ODB functions are defined by

$$\eta_l(\mathbf{x},q) \equiv \varphi_l(\mathbf{y}(\mathbf{x}),q) J^{-\frac{1}{2}}(\mathbf{y}(\mathbf{x})). \quad (17)$$

$\varphi_l(\mathbf{x},q)$ is defined in (8), (10), and (11) and \mathbf{y} is defined by

$$\mathbf{x} = \mathbf{y} + \mathbf{u}(\mathbf{y}), \quad (18)$$

where $\mathbf{u}(\mathbf{y})$ is given¹¹ by (13). We note from (13) and (5) that

$$\mathbf{u}(\mathbf{R}_\nu^0) = \mathbf{u}_\nu,$$

and hence if $\mathbf{x} = \mathbf{R}_\nu$, then $\mathbf{y} = \mathbf{R}_\nu^0$. In this sense then, in the "y space" the ion cores appear to be at their lattice points, and the η_l are essentially Bloch functions in this y space.

J is the Jacobian of the transformation (18):

$$\begin{aligned} J(\mathbf{y}) &\equiv \frac{\partial(x_1(\mathbf{y}), x_2(\mathbf{y}), x_3(\mathbf{y}))}{\partial(y_1, y_2, y_3)} \\ &= 1 + \frac{\partial u_\alpha(\mathbf{y})}{\partial y_\alpha} + \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial y_\alpha} \frac{\partial u_\beta}{\partial y_\beta} - \frac{\partial u_\alpha}{\partial y_\beta} \frac{\partial u_\beta}{\partial y_\alpha} \right) (1 - \delta_{\alpha\beta}) \\ &\quad + \frac{\partial(u_1(\mathbf{y}), u_2(\mathbf{y}), u_3(\mathbf{y}))}{\partial(y_1, y_2, y_3)}. \end{aligned} \quad (19)$$

The Jacobian is included to make the η_l orthogonal. One can, however, develop a similar theory with non-orthogonal functions as is shown in Appendix A, where we discuss the use of the functions $\varphi_l(\mathbf{y}(\mathbf{x}),q)$ as a basis.

As long as $J > 0$ the η_l remain finite and single valued, but the η_l are infinite when $J = 0$ and multivalued when

¹⁰ This similarity between the Bloch and ODB states has been shown only to the lowest order in \mathbf{u} , and may in fact not extend to higher orders.

¹¹ If there is more than one atom per unit cell we would choose the polarization vector so that \mathbf{u}_ν refers to the displacement of the center of mass of the unit cell [i.e., $\mathbf{v}(\mathbf{f},s) = \sum_j \mathbf{v}^j(\mathbf{f},s) M_j / \sum_j M_j$, where j runs over the atoms in the unit cell].

$J < 0$. We can see from (19) that J will be greater than zero except when the strains are of the order of magnitude of 1 or larger, and this sort of very large deformation was not intended to be included in this theory. In fact, for such large deformations the lattice is certainly not harmonic, and even the Bloch functions $\varphi_l(\mathbf{x},q)$ are realistic only in that they are small. It is clear then on physical grounds that this peculiar behavior of the η_l is not a serious problem. These essentially formal difficulties can be avoided by thinking of the η_l as being defined by (17) only in a connected region containing $J=1$ and where $J > \epsilon$, where ϵ is some small fixed number, and setting $\eta_l = 0$ elsewhere. When we do this the η_l are not exactly orthogonal or complete; however for the purposes of this paper they can be thought of as a complete orthonormal set.

Since $\mathbf{u}(\mathbf{y})$ satisfies the same periodic boundary condition as $\varphi_l(\mathbf{x},q)$, we have

$$\eta_l(\mathbf{x},q) = \eta_l(\mathbf{x} + \mathbf{L}_i, q). \quad (20)$$

In short, all the functions involved whether written as functions of \mathbf{x} or \mathbf{y} are periodic in the same set of vectors, \mathbf{L}_i .

Now in order to show that the η_l are essentially orthonormal¹² we consider the integral

$$\int dq \int_{\mathcal{V}} d^3x \eta_l^*(\mathbf{x},q) \eta_{l'}(\mathbf{x},q). \quad (21)$$

Because the η_l satisfy (20), the integral with respect to \mathbf{x} may be taken over any one of many equivalent regions one of which is the region \mathcal{V}' which is defined as the region which maps into \mathcal{V} when mapping from x space to y space. Hence (21) is precisely equal to

$$\int dq \int_{\mathcal{V}'} d^3x \eta_l^*(\mathbf{x},q) \eta_{l'}(\mathbf{x},q),$$

which on changing the variables of integration becomes

$$\int dq \int_{\mathcal{V}} d^3y \varphi_l^*(\mathbf{y},q) \varphi_{l'}(\mathbf{y},q) = \delta_{l,l'}. \quad (22)$$

That the η_l are essentially complete follows in a similar fashion from the completeness of the φ_l .

Because the η_l are complicated functions of \mathbf{x} and q we will not calculate matrix elements in this representation directly but relate them to matrix elements in the Bloch representation. Since $\{\varphi_l\}$ and $\{\eta_l\}$ can be

¹² The integral on q in (21) should be taken only over a region around $J=1$ where $J > \epsilon$, and hence over a similar region in (22). Therefore the right-hand side of (22) is not actually $\delta_{l,l'}$, but differs appreciably only for states with such large values of $\{N(\mathbf{f},s)\}$ that we need not consider them.

regarded as two complete orthonormal sets defined in the same region of space, they form two bases which are related by a unitary transformation T ,

$$|\eta_l\rangle = T|\varphi_l\rangle,$$

where

$$T = \sum_l |\eta_l\rangle\langle\varphi_l|. \quad (23)$$

Then for every operator O there is another

$$O' = T^\dagger O T,$$

such that

$$\langle\varphi_l|O'|\varphi_{l'}\rangle = \langle\eta_l|O|\eta_{l'}\rangle. \quad (24)$$

The usual procedure for handling such a change of basis is to investigate the properties of the unitary operator T . However, as will be shown in Appendix C, this operator can be handled only as a power series in the lattice displacement and this is just the type of expansion we are trying to avoid. We shall instead calculate the primed operators directly from (24), using only power series in the strains. We shall do this now for the dynamical variables, \mathbf{x} , $q_{t,s}$, \mathbf{p} , $P_{t,s}$ to arbitrary order in the strain.

Electron Position

If we set $O = \mathbf{x}$, the right-hand side of (24) becomes

$$\langle\eta_l|\mathbf{x}|\eta_{l'}\rangle = \int d\mathbf{q} \int_{\mathcal{V}} d^3x \eta_l^*(\mathbf{x}, q) \mathbf{x} \eta_{l'}(\mathbf{x}, q).$$

Then introducing the change of variables (18) into the integral, remembering that because of the periodic boundary conditions we need not change the region of integration, we get

$$\begin{aligned} \langle\eta_l|\mathbf{x}|\eta_{l'}\rangle &= \int d\mathbf{q} \int_{\mathcal{V}} d^3x \varphi_l(\mathbf{y}, q) [\mathbf{y} + \mathbf{u}(\mathbf{y})] \varphi_{l'}(\mathbf{y}, q) \\ &= \langle\varphi_l|\mathbf{x} + \mathbf{u}(\mathbf{x})|\varphi_{l'}\rangle. \end{aligned} \quad (25)$$

Comparing (25) and (24), we have

$$\mathbf{x}' = \mathbf{x} + \mathbf{u}(\mathbf{x}). \quad (26)$$

Hence the form of the operator relation (26) suggests that the change from the Bloch to the ODB representation can be thought of as mapping the electron wave function so that it moves with the lattice. Equations (26) and (18) are complementary in the sense that while (26) refers to a mapping of the wave function, (18) is the corresponding mapping of the space.

Normal Coordinate of the Lattice

Following the same procedure as for \mathbf{x}' , we get

$$q_{t,s}' = q_{t,s}.$$

Electron Momentum

Again we start by considering the right-hand side of (24).

$$\begin{aligned} \langle\eta_l|p_\alpha|\eta_{l'}\rangle &= \int d\mathbf{q} \int_{\mathcal{V}} d^3x \eta_l^*(\mathbf{x}, q) \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} \eta_{l'}(\mathbf{x}, q) \\ &= \frac{1}{2} \int d\mathbf{q} \int_{\mathcal{V}} d^3x \left[\eta_l^*(\mathbf{x}, q) \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} \eta_{l'}(\mathbf{x}, q) \right. \\ &\quad \left. - \frac{\hbar}{i} \left(\frac{\partial}{\partial x_\alpha} \eta_l^*(\mathbf{x}, q) \right) \eta_{l'}(\mathbf{x}, q) \right]. \end{aligned} \quad (27)$$

If we write $\eta_l(\mathbf{x}, q) = \varphi_l(\mathbf{y}(\mathbf{x}), q) J^{-1/2}(\mathbf{y}(\mathbf{x}))$ and differentiate the product we see that in (27) the terms involving derivatives of $J^{-1/2}$ cancel and we find

$$\begin{aligned} \langle\eta_l|p_\alpha|\eta_{l'}\rangle &= \frac{\hbar}{2i} \int d\mathbf{q} \int_{\mathcal{V}} d^3x \left[\varphi_l^*(\mathbf{y}(\mathbf{x}), q) \frac{\partial}{\partial x_\alpha} \varphi_{l'}(\mathbf{y}(\mathbf{x}), q) \right. \\ &\quad \left. - \left(\frac{\partial}{\partial x_\alpha} \varphi_l^*(\mathbf{y}(\mathbf{x}), q) \right) \varphi_{l'}(\mathbf{y}(\mathbf{x}), q) \right] J^{-1}(\mathbf{y}(\mathbf{x})). \end{aligned} \quad (28)$$

In order to change the variables in this integral we note that

$$\begin{aligned} \frac{\partial}{\partial x_\alpha} &= \left(\delta_{\alpha\beta} - \frac{\partial u_\beta(\mathbf{y})}{\partial y_\alpha} + \frac{\partial u_i(\mathbf{y})}{\partial y_\alpha} \frac{\partial u_\beta(\mathbf{y})}{\partial y_i} \right. \\ &\quad \left. - \frac{\partial u_i(\mathbf{y})}{\partial y_\alpha} \frac{\partial u_j(\mathbf{y})}{\partial y_i} \frac{\partial u_\beta(\mathbf{y})}{\partial y_j} + \dots \right) \frac{\partial}{\partial y_\beta} \\ &= \left(\frac{1}{1+S(\mathbf{y})} \right)_{\alpha\beta} \frac{\partial}{\partial y_\beta}, \end{aligned} \quad (29)$$

where¹³

$$S^{\alpha\beta}(\mathbf{y}) \equiv \partial u_\beta(\mathbf{y}) / \partial y_\alpha.$$

Using (29) and integrating one of the terms by parts, (28) becomes

$$\begin{aligned} \langle\eta_l|p_\alpha|\eta_{l'}\rangle &= \frac{1}{2} \left\langle \varphi_l \left| p_\beta \left(\frac{1}{1+S(\mathbf{x})} \right)_{\alpha\beta} + \left(\frac{1}{1+S(\mathbf{x})} \right)_{\alpha\beta} p_\beta \right| \varphi_{l'} \right\rangle, \end{aligned}$$

and hence

$$p_\alpha' = \frac{1}{2} \left[p_\beta \left(\frac{1}{1+S(\mathbf{x})} \right)_{\alpha\beta} + \left(\frac{1}{1+S(\mathbf{x})} \right)_{\alpha\beta} p_\beta \right]. \quad (30)$$

¹³ Nowhere in this paper do we distinguish between covariant and contravariant tensors. Superscripts are used for notational convenience.

Lattice Momentum

As above, we start by considering the ODB matrix elements

$$\begin{aligned} \langle \eta_l | P_{f,s} | \eta_{l'} \rangle &= \int dq \int_{\mathcal{V}} d^3x \eta_l^* \left(\frac{\partial}{\partial q_{f,s}} \eta_{l'} \right)_x \\ &= \frac{\hbar}{2i} \int dq \int_{\mathcal{V}} d^3x \left[\eta_l^* \left(\frac{\partial}{\partial q_{f,s}} \eta_{l'} \right)_x \right. \\ &\quad \left. - \left(\frac{\partial}{\partial q_{f,s}} \eta_l^* \right)_x \eta_{l'} \right]. \quad (31) \end{aligned}$$

Again we write $\eta_l = \varphi_l J^{-1/2}$ and note that the terms involving the derivatives of the Jacobian cancel, and (31) becomes

$$\begin{aligned} \frac{\hbar}{2i} \int dq \int_{\mathcal{V}} d^3x \left[\varphi_l^*(\mathbf{y}(\mathbf{x}), q) \left(\frac{\partial}{\partial q_{f,s}} \varphi_{l'}(\mathbf{y}(\mathbf{x}), q) \right)_x \right. \\ \left. - \left(\frac{\partial}{\partial q_{f,s}} \varphi_l^*(\mathbf{y}(\mathbf{x}), q) \right)_x \varphi_{l'}(\mathbf{y}(\mathbf{x}), q) \right] J(\mathbf{y}(\mathbf{x})). \end{aligned}$$

Then by changing the variables in the integral and using the fact that

$$\begin{aligned} \left(\frac{\partial}{\partial q_{f,s}} \varphi(\mathbf{y}(\mathbf{x}), q) \right)_x &= \left(\frac{\partial}{\partial q_{f,s}} \varphi(\mathbf{y}, q) \right)_y - \left(\frac{1}{1+S(\mathbf{y})} \right)_{\alpha\beta} \\ &\quad \times \left(\frac{\partial u_\beta(\mathbf{y})}{\partial q_{f,s}} \right)_y \left(\frac{\partial}{\partial y_\alpha} \varphi(\mathbf{y}, q) \right)_q, \end{aligned}$$

we show that

$$\begin{aligned} P_{f,s}' &= P_{f,s} - \frac{1}{2} \frac{i}{\hbar} \left\{ [P_{f,s}, u_\beta] \left(\frac{1}{1+S} \right)_{\beta\alpha} p_\alpha \right. \\ &\quad \left. + p_\alpha \left(\frac{1}{1+S} \right)_{\beta\alpha} [P_{f,s}, u_\beta] \right\}. \quad (32) \end{aligned}$$

IV. H IN THE ODB REPRESENTATION

In Sec. VI it is shown that, in order to find the transition rates between the ODB states, we must find the matrix elements of H in the ODB representation. We shall do this by using the same procedure as we used in the preceding section, namely find the operator H' whose Bloch matrix elements are equal to the ODB matrix elements of H . As we proceed we will see that it is possible to express H' in powers of $S^{\alpha\beta}$ and the lattice velocity $[H_L, \mathbf{u}]$, and we will keep only terms of the lowest order in these two quantities.

Since H and H' are related by a similarity transformation, H' has the same form as H , i.e.,

$$\begin{aligned} H' &= \frac{p_\alpha' p_\alpha'}{2m} + V'(\mathbf{x}, q) + \frac{P_{f,s}' P_{-f,s}'}{2M} \\ &\quad + \frac{1}{2} M \omega^2(\mathbf{f}, s) q_{f,s}' q_{-f,s}'. \quad (33) \end{aligned}$$

We now evaluate each of the terms of (33), using the results of Sec. III.

(a) Electron Kinetic Energy

From (30) we get, to the first order in strain, that

$$p_\alpha' = p_\alpha - \frac{1}{2} [p_\beta S^{\alpha\beta}(\mathbf{x}) + S^{\alpha\beta}(\mathbf{x}) p_\beta]. \quad (34)$$

Then using the relation

$$[p_\alpha, S^{\beta\gamma}(\mathbf{x})] = [\hbar K_\alpha, S^{\beta\gamma}(\mathbf{x})], \quad (35)$$

where¹⁴ K_α is a diagonal operator in the Bloch representation defined by

$$K_\alpha | \varphi_l \rangle = k_\alpha | \varphi_l \rangle,$$

as well as (34) and the relation¹⁵

$$p_\alpha S^{\alpha\beta} + S^{\alpha\beta} p_\alpha = (2mi/\hbar) [H_e, u_\beta],$$

one can show that, to the lowest order in $S^{\alpha\beta}$ and $[H_e, u_\beta]$,

$$\begin{aligned} \frac{p_\alpha' p_\alpha'}{2m} &= \frac{p_\alpha p_\alpha}{2m} + \frac{1}{2} \left\{ S^{\alpha\beta} \left(-\frac{p_\alpha p_\beta}{m} + \frac{\hbar K_\beta p_\alpha}{m} \right) \right. \\ &\quad \left. + \left(-\frac{p_\alpha p_\beta}{m} + \frac{\hbar K_\beta p_\alpha}{m} \right) S^{\alpha\beta} \right\} \\ &\quad - \frac{i}{2\hbar} (\hbar K_\beta [H_e, u_\beta] + [H_e, u_\beta] \hbar K_\beta). \quad (36) \end{aligned}$$

(b) Lattice Hamiltonian

In order to simplify the last two terms in (33) we note that

$$M[H_L, u_\alpha] = [P_{-f,s}, u_\alpha] P_{f,s}. \quad (37)$$

$(i/\hbar)[H_L, u_\alpha]$ is essentially the velocity of the lattice. Using (37) and (32) we are able to show, to the lowest order¹⁶ in $[H_L, u_\alpha]$ and $S^{\alpha\beta}$, that

$$\begin{aligned} \frac{P_{f,s}' P_{-f,s}'}{2M} &+ \frac{1}{2} M \omega^2(\mathbf{f}, s) q_{f,s}' q_{-f,s}' \\ &= H_L - \frac{i}{2\hbar} (p_\beta [H_L, u_\beta] + [H_L, u_\beta] p_\beta) + \frac{p_\alpha p_\alpha}{2M}. \quad (38) \end{aligned}$$

(c) Electron Potential Energy

Using the ODB representation is equivalent to introducing a mapping of the lattice so that the ion cores now appear (i.e., in \mathbf{y} space) to be at their lattice points and the remaining departure of the mapped potential

¹⁴ This same operator was used by E. N. Adams, J. Chem. Phys. **21**, 2013 (1953). In the case where one wished to consider an Umklapp collision one would have to add $S^{\alpha\beta} \times$ (a reciprocal lattice vector) to the right side of (35).

¹⁵ Note that the order of α and β is different here from that in the similar expression in (36).

¹⁶ Whenever u_α appears in the higher order terms neglected in (38), it appears either in $S^{\alpha\beta}$ or in $[H_L, u_\alpha]$.

function, $V(\mathbf{x}(\mathbf{y}), q)$, from the equilibrium potential function, $V_0(\mathbf{y})$, is small and can be reasonably approximated by a series in the strains and their derivatives. In this paper we keep only terms of the lowest order in strain and neglect terms in the derivatives of the strain. We assume that

$$V(\mathbf{x}(\mathbf{y}), q) = V_0(\mathbf{y}) + U^{\alpha\beta}(\mathbf{y})S^{\beta\alpha}(\mathbf{y}), \quad (39)$$

where $U^{\alpha\beta}(\mathbf{y})$ is an unspecified function with the periodicity of the lattice. This is essentially the same assumption as that made by Bardeen and Shockley,¹ and by Pikus and Bir^{17,18} in the special case of homogeneous strains. We feel that it is a quite realistic assumption when we are dealing with long-wavelength phonons, and that it remains a possibly useful model even for the shortest wavelength phonons.

The model obtained by setting $U^{\alpha\beta}(\mathbf{y}) \equiv 0$ corresponds to the physical notion of deformable ions [but is identical to the standard D.I. model (12) only to the first order in \mathbf{u}]. Setting

$$U^{\alpha\beta}(\mathbf{y}) = \sum_{\nu} (\mathbf{R}_{\nu}^0 - \mathbf{y})_{\beta} \frac{\partial}{\partial y_{\alpha}} v(\mathbf{y} - \mathbf{R}_{\nu}^0)$$

gives a model which is equivalent to the R.I. model (16) for long-wavelength phonons.

In this paper we will not assume any particular form for $U^{\alpha\beta}$ but will, so far as we can, eliminate it from the theory by expressing the required results in terms of the properties of the crystal under *homogeneous* strain.

Using (39) we see that

$$\langle \eta_l | V(\mathbf{x}, q) | \eta_{l'} \rangle = \langle \varphi_l | V_0(\mathbf{x}) + U^{\alpha\beta}(\mathbf{x})S^{\beta\alpha}(\mathbf{x}) | \varphi_{l'} \rangle,$$

and therefore

$$V'(\mathbf{x}, q) = V_0(\mathbf{x}) + U^{\alpha\beta}(\mathbf{x})S^{\beta\alpha}(\mathbf{x}). \quad (40)$$

We could extend (39) to include higher orders by adding terms like $W^{\alpha\beta\gamma\nu}(\mathbf{y})S^{\alpha\beta}(\mathbf{y})S^{\gamma\nu}(\mathbf{y})$ and $Z^{\alpha\beta\gamma}(\mathbf{y}) \times (\partial/\partial y_{\gamma})S^{\alpha\beta}(\mathbf{y})$, etc. The additional parameters Z and W are also related to the properties of statically strained crystals, but it is not clear to what extent they could be eliminated from the theory.

In a crystal with more than one atom per unit cell, the locations of the ion cores in the unit cell will in general shift even for a homogeneous strain. The effect of these shifts on the effective potential, for the case of homogeneous strain, is included in $U^{\alpha\beta}(\mathbf{x})$; but the dependence of these shifts on wave vector has been neglected in (39). Hence, for this reason also, (39) should be regarded as a long-wavelength approximation.

(d) Transformed Hamiltonian

On substituting (35), (38), and (40) in (33), we have

$$H' = E + E^I + E^{II} + E^{III}, \quad (41)$$

¹⁷ G. E. Pikus, J. Tech. Phys. (U.S.S.R.) **28**, 2390 (1958) [translation: Soviet Phys.-Tech. Phys. **3**, 2194 (1958)].

¹⁸ G. E. Pikus and G. L. Bir, Fiz. Tverdogo Tela **1**, 1624 (1959) [translation: Soviet Phys.-Solid State **1**, 1502 (1960)].

where

$$E^I = \frac{1}{2}(S^{\alpha\beta}\mathfrak{D}^{\beta\alpha} + \mathfrak{D}^{\beta\alpha}S^{\alpha\beta}), \quad (42)$$

$$E^{II} = -\frac{i}{2\hbar}(\hbar K_{\beta}[H_e, u_{\beta}] + [H_e, u_{\beta}]\hbar K_{\beta}) - \frac{i}{2\hbar}(p_{\beta}[H_L, u_{\beta}] + [H_L, u_{\beta}]p_{\beta}), \quad (43)$$

$$E^{III} = p_{\alpha}p_{\alpha}/2M; \quad (44)$$

and where

$$\mathfrak{D}^{\beta\alpha} \equiv -p_{\alpha}p_{\beta}/m + \hbar K_{\beta}p_{\alpha}/m + U^{\beta\alpha}(\mathbf{x}). \quad (45)$$

We call $\mathfrak{D}^{\beta\alpha}$ the "deformation potential operator" and will show in Sec. V that its diagonal matrix elements in the Bloch representation are just the deformation potentials.

We will show in Sec. VII that the major part of the electron-phonon coupling comes from E^I and that E^{II} represents a relatively small coupling. Whereas E^I is related to the local change of the electron energy in the crystal, E^{II} expresses the fact that a moving lattice tends to drag the electron with it. E^{III} is a small term which does not contribute to the scattering because it is diagonal in the phonon occupation number¹⁹ and it will be neglected for the rest of this paper (except in Appendix C).

When $V_0(\mathbf{x})$ and $w_{nk}(\mathbf{x})$ approach constants (which are independent of the strain) the electron-phonon coupling should disappear. Although all of the matrix elements of E^I approach zero in this limit, some of the matrix elements of E^{II} do not. In particular the matrix elements of E^{II} between states of different total energy do not approach zero when $V_0(\mathbf{x})$ and w_{nk} do. This is most easily seen if we write E^I using the form of p_{α}^2 in Appendix C. With the help of (C-3) we can show that

$$\lim_{V_0 \rightarrow \text{const}} \langle \varphi_l | E^I | \varphi_{l'} \rangle = (E_l - E_{l'}) \langle \chi_N e^{ik \cdot x} | \mathbf{u} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{u} | \chi_{N'} e^{ik' \cdot x} \rangle,$$

which is zero only when $E_l = E_{l'}$. This results from the fact that the ODB states are not stationary in a lattice with no coupling (which is of course to be expected, since if there is no coupling the electron wave functions should not deform with the lattice as the ODB states do). The time dependence of the ODB states resulting from these matrix elements is very small and represents the type of time dependence which is neglected in first

¹⁹ E^{III} can be regarded as a mass renormalization in that it is accounted for by replacing $1/m$ by $(1/m + 1/M)$ in E . In fact mass renormalization in its earliest form [H. A. Kramers, *Institut Solvay, Huitieme Conseil de Physique, 1948 Rapports et Discussions* (R. Stoops, Brussels, 1950); N. G. Van Kampen, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd **26**, No. 15 (1951)] came about by applying a "displacement operator" to the Hamiltonian which is somewhat analogous to T (see Appendix C).

order perturbation theory when one replaces

$$\frac{\hbar \sin^2[(E_l - E_r)t/2\hbar]}{(E_l - E_r)^2} \quad \text{by} \quad \frac{1}{2}\pi\delta(E_l - E_r)t.$$

Even this small time dependence does not appear in the results of the present work because we limit ourselves to first-order perturbation theory which involves only matrix elements of H' between states of the same total energy.

In Appendix C we introduce the deformable- and rigid-ion models into (41) and show that for these models the Bloch matrix elements of H and H' , between states of the same total energy, differ only by the contribution of E^{III} . Since this is true for both the R.I. and D.I. models it is probably independent of these models, which suggests that E^{III} represents the difference between a theory which is first-order in $S^{\alpha\beta}$ and $[H_L, u_\alpha]$ and a theory which is first-order in u_α .

V. DEFORMATION POTENTIAL

We will now show how the operator $\mathfrak{D}^{\beta\alpha}$ is related to the properties of a homogeneously strained crystal.²⁰

Let $\psi_{nk}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}w_{nk}(\mathbf{x})$ be one of the eigenfunctions of an electron in a stationary crystal,²¹ where the position of the lattice points are given by \mathbf{R}_n^0 which are defined in (6). The $\psi_{nk}(\mathbf{x})$ satisfy the periodic boundary conditions, (11), and are normalized in the volume $\mathfrak{V} = (\mathbf{L}_1 \times \mathbf{L}_2) \cdot \mathbf{L}_3 = L_1 L_2 L_3$. The $w_{nk}(\mathbf{x})$ have the periodicity of the lattice [i.e., $w_{nk}(\mathbf{x} + \mathbf{R}_n^0) = w_{nk}(\mathbf{x})$] and satisfy the equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x_\alpha} + ik_\alpha\right)^2 w_{nk}(\mathbf{x}) + V_0(\mathbf{x})w_{nk}(\mathbf{x}) = \epsilon_n(\mathbf{k})w_{nk}(\mathbf{x}). \quad (46)$$

If we now slightly deform and rotate this crystal, we have another regular crystal with lattice points given by $\mathbf{R}_n^{0d} = \mathbf{R}_n^0 \cdot (\mathbf{1} + \mathbf{a}) = \mathbf{R}_n^0 + \mathbf{u}_n$, where \mathbf{a} is a small, constant (but not symmetric) tensor. In this new crystal there is an electron eigenfunction²²

$$\psi_{nk^d}(\mathbf{x}, \mathbf{a}) = e^{i\mathbf{k}\cdot\mathbf{x}}w_{nk^d}(\mathbf{x}, \mathbf{a}). \quad (47)$$

²⁰ The effect of homogeneous strain on the electron states in a crystal has been discussed by several authors: E. N. Adams, Phys. Rev. **96**, 803 (1954); R. H. Parmenter, Phys. Rev. **99**, 1759 (1955); and **99**, 1767 (1955); and references 17 and 18. In reference 18 the case of degenerate bands (which is omitted in this paper) is discussed.

²¹ We should of course consider a vibrating crystal in which there would be temperature-dependent corrections to the energy and hence to the deformation potentials, due to both the second order term in strain in the Hamiltonian, and the second order of the perturbation theory. We will not include them here because we are doing an entirely first-order theory.

²² Even though the allowed values of \mathbf{k} in this crystal are different from those in the first, since they are practically a continuum we assume that for each value of \mathbf{k} there are eigenfunctions in both. In the case where \mathbf{k} lies near the zone boundary of one crystal, it may be outside the first zone of the other crystal, and the appropriate wave function is then that which corresponds to the reduced \mathbf{k} vector in the second crystal.

To these new Bloch functions we apply the boundary conditions

$$\psi_{nk^d}(\mathbf{x}, \mathbf{a}) = \psi_{nk^d}(\mathbf{x} + \mathbf{L}_i^d, \mathbf{a}),$$

where $\mathbf{L}_i^d \equiv \mathbf{L}_i \cdot (\mathbf{1} + \mathbf{a})$, and we normalize these functions so that

$$\int_{\mathfrak{V}^d} d^3x \psi_{nk^d}^* \psi_{n'k'^d} = (1 + \text{Trace}(\mathbf{a}))^{-1} \delta_{n,n'} \delta_{\mathbf{k},\mathbf{k}'}, \quad (48)$$

where \mathfrak{V}^d is the parallelepiped defined by the vectors \mathbf{L}_i^d .

The w_{nk^d} have the periodicity of the new lattice [i.e., $w_{nk^d}(\mathbf{x}, \mathbf{a}) = w_{nk^d}(\mathbf{x} + \mathbf{R}_n^{0d}, \mathbf{a})$] and satisfy the equation

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial}{\partial x_\alpha} + ik_\alpha \right)^2 + V_0^d(\mathbf{x}, \mathbf{a}) \right\} w_{nk^d}(\mathbf{x}, \mathbf{a}) = \epsilon_n^d(\mathbf{k}) w_{nk^d}(\mathbf{x}, \mathbf{a}). \quad (49)$$

We define the deformation potential²³ $D^{\beta\alpha}(n, \mathbf{k})$ by saying that

$$\epsilon_n^d(\mathbf{k}) = \epsilon_n(\mathbf{k}) + a_{\alpha\beta} D^{\beta\alpha}(n, \mathbf{k}). \quad (50)$$

We evaluate $D^{\beta\alpha}(n, \mathbf{k})$, by solving (49) by first-order perturbation theory. To do this we again make the change of variables

$$\mathbf{x} = \mathbf{y} + \mathbf{u}(\mathbf{y}),$$

but here we define

$$u_\alpha(\mathbf{y}) \equiv a_{\beta\alpha} y_\beta.$$

Then using (39) [with $S^{\alpha\beta}(\mathbf{x}) \equiv a_{\alpha\beta}$] for V^d and keeping only terms to the first order in \mathbf{a} , (49) in terms of the new variables becomes

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial}{\partial y_\alpha} + ik_\alpha \right)^2 + V_0(\mathbf{y}) \right\} w_{nk^d}(\mathbf{y}, \mathbf{a}) + a_{\alpha\beta} \left\{ -\frac{\hbar^2}{m} \frac{\partial^2}{\partial y_\alpha \partial y_\beta} - ik_\alpha \frac{\partial}{\partial y_\beta} + U^{\beta\alpha}(\mathbf{y}) \right\} w_{nk^d}(\mathbf{y}, \mathbf{a}) = \epsilon_n^d(\mathbf{k}) w_{nk^d}(\mathbf{y}, \mathbf{a}), \quad (51)$$

where

$$w_{nk^d}(\mathbf{y}, \mathbf{a}) \equiv w_{nk^d}(\mathbf{y} \cdot (\mathbf{1} + \mathbf{a}), \mathbf{a}).$$

We note that

$$w_{nk^d}(\mathbf{y} + \mathbf{R}_n^0, \mathbf{a}) = w_{nk^d}(\mathbf{y}, \mathbf{a}),$$

and because of (48)

$$\int_{\mathfrak{V}} w_{nk^d}^* w_{nk^d} d^3y = 1,$$

where \mathfrak{V} is the volume defined by the vectors \mathbf{L}_i . We can now solve (51) by perturbation theory²⁴ by assuming

$$w_{nk^d}(\mathbf{y}, \mathbf{a}) = w_{nk^{(0)}}(\mathbf{y}) + a_{\alpha\beta} w_{nk^{(1)\beta\alpha}}(\mathbf{y}) + \dots, \quad (52)$$

²³ The deformation potential is usually defined in terms of the shift of a band edge point, which is not the same as (50). This point is discussed in Appendix B.

²⁴ We are not considering the situation in degenerate bands.

where both $w^{(0)}$ and $w^{(1)}$ are periodic in \mathbf{R}_v^0 , and using (50) for $\epsilon_n^d(\mathbf{k})$. Substituting (50) and (52) in (51) we get, to the lowest order in \mathbf{a} , that

$$w_{n\mathbf{k}}^{(0)}(\mathbf{y}) = w_{n\mathbf{k}}(\mathbf{y}).$$

By equating the terms that are first order in \mathbf{a} and setting

$$w_{n\mathbf{k}}^{(1)\beta\alpha} = \sum_{n'} c_{n',\beta\alpha} w_{n'\mathbf{k}},$$

we can show that

$$D^{\beta\alpha}(n, \mathbf{k}) = \int_{\mathbf{v}} d^3y w_{n\mathbf{k}}^*(\mathbf{y}) \left\{ \frac{\hbar^2}{m} \frac{\partial^2}{\partial y_\alpha \partial y_\beta} + i\hbar^2 k_\alpha \frac{\partial}{\partial y_\beta} + U^{\beta\alpha}(\mathbf{y}) \right\} w_{n\mathbf{k}}(\mathbf{y}) \quad (53)$$

$$= \int_{\mathbf{v}} d^3y \psi_{n\mathbf{k}}^* \left\{ \frac{\hbar^2}{m} \frac{\partial^2}{\partial y_\beta \partial y_\alpha} + \frac{\hbar^2 k_\beta}{im} \frac{\partial}{\partial y_\alpha} + U^{\beta\alpha}(\mathbf{y}) \right\} \psi_{n\mathbf{k}}(\mathbf{y}), \quad (54)$$

which is just one of the diagonal elements $\langle \varphi_l | \mathcal{D}^{\beta\alpha} | \varphi_l \rangle$ of the deformation potential operator defined in (45).

Although $\mathcal{D}^{\beta\alpha}$ is diagonal in \mathbf{k} , it is not diagonal in the band index n and, as will be seen in Sec. VII, these interband elements are important in determining interband scattering probabilities as well as some correction terms for the intraband scattering probabilities. It would therefore be desirable to relate these parameters to the properties of homogeneously strained crystals also. Such a relaxation does exist in that the terms proportional to \mathbf{a}^2 which are neglected in (50) can be seen to involve sums over these interband deformation potentials. But these relations are so complicated [they include terms which come from extending (39) to second order], and the nonlinear energy shifts so small, that there seems to be little hope of determining the interband deformation potentials from homogeneous strain experiments. However, near a point where two bands are degenerate (as in the valence bands of Ge and Si) the energy shifts on homogeneous strain¹⁸ involve the interband elements of $\mathcal{D}^{\beta\alpha}$ (we have not considered the case of degenerate bands here), and scattering near such degenerate points is one instance where interband phonon scattering might be important. Certain of the properties of the matrix elements of $\mathcal{D}^{\beta\alpha}$ can, of course, be deduced from the crystal symmetry.

VI. TRANSPORT THEORY IN THE ODB REPRESENTATION

We have stated previously that the Bloch and ODB representations are very similar. In this section we will establish that this similarity permits us to use the off-diagonal elements of H in either representation to give the transition rates needed for transport theory.

We will consider the electric current caused by the application of a constant electric field \mathcal{E} . This field leads to an extra term, $H_{\text{field}} = -e\mathcal{E}x_1$, in the Hamiltonian, and from (26) we see that

$$H_{\text{field}}' = -e\mathcal{E}[x_1 + u_1(\mathbf{x})]. \quad (55)$$

The second term in (55) can be thought of as appearing because the electric field which is constant in x space is not constant in y space.

1. The usual procedure²⁵ for evaluating the electric current is to solve the Boltzmann equation for the probability $f(n, \mathbf{k})$ that an electron is in the Bloch state $\psi_{n\mathbf{k}}$; namely,

$$\left(\frac{\partial f(n, \mathbf{k})}{\partial t} \right)_{\text{field}} + \left(\frac{\partial f(n, \mathbf{k})}{\partial t} \right)_{\text{coll}} = 0, \quad (56)$$

where

$$\left(\frac{\partial f(n, \mathbf{k})}{\partial t} \right)_{\text{field}} = -\frac{e\mathcal{E}}{\hbar} \frac{\partial \epsilon_n(\mathbf{k})}{\partial k_1} \frac{df^0}{d\epsilon_n}, \quad (57)$$

$$\left(\frac{\partial f(n, \mathbf{k})}{\partial t} \right)_{\text{coll}} = \frac{v}{(2\pi)^3} \sum_{n'} \int d^3k [f^1(n', \mathbf{k}') R_{n'\mathbf{k}' \rightarrow n\mathbf{k}} - f^1(n, \mathbf{k}) R_{n\mathbf{k} \rightarrow n'\mathbf{k}'}], \quad (58)$$

where

$$f(n, \mathbf{k}) = f^0 + f^1 + O(\mathcal{E}^2, S^{-1}, \mathcal{E}S^{-2}),$$

(f^0 being the equilibrium distribution function) and

$$R_{n\mathbf{k} \rightarrow n'\mathbf{k}'} = \frac{2\pi}{\hbar} |\langle \varphi_{n\mathbf{k}}; \{N\} | H_{eL} | \varphi_{n'\mathbf{k}'}; \{N'\} \rangle|^2 \times \delta(\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k}') \pm \hbar\omega(\mathbf{k} - \mathbf{k}', s)). \quad (59)$$

For the sake of simplifying the argument we assume that after calculating the matrix elements in (59) one sets $N(\mathbf{f}, s)$ equal to its equilibrium value

$$N^0(\mathbf{f}, s) = (e^{\hbar\omega/KT} - 1)^{-1}.$$

Then having $f^1(n, \mathbf{k})$, one obtains the current from

$$\bar{J}_\alpha = -\frac{e}{\hbar} \sum_n \int d^3k \frac{v}{(2\pi)^3} f^1(n, \mathbf{k}) \frac{\partial \epsilon_n(\mathbf{k})}{\partial k_\alpha}. \quad (60)$$

The standard derivation²⁰ of this procedure relies on first-order perturbation theory to give (59) for the transition rates between the Bloch states.

By relying on perturbation theory we could easily derive a similar procedure for the ODB states in which the transition rates would be given by (59) with $E^I + E^{II}$ replacing H_{eL} , and the extra terms which comes from putting H_{field} and J_α in the ODB representation may be neglected (see part 3 of this section).

²⁵ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London and New York, 1953), 2nd ed., Chap. IX. For simplicity we will use Boltzmann statistics.

Hence one would calculate the transport phenomenon with a procedure identical to (56)–(60) except that H_{eL} is replaced by $E^I + E^{II}$.

Although the conclusion of this argument is correct, the derivation of the Boltzmann equation upon which it is based is not very convincing.²⁸ Since there have recently appeared much more satisfactory derivations of the Boltzmann equation,^{27–29} we will go on to show that even in these more sophisticated derivations it makes little difference whether one used the Bloch or ODB representation.

2. Kohn and Luttinger²⁷ have derived the Boltzmann equation from the density matrix in the Bloch representation. In their derivation they consider only impurity scattering and assume that the electric field is being turned on adiabatically. We have followed their procedure but use the ODB representation and consider phonon scattering. In doing this we neglect E^{III} and find that the additional term in (55) does not contribute to the lowest order because it is completely off-diagonal. The additional term in (62) which comes from putting the current operator in the ODB representation does not contribute to the lowest order because of the smallness of the off-diagonal elements of the density matrix. Again we conclude that one need merely replace H_{eL} by $E^I + E^{II}$ in (59) and then use the usual procedure. We will not present the details of this argument here because they follow very closely those of the original work.³⁰

3. Since we have not presented the details of the argument of the previous paragraph we will now present a plausibility argument which will show the sort of questions that are involved. We assume that for the procedure (56)–(60) to be valid it must be derivable from the equation of motion of the density matrix

$$i\hbar\dot{\rho} = [H + H_{\text{field}}, \rho], \quad (61)$$

and the fact that

$$\bar{J}_\alpha = \text{Trace}(\rho J_\alpha). \quad (62)$$

In such a derivation $f(n, \mathbf{k})$ will appear as the diagonal elements of the density matrix in the Bloch representation,

$$\langle \varphi_l | \rho | \varphi_l \rangle = f(n, \mathbf{k}) N^0(\mathbf{f}, s).$$

By assuming that (61), (62) in the Bloch representation lead to (56)–(60) we will show that (61), (62) in the ODB representation will, to a sufficient approximation, lead to a procedure identical to (56)–(60) except that $E^I + E^{II}$ replaces H_{eL} . In order to do this

we first compare (61) in the two representations. In the Bloch representation, using (1), (61) becomes

$$\begin{aligned} i\hbar \langle \varphi_l | \dot{\rho} | \varphi_l \rangle &= \sum_{l'} \langle \varphi_l | E + H_{eL} - e\mathcal{E}x_1 | \varphi_{l'} \rangle \langle \varphi_{l'} | \rho | \varphi_l \rangle \\ &\quad - \langle \varphi_l | \rho | \varphi_{l'} \rangle \langle \varphi_{l'} | E + H_{eL} - e\mathcal{E}x_1 | \varphi_l \rangle, \end{aligned} \quad (63)$$

and in the ODB representation, using (41) and (55) and remembering that $\langle \eta_l | O | \eta_{l'} \rangle = \langle \varphi_l | O' | \varphi_{l'} \rangle$, (61) becomes

$$\begin{aligned} i\hbar \langle \eta_l | \dot{\rho} | \eta_l \rangle &= \sum_{l'} \langle \varphi_l | E + E^I + E^{II} + E^{III} - e\mathcal{E}(x_1 + u_1) | \varphi_{l'} \rangle \\ &\quad \times \langle \eta_{l'} | \rho | \eta_l \rangle - \langle \eta_l | \rho | \eta_{l'} \rangle \\ &\quad \times \langle \varphi_{l'} | E + E^I + E^{II} + E^{III} - e\mathcal{E}(x_1 + u_1) | \varphi_l \rangle. \end{aligned} \quad (64)$$

The term $-e\mathcal{E}u_1$ in (64) is like a scattering term in that it connects states that differ by one phonon and conserves pseudomomentum, and hence can be grouped with $E^I + E^{II}$ in comparison to which it is negligible for any reasonable electric field. The term E^{III} does not give scattering (because it is diagonal in the phonon occupation numbers), and may be neglected in comparison to E . When we neglect E^{III} and $-e\mathcal{E}u_1$ in (64), we see that the equation of motion of ρ is the same in the two representations except that where H_{eL} appears in (63), $E^I + E^{II}$ appear in (64). Now, although we will not attempt to derive the Boltzmann equation here, it is clear that as far as the form of $\langle \varphi_l | H_{eL} | \varphi_{l'} \rangle$ is concerned, such a derivation would require only some very general properties³¹ that $\langle \varphi_l | E^I + E^{II} | \varphi_{l'} \rangle$ would also have. Hence we conclude that a Boltzmann equation for the probabilities of occupation of the ODB states would be the same as (56) except that H_{eL} would be replaced by $E^I + E^{II}$ in the transition rates (59).

Now assuming we have the ODB density matrix we can calculate the current from (52). Remembering to put J_α also in the ODB representation, we get from (34) that

$$\bar{J}_\alpha = \frac{e}{m} \sum_{l, l'} \langle \eta_l | \rho | \eta_{l'} \rangle \langle \varphi_{l'} | p_\alpha - (S^{\beta\alpha} p_\beta + p_\beta S^{\beta\alpha}) | \varphi_l \rangle. \quad (65)$$

Since $\langle \varphi_l | S^{\beta\alpha} p_\beta + p_\beta S^{\beta\alpha} | \varphi_{l'} \rangle$ is completely off-diagonal and provided that the off-diagonal elements of ρ are one order (with respect to $S^{\beta\alpha}$) smaller than the diagonal elements (this is the case in both Kohn and Luttinger's derivation²⁷ and Adams' extension of van Hove's²⁸ work), neither the second term in (65) nor the off-diagonal elements of p_β contribute to the lowest order

³¹ (a) According to van Hove, it is necessary only that the matrix elements $\langle \varphi_l | H_{eL} | \varphi_{l'} \rangle$ be continuous functions of their index (and in this respect the Bloch and ODB states are the same) and that the diagonal elements of the matrix,

$$\sum_{l'} \langle \varphi_l | H_{eL} | \varphi_{l'} \rangle \langle \varphi_{l'} | H_{eL} | \varphi_{l'} \rangle,$$

be larger than the off-diagonal elements by a factor of the square root of the number of ion cores in the sample. (b) The fact that the Boltzmann equation has the same form for many different kinds of scattering strongly suggests that its validity is not sensitive to the form of the scattering matrices.

²⁶ N. G. van Kampen, *Physica* **20**, 603 (1954).

²⁷ W. Kohn and J. M. Luttinger, *Phys. Rev.* **108**, 590 (1957); and D. A. Greenwood, *Proc. Phys. Soc. (London)* **71**, 585 (1958).

²⁸ Leon Van Hove, *Physica* **21**, 517 (1955).

²⁹ E. N. Adams, Westinghouse Research Laboratory Scientific Paper 6-43001-1-Pl (unpublished).

³⁰ E. N. Adams, reference 29, has criticized some aspects of Kohn and Luttinger's derivation, but these comments do not affect the validity of the conclusions of the present paper.

of the current. Also we have that

$$\bar{J}_\alpha = -\frac{e}{m} \sum_l \langle \eta_l | \rho | \eta_l \rangle \langle \varphi_l | p_\alpha | \varphi_l \rangle \\ = -\frac{e}{\hbar} \frac{v}{(2\pi)^3} \sum_n \int d^3k f''(n, \mathbf{k}) \frac{\partial \epsilon_n(\mathbf{k})}{\partial k_\alpha},$$

where $f''(n, \mathbf{k})$ is the solution of (56) with H_{eL} replaced by $E^I + E^{II}$.

The conclusion of these arguments is that, in order to use the ODB representation to calculate transport properties, one replaces H_{eL} by $E^I + E^{II}$ and then proceeds exactly as if the Bloch representation were being used.

$$S^{\alpha\beta}(\mathbf{k}, \mathbf{k}') \equiv \frac{1}{v} \int d^3x dq \chi_N^* e^{-i\mathbf{k} \cdot \mathbf{x}} \frac{\partial u_\beta(\mathbf{x})}{\partial x_\alpha} \chi_N e^{i\mathbf{k}' \cdot \mathbf{x}}$$

$$= \sum_s i \left(\frac{\hbar}{2NM\omega(\mathbf{k} - \mathbf{k}', s)} \right)^{\frac{1}{2}} \left[\pm (\mathbf{k} - \mathbf{k}')_\alpha V_\beta(\pm(\mathbf{k} - \mathbf{k}'), s) \left\{ \frac{[N'(\mathbf{k} - \mathbf{k}', s) + 1]^{\frac{1}{2}}}{[N'(\mathbf{k} - \mathbf{k}', s)]^{\frac{1}{2}}} \right\} \right], \quad (67)$$

$$I(n\mathbf{k}; n'\mathbf{k}') \equiv \int d^3x w_{n\mathbf{k}}^*(\mathbf{x}) w_{n'\mathbf{k}'}(\mathbf{x}), \quad (68)$$

and

$$\mathcal{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}') \equiv \langle \psi_{n\mathbf{k}} | \mathcal{D}^{\beta\alpha} | \psi_{n'\mathbf{k}'} \rangle = \delta_{\mathbf{k}, \mathbf{k}'} \mathcal{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}).$$

There are two special cases where (66) reduces to a particularly simple form.

1. Scattering by Long-Wavelength Phonons

In order to consider scattering by long-wavelength phonons, we expand I and \mathcal{D} in powers of $\mathbf{k}' - \mathbf{k}$.

$$\mathcal{D}^{\beta\alpha}(n\mathbf{k}'; n'\mathbf{k}') = \mathcal{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}) + (\mathbf{k}' - \mathbf{k})_\gamma \frac{\partial}{\partial k_\gamma} \mathcal{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}) + \dots, \quad (69)$$

and

$$I(n\mathbf{k}; n'\mathbf{k}') = \delta_{n, n'} + (\mathbf{k}' - \mathbf{k})_\gamma I^\gamma(n\mathbf{k}; n'\mathbf{k}) + \frac{1}{2} (\mathbf{k}' - \mathbf{k})_\gamma (\mathbf{k}' - \mathbf{k})_\nu I^{\gamma\nu}(n\mathbf{k}; n'\mathbf{k}) + \dots, \quad (70)$$

where

$$I^\gamma(n\mathbf{k}; n'\mathbf{k}) \equiv \int d^3x w_{n\mathbf{k}}^* \frac{\partial}{\partial k_\gamma} w_{n'\mathbf{k}}, \\ I^{\gamma\nu}(n\mathbf{k}; n'\mathbf{k}) \equiv \int d^3x w_{n\mathbf{k}}^* \frac{\partial^2}{\partial k_\gamma \partial k_\nu} w_{n'\mathbf{k}}.$$

By using the Schrödinger equation satisfied by $w_{n\mathbf{k}}$ and making a convenient choice of the arbitrary phase factor we can show that

$$I^\gamma(n\mathbf{k}; n'\mathbf{k}) = -\frac{\hbar}{m} \frac{p_{nn'}^\gamma(\mathbf{k})}{\epsilon_{n'}(\mathbf{k}) - \epsilon_n(\mathbf{k})}, \quad n \neq n' \\ = 0, \quad n = n', \quad (71)$$

VII. PROPERTIES OF E^I AND E^{II}

A. Deformation Potential Theorem

We have now only to investigate the Bloch matrix elements of E^I and E^{II} . In part (B) of this section we will show that E^{II} is usually small; hence the form of E^I leads directly to a generalized deformation potential theorem³²:

$$\langle \varphi_l | E^I | \varphi_{l'} \rangle = \frac{1}{2} \sum_{\alpha, \beta, n''} S^{\alpha\beta}(\mathbf{k}, \mathbf{k}') \{ I(n\mathbf{k}; n''\mathbf{k}') \\ \times \mathcal{D}^{\beta\alpha}(n''\mathbf{k}'; n'\mathbf{k}') + \mathcal{D}^{\beta\alpha}(n\mathbf{k}; n''\mathbf{k}') I(n''\mathbf{k}; n'\mathbf{k}') \}, \quad (66)$$

where

and that

$$I^{\gamma\nu}(n\mathbf{k}; n'\mathbf{k}) = -\frac{2\hbar}{m} \sum_{n''} \frac{p_{nn''}^\gamma I^\nu(n''\mathbf{k}; n'\mathbf{k})}{\epsilon_{n''} - \epsilon_n}, \quad n \neq n' \\ = \sum_{n''} I^\gamma(n\mathbf{k}; n''\mathbf{k}) I^\nu(n''\mathbf{k}; n\mathbf{k}), \quad n = n', \quad (72)$$

where $p_{nn'}^\gamma(\mathbf{k}) = \langle \varphi_{n\mathbf{k}} | p_\gamma | \varphi_{n'\mathbf{k}} \rangle$.

Hence $I(n\mathbf{k}; n'\mathbf{k}')$ is expressed entirely in terms of the familiar matrix elements of \mathbf{p} (which determine the optical absorption, dielectric constant, and part of the deformation potential) and the energy bands, $\epsilon_n(\mathbf{k})$.

If we keep only the lowest order in $\mathbf{k} - \mathbf{k}'$, Eq. (66) reduces to

$$\langle \varphi_l | E^I | \varphi_{l'} \rangle \simeq \sum_{\alpha\beta} \mathcal{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}) S^{\alpha\beta}(\mathbf{k}, \mathbf{k}'); \quad (73)$$

or if \mathbf{k} and \mathbf{k}' are both close to some special point \mathbf{k}^0 , (73) can be written

$$\langle \varphi_l | E^I | \varphi_{l'} \rangle \simeq \sum_{\alpha\beta} \mathcal{D}^{\beta\alpha}(n\mathbf{k}^0; n'\mathbf{k}^0) S^{\alpha\beta}(\mathbf{k}, \mathbf{k}'). \quad (74)$$

Equation (73) or (74) (together with the facts that E^{II} and E^{III} are negligible and that these matrix elements give transition rates in the usual way) constitutes a generalized deformation potential theorem. These equations are a generalization of the original theorem³³ in that they do not require that the two \mathbf{k} values be close to a band edge point, and in that they include

³² In this section all summations will be indicated explicitly.

³³ The original theorem stated by Bardeen and Shockley was restricted to compressional waves and crystals with a band edge point at the center of the zone. However, the theorem has been used for all modes and an arbitrary band edge point. See reference 5.

interband transitions and all acoustic lattice modes. The interband transitions and the corrections to (73) or (74) for higher powers of $(\mathbf{k}-\mathbf{k}')$, involve the parameters $\mathfrak{D}^{\beta\alpha}(n\mathbf{k}; n'\mathbf{k}')$ where $n \neq n'$ which probably cannot be determined from homogeneous strain experiments except possibly near a point of degeneracy.¹⁸ Nevertheless, calculations which treat them as adjustable parameters should still be an improvement on the existing⁴ calculations.

The first two corrections to (73) and (74) are obtained

$$\langle \varphi_l | E^I | \varphi_{l'} \rangle \simeq \sum_{\alpha\beta} D^{\beta\alpha}(n, \mathbf{k}) S^{\alpha\beta}(\mathbf{k}, \mathbf{k}') + \sum_{\alpha\beta\gamma} \frac{\partial D^{\beta\alpha}(n, \mathbf{k})}{\partial k_\gamma} (\mathbf{k}' - \mathbf{k})_\gamma S^{\alpha\beta}(\mathbf{k}, \mathbf{k}') + \sum_{\alpha\beta\gamma\nu} \frac{1}{2} \left[\frac{\partial^2 D^{\beta\alpha}(n, \mathbf{k})}{\partial k_\gamma \partial k_\nu} - \frac{2\hbar^2}{m^2} D^{\beta\alpha}(n, \mathbf{k}) \sum_{m \neq n} \frac{p_{nm\gamma} p_{mn\nu}}{(\epsilon_n - \epsilon_m)^2} \right] (\mathbf{k}' - \mathbf{k})_\gamma (\mathbf{k}' - \mathbf{k})_\nu S^{\alpha\beta}(\mathbf{k}, \mathbf{k}').$$

By differentiating (50) with respect to \mathbf{k} , we see that the first two derivatives of $D^{\beta\alpha}(n, \mathbf{k})$ are given by the shift of electron velocity and effective mass with respect to strain. Hence, these corrections are given entirely by the measurable properties of the energy bands under strain and the matrix elements of \mathbf{p} .

We note that the term $(\mathbf{k}' - \mathbf{k})_\gamma S^{\alpha\beta}(\mathbf{k}, \mathbf{k}')$ is essentially the derivative of the strain with respect to x_γ , and hence the corrections that we are discussing here are in this sense of the same order as terms neglected in the assumed form of the potential (39).

2. Intraband Scattering by Short-Wavelength Phonons

The assumed form of the crystal potential in a vibrating lattice, (39), is much more limiting for short-wavelength phonons. [It is, however, always better than the D.I. model which is a special case of (39).] For short-wavelength phonons, terms involving the derivatives of the strains may well be important and shifts of the atoms within the unit cell may be different from those extrapolated from the shifts under homogeneous strain. Nevertheless, since with one more assumption we obtain a simple result for this case, and since we feel that the scattering by short-wavelength phonons is an inherently difficult problem for which it would be hard to make a much better theory, we will briefly consider this case.

In order to reduce (66) to a simple result we assume that the interband matrix elements of $\mathfrak{D}^{\beta\alpha}$ may be neglected in comparison to the intraband matrix elements. With this assumption, (66) reduces to

$$\langle \varphi_l | E^I | \varphi_{l'} \rangle \simeq \sum_{\alpha\beta} S^{\alpha\beta}(\mathbf{k}, \mathbf{k}') I(n\mathbf{k}; n\mathbf{k}') \times \left\{ \frac{D^{\beta\alpha}(n, \mathbf{k}) + D^{\beta\alpha}(n, \mathbf{k}')}{2} \right\}. \quad (75)$$

Hence the scattering is determined by the mean value of the measurable deformation potentials and $I(n\mathbf{k}; n\mathbf{k}')$, which would have to be estimated theoretically or

directly by substituting (69), (70), (71), and (72) into (66). Since the resulting expression is very long, we will consider just the special case of intraband transition and also neglect all of the interband matrix elements of $\mathfrak{D}^{\beta\alpha}$ in comparison to the diagonal matrix elements. (The neglect of these interband matrix elements is probably not justified and we do so merely to present a tractable formula which will indicate the nature of the corrections to (73) and (74). Under these assumptions, (66) up to the order $(\mathbf{k}' - \mathbf{k})^2$ is

treated as an adjustable parameter. In the case of intervalley scattering in a semiconductor, one would simply replace \mathbf{k} and \mathbf{k}' by the respective band edge wave vectors everywhere in (75).

B. E^{II} and the Effective Mass Equation

1. We wish first to compare the size of $\langle \varphi_l | E^{II} | \varphi_{l'} \rangle$ and $\langle \varphi_l | E^I | \varphi_{l'} \rangle$.

The first term of $\langle \varphi_l | E^{II} | \varphi_{l'} \rangle$ in (43) is composed of two terms like

$$ik_\beta [\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k}')] \langle \varphi_{n\mathbf{k}; N} | u_\beta | \varphi_{n'\mathbf{k}'; N'} \rangle. \quad (76)$$

In the case of transitions between two states which are of the same total energy and which involve an acoustic phonon (which is the only type of transition that we will consider in this paper),

$$\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k}') = \hbar\omega(\mathbf{k} - \mathbf{k}') \leq s\hbar|\mathbf{k} - \mathbf{k}'|,$$

where s is the maximum sound velocity in the crystal. Then (76) is always less than

$$\hbar k_\beta s |\mathbf{k} - \mathbf{k}'| \langle \varphi_{n\mathbf{k}; N} | u_\beta | \varphi_{n'\mathbf{k}'; N'} \rangle.$$

Since $|\mathbf{k} - \mathbf{k}'| \langle \varphi_{n\mathbf{k}; N} | u_\beta | \varphi_{n'\mathbf{k}'; N'} \rangle$ is of the order of magnitude of $I(n\mathbf{k}; n'\mathbf{k}') S^{\alpha\beta}(\mathbf{k}, \mathbf{k}')$, we need only compare $\hbar k_\beta s$ to the deformation potentials in order to estimate the importance of this part of E^{II} . Even where \mathbf{k} is a reciprocal lattice vector this term is only of the order of 0.1 ev, and hence may be neglected in comparison to the typical deformation potentials which are of the order of several ev (17 ev for Ge).^{2,5}

The second term of E^{II} is more difficult to estimate in general. It is composed of two terms like

$$(i/\hbar) \sum_{n''} \langle \psi_{n\mathbf{k}} | p_\beta | \psi_{n''\mathbf{k}} \rangle \hbar\omega(\mathbf{k} - \mathbf{k}') \langle \varphi_{n''\mathbf{k}'; N} | u_\beta | \varphi_{n'\mathbf{k}'; N'} \rangle. \quad (77)$$

Again setting $\omega(\mathbf{k} - \mathbf{k}') = s|\mathbf{k} - \mathbf{k}'|$, we have for (77)

$$\{ |\mathbf{k} - \mathbf{k}'| \langle \chi_N e^{i\mathbf{k} \cdot \mathbf{x}} | u_\beta | \chi_{N'} e^{i\mathbf{k}' \cdot \mathbf{x}} \rangle \times \sum_{n''} s \langle \psi_{n\mathbf{k}} | p_\beta | \psi_{n''\mathbf{k}} \rangle I_{n''\mathbf{k}; n'\mathbf{k}'} \}. \quad (78)$$

The term in braces is of the same order of magnitude as $S^{\alpha\beta}(\mathbf{k}, \mathbf{k}')$. Then by comparing (78) with (66) we see that we must compare $s\langle\psi_{n\mathbf{k}}|p_{\beta}|\psi_{n''\mathbf{k}}\rangle$ to $\mathcal{D}^{\beta\alpha}(n\mathbf{k}; n''\mathbf{k})$ to estimate the importance of this part of E^{II} .

In the special case of intraband scattering by long-wavelength phonons, we need consider only the case $n=n''$, where for thermal electrons in a semiconductor

$$s\langle\psi_{n\mathbf{k}}|p_{\beta}|\psi_{n\mathbf{k}}\rangle \approx 10^{-3} \text{ ev},$$

and even for a metal is only about 10^{-2} ev. Hence, for this special case the term is certainly negligible in comparison to the known values of the diagonal elements of $\mathcal{D}^{\beta\alpha}$ (several electron volts).

To obtain the order of magnitude of this part of E^{II} in general we could compare $s\langle\psi_{n\mathbf{k}}|p_{\alpha}|\psi_{n''\mathbf{k}}\rangle$ to just one of the terms in the deformation potential, say $(\hbar k_{\beta}/m)\langle\psi_{n\mathbf{k}}|p_{\alpha}|\psi_{n''\mathbf{k}}\rangle$. The E^{II} term is smaller than the deformation potential term by a factor $s/(\hbar k_{\beta}/m)$, or the ratio of the speed of sound to the electron velocity which is usually about 1/20 for thermal electrons in a semiconductor at room temperature, and much smaller for a metal. Hence, we can conclude that the E^{II} term is negligible, at all but very low temperatures, unless the part of the deformation potential to which we are comparing it almost cancels some other part of the deformation potential. Even at very low temperature there are other parts of the deformation potential which would probably be much larger than $s\langle\psi_{n\mathbf{k}}|p_{\beta}|\psi_{n''\mathbf{k}}\rangle$ (i.e., $\langle\psi_{n\mathbf{k}}|U^{\beta\alpha}|\psi_{n''\mathbf{k}}\rangle$).

2. Secondly, we wish to show how the E^{II} term may be included in an effective-mass equation and thus acquire a physical interpretation. We do this only in the simple model where we are considering only one band which has the shape

$$\epsilon(\mathbf{k}) = \epsilon(0) + \sum_{\alpha} \frac{\hbar^2 k_{\alpha}^2}{2m^*},$$

and therefore

$$\langle\psi_{\mathbf{k}}|p_{\beta}|\psi_{\mathbf{k}}\rangle = (m/m^*)\hbar k_{\beta}.$$

We consider only matrix elements between states of the same total energy and therefore,

$$\langle\varphi_l|[H_e, u_{\beta}]|\varphi_{l'}\rangle = -\langle\varphi_l|[H_L, u_{\beta}]|\varphi_{l'}\rangle.$$

The local velocity of the lattice is

$$V_{\beta}^L = (i/\hbar)[H_L, u_{\beta}],$$

and then we can write

$$\begin{aligned} \langle\varphi_l|E^{\text{II}}|\varphi_{l'}\rangle = & \sum_{\beta} \frac{1}{2} \left\{ \hbar k_{\beta} \left(1 - \frac{m}{m^*} \right) \langle\varphi_l|V_{\beta}^L|\varphi_{l'}\rangle \right. \\ & \left. + \left(1 - \frac{m}{m^*} \right) \langle\varphi_l|V_{\beta}^L|\varphi_{l'}\rangle \hbar k_{\beta}' \right\}. \end{aligned}$$

Then noting that to the lowest order in $(\mathbf{k}-\mathbf{k}')$

$$\langle\varphi_l|V_{\beta}^L|\varphi_{l'}\rangle = \langle\chi_N e^{i\mathbf{k}\cdot\mathbf{x}}|V_{\beta}^L|\chi_{N'} e^{i\mathbf{k}'\cdot\mathbf{x}}\rangle,$$

we see that $H_e + E^{\text{II}}$ may be replaced by the effective Hamiltonian

$$\sum_{\alpha} \frac{1}{2m^*} \left[p_{\alpha} + \left(1 - \frac{m}{m^*} \right) m^* V_{\alpha}^L \right]^2,$$

neglecting the $(V^L)^2$ term. Hence we see that, but for factor $(1-m/m^*)$, E^{II} enters the effective Hamiltonian like a term which transforms to a moving coordinate system. The factor $1-m/m^*$ expresses the reluctance of the electrons to follow the lattice.

VIII. ACKNOWLEDGMENTS

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APPENDIX A

We have stated that the introduction of the ODB representation is essentially equivalent to mapping the electron wave function so that it deforms with the lattice as it vibrates. In this Appendix we will discuss the introduction of such a mapping and show explicitly how this approach is related to the introduction of the ODB representation.³⁴

First we consider the boundary value problem:

$$\begin{aligned} H^{(x)}\Psi(\mathbf{x}, q, t) &= i\hbar(\partial/\partial t)\Psi(\mathbf{x}, q, t), \\ \Psi(\mathbf{x}, q, t) &= \Psi(\mathbf{x} + \mathbf{L}_i, q, t), \end{aligned} \quad (\text{A-1})$$

where $H^{(x)}$ is the differential form of the operator H defined in (1)–(4). We then introduce the change of variables (18) and obtain the boundary value problem:

$$\begin{aligned} H^{(y)}Z(\mathbf{y}, q, t) &= i\hbar\partial/\partial t Z(\mathbf{y}, q, t), \\ Z(\mathbf{y}, q, t) &= Z(\mathbf{y} + \mathbf{L}_i, q, t), \end{aligned} \quad (\text{A-2})$$

where

$$\begin{aligned} H^{(x)}\Psi(\mathbf{x}, q, t) &= H^{(y)}\Psi(\mathbf{x}(\mathbf{y}), q, t) \\ &= H^{(y)}Z(\mathbf{y}, q, t). \end{aligned} \quad (\text{A-3})$$

We call $H^{(y)}$ the Hamiltonian in “y space” and it can be written as

$$H^{(y)} = H_0^{(y)} + H_1^{(y)},$$

where $H_0^{(y)}$ is the differential operator which can be obtained from the differential form of E [Eqs. (1–3)],

³⁴ E. I. Blount [Phys. Rev. **114**, 418 (1959)], in the course of developing a theory of ultrasonic attenuation in metals, introduces a change of variables very similar to the one used in this paper. He gives a discussion of the transformed Hamiltonian in which he tacitly neglects the non-Hermitian part (which we feel is probably quite appropriate for the special case of ultrasonic attenuation). The reasons he gives for introducing the change of variables are to a large extent the same reasons that motivated this work.

by replacing all the x 's by y 's, (including, of course, the variables which are held constant when differentiating with respect to q). $H_1^{(y)}$ is a complicated non-Hermitian³⁵ differential operator proportional to $S^{\alpha\beta}$ and $[H_L, u_\alpha]$, which we will not write down explicitly, but we will show below that to the first order in $S^{\alpha\beta}$ the Hermitian part of $H_1^{(y)}$ is just $E^I + E^{II} + E^{III}$ (written as a differential operator with y replacing x).

Having introduced the change of variables, we could now use (38) for the crystal potential and solve the boundary value problem (A-2) by perturbation methods, obtaining a set of eigenfunctions $Z_l(y, q, t)$ and eigenvalues \mathcal{E}_l .

For each eigenfunction in "y space" there is a corresponding eigenfunction $\Psi_l(x, q, t) \equiv Z_l(y(x), q, t)$, in "x space" having the same eigenvalue \mathcal{E}_l . Then the expected value of some operator $O^{(x)}$ for a system in the state $\Psi_l(x, q, t)$ is given by

$$\langle \Psi_l(x) | O^{(x)} | \Psi_l(x) \rangle = \int d^3y dq Z_l^*(y, q, t) \times J^{-1}(y) O^{(y)} Z_l(y, q, t), \quad (\text{A-4})$$

where $O^{(y)}$ is defined in the same way as $H^{(y)}$ and $J^{-1}(y)$ is easily expressed in powers of the strain [see (19)]. If $O^{(x)}$ is Hermitian, (A-4) will, of course, always be real even though $O^{(y)}$ is in general not Hermitian. This then constitutes an entirely adequate procedure for solving a problem in the "y space," which we will show is essentially the same as introducing the ODB functions.

Since the above procedure can be thought of as a mapping of the quantum operators, we would expect that there is an equivalent procedure which involves a mapping of the basis states. In order to see what these new basis states are, we first define the matrix elements of an operator O in "y space" as

$$[\theta_m | O | \theta_n] \equiv \int \theta_m^*(y, q) O^{(y)} \theta_n(y, q) d^3y dq,$$

where $\{\theta_n(y, q)\}$ is some complete orthonormal set in the "y space" (i.e., $[\theta_m | \theta_n] = \delta_{m,n}$ and $\sum_n |\theta_n\rangle [\theta_n|$ is the identity operator). It is then easily seen that

$$[\theta_m | O | \theta_n] = \langle \theta_m(y(x)) | J^{-1} O | \theta_n(y(x)) \rangle,$$

from which it is clear that $\langle \theta_m(y(x)) | J^{-1}$ and $|\theta_n(y(x))\rangle$ are the covariant and contravariant basis vectors of a nonorthogonal representation in the "x space," the use of which is equivalent to mapping the operators into the "y space."

We are concerned here with the Bloch functions $\varphi_l(x, q)$ and the corresponding mapped $\varphi_l(y(x), q)$,

³⁵ It is not surprising that $H^{(y)}$ is not Hermitian since it is easily seen that even the momentum in "y space,"

$$p_\alpha^{(y)} = -\frac{\hbar}{i} \frac{\partial}{\partial y_\alpha} + \frac{\hbar}{i} \frac{\partial u_\beta(y)}{\partial y_\alpha} \frac{\partial}{\partial y_\beta}$$

(to the first order in strain), is non-Hermitian.

which we call the deformed Bloch (DB) functions, and which may be thought of as Bloch functions that deform with the lattice. The fact that the DB functions are not orthogonal is no serious obstacle to their use, although it leads to some awkwardness when talking about transition rates. We have chosen to orthogonalize them because it can easily be done without essentially changing their character. In fact, we will now show that to the first order in $S^{\alpha\beta}$ an operator in the ODB representation is just the Hermitian part of the corresponding operator in "y space," and it is in this sense that the use of the ODB representation is equivalent to introducing a change of variables in the Hamiltonian.

Proof: First we note that the operator O'' , defined so that

$$\langle \varphi_l(x) | O'' | \varphi_{l'}(x) \rangle = [\varphi_l | O | \varphi_{l'}],$$

is given by

$$O'' = S^{-1} O S,$$

where

$$S = \sum_l |\varphi_l(y(x))\rangle \langle \varphi_l(x)|,$$

$$S^{-1} = \sum_l |\varphi_l(x)\rangle \langle \varphi_l(y(x))| J^{-1},$$

and that

$$S S^\dagger = J, \quad (S^{-1})^\dagger S^{-1} = J^{-1}.$$

Then since $J^{-\frac{1}{2}}$ transforms from DB to the ODB representation, we have that

$$O' = J^{-\frac{1}{2}} S O S^\dagger J^{\frac{1}{2}}.$$

But we have to the first order in $S^{\alpha\beta}$ that

$$J^{-\frac{1}{2}} = 1 + \frac{1}{2} S,$$

and hence

$$\frac{1}{2} (O'' + O''^\dagger) = O',$$

or an operator in the ODB representation is just the Hermitian part of the corresponding operator in "y space."

APPENDIX B

There are two other reasonable definitions of the deformation potential besides (50). The first of these, $D_{\text{exp}}^{\beta\alpha}$, is the one directly obtained from most homogeneous strain experiments and can be defined:

$$\epsilon_n^d(k_0^d) = \epsilon_n(k_0) + a_{\alpha\beta} D_{\text{exp}}^{\beta\alpha}(n, k_0), \quad (\text{B-1})$$

where k_0 and k_0^d are the band edge points in the unstrained and strained crystals, respectively. This definition is not convenient for theoretical work because one does not know where the new band edge point will be. Another choice for the deformation potential which is close to $D_{\text{exp}}^{\beta\alpha}$ and yet convenient for theoretical use is $B^{\beta\alpha}$ defined by:

$$\epsilon_n^d(k \cdot (1 - a)) = \epsilon_n(k) + a_{\alpha\beta} B^{\beta\alpha}(n, k). \quad (\text{B-2})$$

Then to the first order in a , we have that

$$D^{\beta\alpha}(n, k) = B^{\beta\alpha}(n, k) + \frac{\hbar k_\beta}{m} \langle \psi_{nk} | p_\alpha | \psi_{nk} \rangle. \quad (\text{B-3})$$

When \mathbf{k} is a band edge point,

$$\langle \psi_{n\mathbf{k}} | p_\alpha | \psi_{n\mathbf{k}} \rangle = m \frac{\partial \epsilon_n(\mathbf{k})}{\partial (\hbar k_\alpha)} = 0,$$

and $D^{\beta\alpha} = B^{\beta\alpha}$. If \mathbf{k} is close to a band edge point which is at the center of the zone, the two deformation potentials are still very close [e.g., for a thermal electron in a semiconductor $(\hbar k_\beta/m) \langle n, \mathbf{k} | p_\alpha | n, \mathbf{k} \rangle \approx (m^*/m)KT$, which is about 0.02 eV at room temperature when $m^* = m$]. If \mathbf{k} is close to a band edge point which is not near the center of the zone, $D^{\beta\alpha} - B^{\beta\alpha}$ would be about $\frac{1}{2}$ eV at room temperature, which although it is not a large term may not always be negligible. However for a completely general point in the zone $D^{\beta\alpha} - B^{\beta\alpha}$ may be as large as several eV, which is the same order of magnitude as $D^{\beta\alpha}$.

By comparing (B-3) with (45) we see that we can define another deformation potential operator,

$$\mathcal{B}^{\beta\alpha} \equiv -p_\beta p_\alpha / m + U^{\beta\alpha}(\mathbf{x}), \quad (\text{B-4})$$

such that

$$B^{\beta\alpha}(n, \mathbf{k}) = \langle \psi_{n\mathbf{k}} | \mathcal{B}^{\beta\alpha} | \psi_{n\mathbf{k}} \rangle. \quad (\text{B-5})$$

It is possible to write H' in terms of $\mathcal{B}^{\beta\alpha}$ and develop an adequate scattering theory based on this form of H' . We have chosen to formulate the theory in terms $D^{\beta\alpha}$ instead of $\mathcal{B}^{\beta\alpha}$, largely because $B^{\beta\alpha}(n, \mathbf{k})$ does not approach zero when the electron-phonon coupling does [i.e., when $V_0(\mathbf{x})$ and $w_{n\mathbf{k}}(\mathbf{x})$ approach constants independent of strain, $B^{\beta\alpha}(n, \mathbf{k})$ approaches $-\hbar^2 k_\alpha k_\beta / m$]; whereas $D^{\beta\alpha}(n, \mathbf{k})$ does approach zero when the coupling does.

APPENDIX C

In order to compare the present work with the standard theory,⁴ we will now rewrite H' using the deformable- and rigid-ion models. From the statement of the deformable-ion model in (12) we get that

$$V(\mathbf{x}(\mathbf{y}), q) = V_0(\mathbf{y} + \mathbf{u}(\mathbf{y}) - \mathbf{u}(\mathbf{x}(\mathbf{y}))),$$

which to the lowest order in \mathbf{u} gives that

$$V(\mathbf{x}(\mathbf{y}), q) = V_0(\mathbf{y}). \quad (\text{C-1})$$

Therefore

$$V_{\text{DI}}'(\mathbf{x}, q) = V_0(\mathbf{x}),$$

where the prime has the same meaning as in (24). From (15) we see that the rigid-ion model gives, to the first order in $\mathbf{u}(\mathbf{y}) - \mathbf{u}_r$, that

$$V(\mathbf{x}(\mathbf{y}), q) = V_0(\mathbf{y}) + \sum_r [\mathbf{u}(\mathbf{y}) - \mathbf{u}_r]_\alpha \frac{\partial}{\partial y_\alpha} v(\mathbf{y} - \mathbf{R}_r^0),$$

and hence

$$V_{\text{RI}}'(\mathbf{x}, q) = V_0(\mathbf{x}) - H_{eL}^{\text{DI}} + H_{eL}^{\text{RI}}, \quad (\text{C-2})$$

where H_{eL}^{DI} and H_{eL}^{RI} are defined in (14) and (16).

It is convenient for our present purpose to use a slightly different form of the electron kinetic energy

than we did in Sec. IV. Using (34) and noting that

$$S^{\alpha\beta} = (i/\hbar) [p_\alpha, u_\beta],$$

we can show that

$$\frac{p'_\alpha p'_\alpha}{2m} = \frac{p_\alpha p_\alpha}{2m} + \frac{i}{4m\hbar} [p_\alpha p_\alpha, (u_\beta p_\beta + p_\beta u_\beta)].$$

Then adding and subtracting

$$\frac{i}{2\hbar} [V_0, (u_\beta p_\beta + p_\beta u_\beta)] = -u_\beta \frac{\partial V_0(\mathbf{x})}{\partial x_\beta} = H_{eL}^{\text{DI}},$$

we get that

$$\frac{p'_\alpha p'_\alpha}{2m} = \frac{p_\alpha p_\alpha}{2m} + H_{eL}^{\text{DI}} - \frac{i}{2\hbar} [H_e, (u_\beta p_\beta + p_\beta u_\beta)]. \quad (\text{C-3})$$

Then combining (C-3), (C-1), (C-2), and (38), we get that

$$H' = E + \mathcal{H} - \frac{i}{2\hbar} [E, (u_\beta p_\beta + p_\beta u_\beta)] - \frac{p_\alpha p_\alpha}{2M}, \quad (\text{C-4})$$

where \mathcal{H} is either H_{eL}^{DI} or H_{eL}^{RI} , depending on which model we are using. (C-4) is then (41) in the R.I. or D.I. models. The standard theory (Sec. II) is based on the Hamiltonian

$$H = E + \mathcal{H}. \quad (\text{C-5})$$

We will now discuss the difference between (C-4) and (C-5). The last term of (C-4) is a small term that may be thought of as the correction to the electron energy in "y space" due to the mapping away of the zero-point motion of the lattice. It is diagonal in the electron wave vector \mathbf{k} and hence gives no intraband transitions, but it does give a correction to the $\epsilon_n(\mathbf{k})$ which we neglect here but which we expect will be important in a self-energy calculation. The term does have interband matrix elements, but since it is diagonal in the phonon number these matrix elements cannot be thought of as giving transitions either. This term is of interest to us in that it expresses the difference between a theory which is taken to the first order in u_α , i.e., (C-5), and a theory, like that in the body of this paper and in (C-4) excepting the potential energy part, which is taken to first order in $S^{\alpha\beta}$ and $[E_L, \mathbf{u}]$.

That there should in fact be a difference is not surprising when we remember that in Sec. III we introduced a change of variables so that certain terms involving all powers of \mathbf{u} are absorbed into the variable \mathbf{y} and then treated exactly.

If we neglect the last term in (C-4) we see that H and H' are related, to the first order in \mathbf{u} , by a unitary transformation:

$$H' = T^\dagger H T,$$

where

$$T = 1 - \frac{i}{2\hbar}(u_\beta p_\beta + p_\beta u_\beta).$$

It is easy to show that this is the same T (to the first order in u_β) as was defined in (23), and it is clear from its form that it is an operator that translates the electron a distance \mathbf{u} . We also note that the electric field operator H_{elec}' (55) and p_α' (34) are obtained, to the first order in u_α , by application of T to H_{elec} and p_α .

Since in the body of this paper we neglect the last term in (C-4) (i.e., E^{III}) the only difference in the physical approximation made when using the ODB instead of the Bloch functions, is the use of (39) instead of the R.I. or D.I. models (i.e., except for E^{III} and the model used for the effective potential, H and H' are related by a similarity transformation and therefore are equivalent). We note further that since the third term

in (C-4) involves a factor $(E_l - E_r)$, it is zero for matrix elements between states of the same total energy. Hence, the matrix elements of H , to the first order in \mathbf{u} , in the D.I. and R.I. models and between states of the same energy, are exactly the same in the Bloch and ODB representations. Since this property is true for both the R.I. and D.I. models, it is probably independent of the model used. These similarities probably do not extend to higher orders.³⁶

³⁶ In second order perturbation theory, matrix elements between states of different energy are important and one may think that terms like the third term in (C-4) will become very large. The fact that these terms result from a change of representation rather than a different physical approximation suggests that they will have no profound effect on the observables. A situation somewhat similar to this was encountered by J. M. Ziman, Proc. Cambridge Phil. Soc. **51**, 707 (1955), and it became clear that these terms did not lead to an important physical effect. Bernard Goodman, Phys. Rev. **110**, 888 (1958); J. C. Taylor, Proc. Cambridge Phil. Soc. **52**, 693 (1956). In a situation like ultrasonic absorption where \mathbf{u} is large, and the theory must be expanded in powers of $S^{a\beta}$, there might be some real effect.

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Decay of Excess Carriers in Semiconductors. II

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A physical interpretation is given of the nonlinear differential equations which govern the decay of excess carrier populations through recombination centers. No restrictions are placed on the magnitudes of the excess carrier densities or the center density. Criteria for trapping are presented; with semiconductors for which the trapping level lies in the opposite half of the intrinsic gap from the Fermi level, it is shown that trapping can be described as being of either a temporary or permanent nature. The variety of possible modes of decay are illustrated with the aid of numerical solutions and approximate analytic solutions.

I. INTRODUCTION

THE lifetime of an excess carrier population is for many semiconductors controlled by a process in which the charge of a recombination center changes by $+e$ and $-e$ alternately. For example, when a recombination center captures a hole of charge $+e$, the next process experienced by this center may be either the reliberation of the hole or the capture of a previously free electron. Either process will restore the center to its original charge state.

The details of the carrier dynamics will depend on a number of parameters and variables. As parameters we should list the absolute and relative magnitudes of the electron and hole capture cross sections, and the density and energy of recombination levels. Variables which enter into the problem comprise the equilibrium Fermi level (which characterizes the thermal-equilibrium carrier densities n_0 and p_0) and the concentrations of excess carriers. The excess free carrier densities $\Delta n = (n - n_0)$ and $\Delta p = (p - p_0)$ are not necessarily the same, since intermediate levels tend to indulge in

trapping as well as recombination. For this reason, we shall use the terms "trap" and "recombination center" interchangeably in this paper.

The kinetics of the excess carriers during buildup, maintenance and decay may be described in terms of two coupled first order differential equations which are expressed in terms of the above mentioned parameters and variables. Solutions of these equations for the special case of steady state nonequilibrium have been presented by Shockley and Read¹ and by Hall.² Even then, these published solutions are valid only for the limiting conditions of vanishing trap density or vanishing excess carrier density. More recently the transient behavior of excess carrier populations confronted with arbitrary trap density has been discussed by us³ in a paper to which we shall in future refer as NB1.

From the study of the general decay equations in

¹ W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

² R. N. Hall, Phys. Rev. **87**, 387 (1952).

³ K. C. Nomura and J. S. Blakemore, Phys. Rev. **112**, 1607 (1958).