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Deformation potentials and electron-phonon scattering: Two new theorems

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This paper gives two new theorems about the band deformation potential $D^{b}_{\alpha\beta}(\vec{k},n)$ which expresses the shift of electron energies under external strains, $\partial\epsilon_{\vec{k}n}/\partial S_{\alpha\beta}$, and the electron-phonon deformation potential $D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)$ which gives the matrix element for an electron to scatter from state $(\vec{k},n)$ to a nearby state $(\vec{k}+\vec{Q},\ n)$ by absorption of an acoustic phonon of branch j and amplitude $\vec{u}(\vec{Q}j)$, namely $\langle\vec{k}+\vec{Q},\ n\,|\,\mathscr{H}_{e\text{-ph}}\,|\,\vec{k},n\rangle = iu_{\alpha}(\vec{Q}j)Q_{\beta}D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)$. First, it is shown for a rigid ion model that $D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)$ equals $D^{b}_{\alpha\beta}(\vec{k},n)+mv_{\vec{k}n\alpha}v_{\vec{k}n\beta}$, where $\vec{v}_{\vec{k}n}$ is the electron group velocity. Second, it is shown that the Fermi surface average of $D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)$ equals the Fermi surface average of $mv_{\vec{k}n\alpha}v_{\vec{k}n\beta}$. From the second theorem, it is deduced that the first theorem is probably generally valid in a metal [i.e., not restricted to a rigid-ion model) provided the band deformation potential $D^{b}_{\alpha\beta}(\vec{k},n)$ is defined relative to an energy which moves with the Fermi energy under strains. The first theorem contradicts the common belief that the two deformation potentials are always the same, but preserves the usual form of the deformation-potential theorem at band edges where $v_{\vec{k}n\alpha}$ vanishes.

I. INTRODUCTION

Bardeen and Shockley[1] introduced the useful notion, known as the "deformation-potential theorem," that the electron—acoustic-phonon matrix element is directly related to the shift in energy of the relevant electron energy level with an externally imposed strain of the same symmetry as the acoustic phonon. This paper derives a rigorous form of that theorem valid for any Bloch state $(\vec{k},n)$ and any acoustic phonon $(\vec{Q},j)$ or strain tensor component $S_{\alpha\beta}$. The theorem is not quite as simple in general as the original Bardeen-Shockley idea, but is still very simple, and reduces to the Bardeen-Shockley version at semiconductor band edges. The original theorem of Ref. 1 was only stated for the case of a nondegenerate band extremum at $\vec{k}=\vec{0}$, and the proof was only for longitudinal phonons.

It is hard to locate a proof of the deformation-potential theorem in the literature. The proof of Ref. 1 is repeated in Shockley's book.[2] Herring and Vogt[3] assert that for nonpiezoelectric crystals the theorem should be valid for longitudinal and transverse phonons, but offer no proof, and use the theorem for many-valley semiconductors with band edges away from $\vec{k}=\vec{0}$. Blount[4] states without any proof that a Hartree-Fock analysis verifies the Bardeen-Shockley theorem for general $(\vec{k},n)$ and branch j. Hunter and Nabarro[5] and Ziman[6] show that in a metal, screening will cause a significant alteration of the deformation-potential theorem. Whitfield[7] gives a full justification of the theorem using the method of "orthogonalized deformed Bloch waves," but Sham and Ziman[8] claim that this proof is not completely right; they argue that, away from band extrema, correction terms occur.

Our conclusions agree with Ref. 8 about the existence of correction terms away from band extrema. We find a simple explicit form for the correction which differs from the one stated (without proof) in Ref. 8. We find no fault with Refs. 1–3, which are explicitly confined to the neighborhood of band extrema, but disagree with Refs. 4 and 7. Our work provides an alternate and more complete method for metals than the one given in Refs. 5 and 6.

There seems to be no reliable general proof of the deformation-potential theorem. The only attempt known to us is that of Whitfield.[7] One reason for the neglect of this subject is because the theorem can be made to seem trivially obvious. Assume there is a homogeneous strain $S_{\mu\nu}$ in a crystal. The strain will cause a shift $\delta V(r)$ in the effective one-electron potential, and to first order in strain we should be able to write this as $\mathscr{H}'=\delta V(\vec{r})=\delta V^{\mu\nu}(\vec{r})S_{\mu\nu}$. This strain will cause an electron energy $\epsilon_{\vec{k}n}$ to shift by an amount

$$\begin{aligned}\delta\epsilon_{\vec{k}n}&=\langle\vec{k},n\,|\,\mathscr{H}'\,|\,\vec{k},n\rangle=D_{\mu\nu}(\vec{k},n)S_{\mu\nu}\ ,\\ D_{\mu\nu}(\vec{k},n)&=\langle\vec{k},n\,|\,\delta V^{\mu\nu}(\vec{r})\,|\,\vec{k},n\rangle\ ,\end{aligned}\tag{1.1}$$

where $\underline{D}(\vec{k},n)$ is the deformation potential for the state $(\vec{k},n)$. Next consider a long-wavelength acoustic wave in a solid, with space and time-dependent displacements given by $\vec{u}e^{i\vec{Q}\cdot\vec{r}-\omega_{Q}t}$. This wave causes a strain $S_{\mu\nu}(\vec{r})=iu_{\mu}Q_{\nu}e^{i\vec{Q}\cdot\vec{r}}$ which varies slowly in space. One expects that the electrons should feel a perturbation $\mathscr{H}_{e\text{-ph}}=\delta V^{\mu\nu}(\vec{r})S_{\mu\nu}(\vec{r})$, where $\delta V^{\mu\nu}(\vec{r})$ is the same as when the strain was homogeneous. The electron-phonon matrix element is

$$\langle \vec{k}+\vec{Q},n\,|\mathscr{H}_{e\text{-ph}}|\,\vec{k}n\rangle \equiv D^{e\text{-ph}}_{\mu\nu}(\vec{k},n)(iu_\mu Q_\nu)\,. \tag{1.2}$$

This simple argument suggests that the same deformation potential should occur in the electron-phonon problem as in the static-strain problem, $D^{e\text{-ph}}_{\mu\nu}=D_{\mu\nu}$.

Unfortunately nature is not this simple, and the argument above fails, except in the special case of states near a band edge. (In Sec. II it is shown that a corresponding argument for optic phonons is successful.) One major difficulty is that there is no unique definition of the band deformation potential for the case of uniform strain. There are two ambiguities. One is that the reciprocal-space unit cell changes its dimensions under the influence of strain. The lattice vectors $\vec{R}_i$ and reciprocal lattice vectors $\vec{G}$ change to

$$\vec{R}_i\to\vec{R}_i'=(\underline{1}+\underline{S})\vec{R}_i\;, \tag{1.3a}$$

$$\vec{G}\to\vec{G}'=(\underline{1}+\underline{S})^{-1}\vec{G}\approx(\underline{1}-\underline{S})\vec{G}\;. \tag{1.3b}$$

The band deformation potential used in this paper will be defined as

$$\begin{aligned}D^b_{\alpha\beta}(\vec{k},n)&=\lim_{S_{\alpha\beta}\to 0}\frac{\epsilon(\vec{k}\,',n;S_{\alpha\beta})-\epsilon(\vec{k},n;0)}{S_{\alpha\beta}}\\&=\left.\frac{d\epsilon((\underline{1}-\underline{S})\vec{k},n;\underline{S})}{dS_{\alpha\beta}}\right|_{\underline{S}=\underline{0}}\,,\end{aligned} \tag{1.4}$$

that is, the wave vector is taken to scale with the strain, rather than remain fixed. This has the virtue that a zone-boundary energy before the strain is being compared with a zone-boundary energy after the strain. However, alternate definitions have been used often without explicit mention (see Ref. 8). The qualitative notions of Eq. (1.1) do not scale the wave vector as in Eq. (1.4).

The second more serious ambiguity in both Eqs. (1.1) and (1.4) is the question of the zero relative to which energy is measured.[9] It is hard to identify the vacuum zero of energy in an infinite crystal. If the muffin-tin zero is used, this zero changes when the crystal is strained. Thus, the definitions (1.1) or (1.4) are reference dependent. Differences of deformation potentials $\underline{D}^b(2)-\underline{D}^b(1)$ are well defined, and experimentally measurable, but absolute values $\underline{D}^b(1)$ are not measurable, and so far not even defined. We shall largely avoid this difficulty by a trick to be described below. By contrast to $\underline{D}^b$, the electron-phonon deformation potential $\underline{D}^{e\text{-ph}}$ defined in Eq. (1.2) has no ambiguity.

We now state our principle results. In Sec. II the deformation-potential theorem is examined in a rigid-ion model, and the result

$$D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)=D^b_{\alpha\beta}(\vec{k},n)+mv_{\vec{k}n\alpha}v_{\vec{k}n\beta} \tag{1.5}$$

is proved, where $\vec{v}_{\vec{k}n}$ is the group velocity of the electron state $(\vec{k},n)$. At this stage the reference zero of energy for $\underline{D}^b$ has not been clearly specified. The constant background potential which remains behind when atoms are slightly moved has been taken to be zero. In Sec. III, a sum rule is proved,

$$\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)=\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]mv_{\vec{k}n\alpha}v_{\vec{k}n\beta}\,, \tag{1.6}$$

where f is the Fermi-Dirac occupation function $(e^{\beta(\epsilon_{\vec{k}n}-\mu)}+1)^{-1}$. This sum rule is a consequence of translational invariance, specifically, the requirement that when the nuclei of a crystal are translated rigidly in space, the electrons follow adiabatically giving zero net electrical current. Finally, by comparing Eqs. (1.5) and (1.6) we are able to identify what the physical zero of energy was in Eq. (1.5). First note that (1.5) and (1.6) require that

$$\sum_{\vec{k},n}D^b_{\alpha\beta}(\vec{k},n)\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]=0\;. \tag{1.7}$$

From this it follows that the reference zero implicit in $\underline{D}^b$ as used in (1.5) is the Fermi energy (or some energy that moves with the Fermi energy under strains). This can be seen by observing that the total number of electrons is not changed by the strain

$$0=\frac{d}{dS_{\alpha\beta}}\sum_{\vec{k},n}f_{\vec{k}n}=\sum_{\vec{k},n}\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\frac{d}{dS_{\alpha\beta}}(\epsilon_{\vec{k}n}-\mu)\;. \tag{1.8}$$

To be completely unambiguous, we now rewrite the definition (1.4) of $\underline{D}^b$:

$$D^b_{\alpha\beta}(\vec{k},n)=\left.\frac{d[\epsilon((\underline{1}-\underline{S})\vec{k},n;\underline{S})-\mu(\underline{S})]}{dS_{\alpha\beta}}\right|_{\underline{S}=0}\,. \tag{1.9}$$

The set of equations (1.2), (1.5), (1.6), and (1.9) together provide a new rigorous basis for the deformation-potential theory. In a separate paper[10] we intend to show how these equations are necessary to give a simple unified version of Pippard's theory[11] of ultrasonic attenuation in metals.

II. THE RIGID-ION DEFORMATION-POTENTIAL THEOREM

Let us assume that the crystal potential $V(\vec{r})$ felt by an electron is given by a sum of atomlike potentials V_a,

$$V(\vec{r})=\sum_{i,a}V_a(\vec{r}-\vec{R}_{ia})\;, \tag{2.1}$$

where $\vec{R}_{ia}=\vec{R}_i+\vec{\tau}_a$ locates the ath atom at location $\vec{\tau}_a$ relative to the origin $\vec{R}_i$ of the ith unit cell. We further assume that (2.1) remains valid, with V_a unchanged, while the atoms undergo small displacements $\vec{u}_{ia}$ from their equilibrium positions $\vec{R}_{ia}$. Within this model we can compute both energy shifts caused by strains (Sec. II A) and electron-phonon matrix elements (Sec. II B). Then by explicit comparison a deformation-potential theorem (1.5) is constructed. It should be noted that this rigid-ion model is certainly not exact. However, to first order in the displacements $\vec{u}_{ia}$ it seems often to be an excellent approximation. Nevertheless, the reader is cautioned that theorem (1.5) has not been proved exactly, but only within the rigid-ion model.

A. Static energy shift

The energy eigenvalues $\epsilon_{\vec{k}n}$ of perfect and strained crystals are given by

$$\det\{[(\vec{k}+\vec{G}_1)^2-\epsilon_{\vec{k}n}]\delta(\vec{G}_1,\vec{G}_2)+V(\vec{G}_1-\vec{G}_2)\}=0\ , \tag{2.2}$$

$$\det\{[(\vec{k}\,'+\vec{G}\,'_1)^2-\epsilon'_{\vec{k}\,'n}]\delta(\vec{G}\,'_1,\vec{G}\,'_2)+V'(\vec{G}\,'_1-\vec{G}\,'_2)\}=0\ . \tag{2.3}$$

The plane-wave representation is used only for convenience. It is not assumed that there is a weak pseudopotential or that Eqs. (2.2) and (2.3) are necessarily viable for an actual calculation. Primes are used to denote quantities in the strained crystal and are given as in Eq. (1.3a) for lattice vectors $\vec{R}_i$ and Eq. (1.3b) for reciprocal lattice vectors $\vec{G}_i$. The unit-cell volume is

$$\vec{R}_1\cdot\vec{R}_2\times\vec{R}_3=\Omega_c\to\Omega'_c=(1+\mathrm{tr}\underline{S})\Omega_c\ . \tag{2.4}$$

The potential (2.1) of the unstrained crystal has a Fourier transform given by

$$V(\vec{G})\equiv\frac{1}{\Omega_c}\int d\vec{r}\,e^{-i\vec{G}\cdot\vec{r}}\sum_a V_a(\vec{r}-\vec{\tau}_a) \tag{2.5}$$

$$=\sum_a V_a(\vec{G})e^{-i\vec{G}\cdot\vec{\tau}_a}\ . \tag{2.6}$$

To work out the corresponding quantity for the strained crystal, we need an explicit formula for the location of the atoms:

$$R_{ia}\to R'_{ia}=(\mathbb{1}+\underline{S})\vec{R}_{ia}+\vec{\delta}_a \tag{2.7}$$

$$=\vec{R}\,'_i+(\mathbb{1}+\underline{S})\vec{\tau}_a+\vec{\delta}_a\ . \tag{2.8}$$

Here $\vec{\delta}_a$ is the "internal shift" of atom coordinates within a cell which in general must accompany a strain, except in Bravais lattices or simple crystal structures such as rock salt where there are no optic modes at $\vec{Q}=\vec{0}$ which transform in the same way as $\underline{S}$ under point group operations. The internal shift $\vec{\delta}_a$ has the same order of magnitude as $\underline{S}\vec{\tau}_a$ and can be regarded as a $\vec{Q}=\vec{0}$ optic-mode displacement which mixes with the external strain. The Fourier transform for the strained crystal which corresponds to Eq. (2.5) is

$$V'(\vec{G}\,')=(1-\mathrm{tr}\underline{S})\sum_a V_a[(\mathbb{1}-\underline{S})\vec{G}]e^{-i\vec{G}\cdot(\vec{\tau}_a+\vec{\delta}_a)}\ , \tag{2.9}$$

$$\begin{aligned}V'(\vec{G}\,')\approx{}& V(\vec{G})-\mathrm{tr}(\underline{S})V(G)\\ &-\sum_a \vec{G}\cdot\overleftrightarrow{S}\cdot\vec{\nabla}_G V_a(\vec{G})e^{-i\vec{G}\cdot\vec{\tau}_a}\\ &-i\sum_a \vec{G}\cdot\vec{\delta}_a V_a(\vec{G})e^{-i\vec{G}\cdot\vec{\tau}_a}\ ,\end{aligned} \tag{2.10}$$

where Eq. (2.10) is the linearized version of (2.9).

Now we can compute the energy shift $\delta\epsilon_{\vec{k}n}$ to lowest order in strain by starting with the eigenvector $|\vec{k},n\rangle$ to (2.2) and treating (2.3) in first-order perturbation theory. Note that $\delta\epsilon_{\vec{k}n}$ is defined as $\epsilon'_{\vec{k}\,'n}-\epsilon_{\vec{k}n}$, i.e., it is the shift of the state labeled by quantum numbers $\vec{k}$, taking into account that under strain, $\vec{k}$ shifts to $\vec{k}\,'=(\mathbb{1}-\underline{S})\vec{k}$. The formula is

$$\delta\epsilon_{\vec{k}n}=\sum_{\vec{G}_1,\vec{G}_2}\langle\vec{k},n\,|\,\vec{G}_1\rangle\Delta H(\vec{G}_1,\vec{G}_2)\langle\vec{G}_2\,|\,\vec{k},n\rangle\ , \tag{2.11}$$

$$\begin{aligned}\Delta H(\vec{G}_1,\vec{G}_2)={}&[(\vec{k}\,'+\vec{G}\,'_1)^2-(\vec{k}+\vec{G}_1)^2]\delta(\vec{G}_1,\vec{G}_2)\\ &+[V'(\vec{G}\,'_1-\vec{G}\,'_2)-V(\vec{G}_1-\vec{G}_2)]\ .\end{aligned} \tag{2.12}$$

The kinetic energy term of (2.12) can be written as $-2(\vec{k}+\vec{G})\cdot\overleftrightarrow{S}\cdot(\vec{k}+\vec{G})$. Taking Eq. (2.10) into account, the answer (2.11) can be written in operator form as

$$\delta\epsilon_{\vec{k}n}=\langle\vec{k},n\,|\,(\mathscr{H}_1+\mathscr{H}_2+\mathscr{H}_3+\mathscr{H}_4)\,|\,\vec{k},n\rangle\ , \tag{2.13}$$

$$\mathscr{H}_1=-\vec{p}\cdot\overleftrightarrow{S}\cdot\vec{p}/m\ , \tag{2.14a}$$

$$\mathscr{H}_2=-\mathrm{tr}(\underline{S})V(\vec{r})\ , \tag{2.14b}$$

$$\mathscr{H}_3=-\sum_{\vec{G}}\sum_{i,a}\vec{G}\cdot\overleftrightarrow{S}\cdot\vec{\nabla}_G V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\ , \tag{2.14c}$$

$$\mathscr{H}_4=-i\sum_{\vec{G}}\sum_{i,a}\vec{G}\cdot\vec{\delta}_a V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\ . \tag{2.14d}$$

The quantities $1=\hbar^2=2m$ have been restored in Eq. (2.14a). In order to extract the deformation potential from these equations, it is necessary to find explicitly the internal strain coordinates $\vec{\delta}_a$ which accompany the applied external strain. Procedures for doing this are in the books by Born and Huang,[12] Venkataraman *et al.*,[13] and by Lax.[14] It suffices to know that for each crystal there is a unique linear relation, which we can write symbolically as

$$\delta_{a\alpha}=L^a_{\alpha\beta\gamma}S_{\beta\gamma}\ . \tag{2.15}$$

The final formula for the band deformation potential $\underline{D}^b$, defined in Eq. (1.4), follows from Eqs. (2.13)—(2.15):

$$\underline{D}^b=\langle\vec{k},n\,|\,(\hat{\overleftrightarrow{D}}_1+\hat{\overleftrightarrow{D}}_2+\hat{\overleftrightarrow{D}}_3+\hat{\overleftrightarrow{D}}_4)\,|\,\vec{k},n\rangle\ , \tag{2.16}$$

$$(\hat{D}_1)_{\alpha\beta}=-p_\alpha p_\beta/m\ , \tag{2.17a}$$

$$(\hat{D}_2)_{\alpha\beta}=-V(r)\delta_{\alpha\beta}\ , \tag{2.17b}$$

$$(\hat{D}_3)_{\alpha\beta}=-\sum_{\vec{G}}\sum_{i,a}G_\alpha\nabla_{G\beta}V_a(\vec{G})e^{-i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\ , \tag{2.17c}$$

$$(\hat{D}_4)_{\alpha\beta}=-i\sum_{\vec{G}}\sum_{i,a}G_\gamma L^a_{\gamma\alpha\beta}V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\ . \tag{2.17d}$$

In a piezoelectric crystal the $\vec{G}=\vec{0}$ term of (2.17d) will not cancel in the sum over a, because the internal shifts generate a macroscopic $\vec{E}$ field. In this case the deformation potential cannot be strictly defined, and the deformation-potential theorem does not exist. Thus, we restrict attention to cases like metals or homopolar semiconductors where atoms are neutral and $V_a(G=0)$ is a constant, or else to nonpiezoelectrics where $\vec{\delta}_a=\vec{0}$ by symmetry.

Jones and March[15] give an expression for D^b which reduces in the rigid-ion model to a form equivalent to Eqs.

(2.16) and (2.17), except that (2.17d) is missing because they have only one atom per cell. The relation between our work and theirs is explored in the Appendix.

B. Electron-phonon matrix element

When a phonon of mode $(\vec{Q},j)$ is present in the crystal, the atoms have displacements given by

$$\vec{u}_{ia}=[\vec{u}(\vec{Q},j)+\vec{\delta}_a(\vec{Q},j)]e^{i\vec{Q}\cdot\vec{R}_{ia}} , \tag{2.18}$$

where $\vec{u}$ is the "acoustic" component and $\vec{\delta}_a$ the "optic" component. These can be defined by requiring that the optic component have no center-of-mass displacement:

$$\sum_a M_a\vec{\delta}_a(\vec{Q},j)=0 . \tag{2.19}$$

The macroscopic strain $\underline{S}$ is the gradient of the local displacement $\vec{u}_{ia}$, namely,

$$S_{\alpha\beta}(\vec{x})=iQ_\beta u_\alpha(\vec{Q},j)e^{i\vec{Q}\cdot\vec{x}} . \tag{2.20}$$

In the $\vec{Q}\rightarrow\vec{0}$ limit, $\vec{u}$ vanishes for optic modes and $\vec{\delta}_a$ vanishes for acoustic branches. However, for acoustic branches with small but finite $\vec{Q}$, $\vec{\delta}_a$ is proportional to $\underline{S}$ and is given by the static formula (2.15), with nonadiabatic corrections being negligibly small (and higher order in $\vec{Q}$).

The perturbation felt by an electron at $\vec{r}$ because of the phonon $(\vec{Q},j)$ is fixed by the rigid-ion model (2.1) to be

$$\mathscr{H}_{e\text{-ph}}(\vec{Q},j)=\sum_{i,a}[V_a(\vec{r}-\vec{R}_{ia}-\vec{u}_{ia}(\vec{Q},j)) - V_a(\vec{r}-\vec{R}_{ia})] . \tag{2.21}$$

We wish to find the matrix element [Eq. (1.2)] of this perturbation between the electron state $|\vec{k},n\rangle$ and the nearby state $\langle\vec{k}+\vec{Q},n|$:

$$\langle\vec{k}+\vec{Q},n|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k},n\rangle=-i\left\langle\vec{k}+\vec{Q},n\left|e^{i\vec{Q}\cdot\vec{r}}\sum_{\vec{G}}\sum_{i,a}[\vec{u}(\vec{Q},j)+\vec{\delta}_a(\vec{Q},j)]\cdot(\vec{Q}+\vec{G})V_a(\vec{Q}+\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\right|\vec{k},n\right\rangle . \tag{2.22}$$

In the limit $\vec{Q}\rightarrow\vec{0}$, the result for an acoustic branch j vanishes linearly with $\vec{Q}$. To prove this, note that since $\vec{\delta}_a$ is linear in $S_{\alpha\beta}=iQ_\beta u_\alpha$, the only part of (2.22) which is zeroth order in $\vec{Q}$ is

$$-i\left\langle\vec{k},n\left|\sum_G\sum_a\vec{u}(\vec{0},j)\cdot\vec{G}V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{\tau}_a)}\right|\vec{k},n\right\rangle=-\vec{u}(\vec{0},j)\cdot\langle\vec{k},n|\vec{\nabla}_rV_{\text{tot}}(\vec{r})|\vec{k},n\rangle .$$

This vanishes because ∇_rV_{tot} is $(i/\hbar)[p,\mathscr{H}]$ which has vanishing diagonal matrix elements. This is just an awkward way of stating the familiar truth that a $\vec{Q}=\vec{0}$ acoustic phonon is a rigid translation of the lattice, which cannot perturb the electrons.

Our task is to examine the parts of (2.22) which are linear in $\vec{Q}$. There are four, which we label M_1 through M_4:

$$\langle\vec{k}+\vec{Q},n|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k},n\rangle=M_1+M_2+M_3+M_4 , \tag{2.23}$$

$$M_1=-i\vec{u}(\vec{Q},j)\cdot\delta\{\langle\vec{k}+\vec{Q},n|e^{i\vec{Q}\cdot\vec{r}}\}\sum_G\sum_{i,a}\vec{G}V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}|\vec{k},n\rangle , \tag{2.24a}$$

$$M_2=-i\vec{u}(\vec{Q},j)\cdot\vec{Q}\left\langle\vec{k},n\left|\sum_G\sum_{i,a}V_a(G)e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\right|\vec{k},n\right\rangle , \tag{2.24b}$$

$$M_3=-i\vec{u}(\vec{Q},j)\cdot\left\langle\vec{k},n\left|\sum_{\vec{G}}\sum_{i,a}\vec{G}[\vec{Q}\cdot\vec{\nabla}_{\vec{G}}V_a(\vec{G})]e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\right|\vec{k},n\right\rangle , \tag{2.24c}$$

$$M_4=-i\left\langle\vec{k},n\left|\sum_{\vec{G}}\sum_{i,a}\vec{\delta}_a(\vec{Q},j)\cdot\vec{G}V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\right|\vec{k},n\right\rangle , \tag{2.24d}$$

where in (2.24a), $\delta\{\cdots\}$ means the term first order in $\vec{Q}$ in the Taylor expansion of $\{\cdots\}$. We can immediately see a correspondence between M_2,M_3,M_4 and the corresponding parts $\mathscr{H}_2,\mathscr{H}_3,\mathscr{H}_4$ of Eqs. (2.13) and (2.14). This correspondence can be written

$$M_2+M_3+M_4=S_{\alpha\beta}\langle\vec{k},n|(\hat{D}_2+\hat{D}_3+\hat{D}_4)_{\alpha\beta}|\vec{k},n\rangle , \tag{2.25}$$

where $S_{\alpha\beta}$ is $iQ_\beta u_\alpha(\vec{Q},j)$ following (2.20) and $\hat{D}_i$ is defined in Eq. (2.17). It remains to find whether M_1 corresponds to $S_{\alpha\beta}\langle\vec{k},n|(\hat{D}_1)_{\alpha\beta}|\vec{k},n\rangle$. The impossibility of such a correspondence can be seen immediately by considering the weak pseudopotential limit of Eqs. (2.17a) and (2.24a), i.e., the case when the wave function $|\vec{k},n\rangle$ is approximately a plane wave $|\vec{k}+\vec{G}_n\rangle$. Then $\langle\vec{k},n|(\hat{D}_1)_{\alpha\beta}|\vec{k},n\rangle$ is approximately $-(\vec{k}+\vec{G}_n)_\alpha(\vec{k}$

$+\vec{G}_n)_\beta/m$ while M_1 is approximately zero because $\langle\vec{k}+\vec{Q},n\,|\,e^{i\vec{Q}\cdot\vec{r}}$ is the same plane wave as $\langle\vec{k},n\,|$, i.e., the correction linear in $\vec{Q}$ is small.

The expression (2.24a) for M_1 can be written as

$$M_1=-\vec{u}(\vec{Q},j)\cdot\langle\delta\psi_{\vec{k}n}\,|\,\vec{\nabla}_{\vec{r}}V(\vec{r})\,|\,\vec{k},n\rangle\ , \tag{2.26}$$

$$|\,\delta\psi_{\vec{k}n}\rangle\equiv e^{-i\vec{Q}\cdot\vec{r}}\,|\,\vec{k}+\vec{Q},n\rangle-|\,\vec{k},n\rangle\ . \tag{2.27}$$

Using $\vec{k}\cdot\vec{p}$ perturbation theory, the formula for $|\,\delta\psi_{\vec{k}n}\rangle$ to first order in $\vec{Q}$ is

$$|\,\delta\psi_{\vec{k}n}\rangle=\sum_{n'\,(\neq n)}|\,\vec{k},n'\rangle\langle\vec{k},n'\,|\,\vec{p}\,|\,\vec{k},n\rangle\cdot(\hbar\vec{Q}/m)(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}n'})^{-1}\ . \tag{2.28}$$

Using (2.28) in (2.26), and using the fact that $\vec{\nabla}_{\vec{r}}\vec{V}(\vec{r})$ is equal to $(i/\hbar)[\vec{p},\mathscr{H}]$, M_1 can be written as

$$M_1=-iQ_\beta u_\alpha(\vec{Q},j)\times\sum_{n'\,(\neq n)}\langle\vec{k},n\,|\,p_\beta\,|\,\vec{k},n'\rangle\langle\vec{k},n'\,|\,p_\alpha\,|\,\vec{k},n\rangle/m\ . \tag{2.29}$$

If we now add and subtract the $n'=n$ term in the sum over intermediate states in (2.29), and use the completeness relation, the result is

$$M_1=S_{\alpha\beta}(\langle\vec{k},n\,|\,(\hat{D}_1)_{\alpha\beta}\,|\,\vec{k},n\rangle+mv_{\vec{k}n\alpha}v_{\vec{k}n\beta})\ . \tag{2.30}$$

The correction term in (2.30) involves the group velocity $v_{\vec{k}n\alpha}=\langle\vec{k},n\,|\,(p_\alpha/m)\,|\,\vec{k},n\rangle$ and has just the right form to cancel the first term $\hat{D}_1$ of M_1 in the nearly-free-electron limit, as is required by the argument given above.

Combining (2.25) and (2.30), we now have a complete expression for the electron-phonon matrix element. This matrix element is written in terms of an electron-phonon deformation potential $D^{e\text{-ph}}_{\alpha\beta}$ in Eq. (1.2). Comparing with Eq. (2.16) for the band-structure deformation potential, we find the fundamental form of the deformation-potential theorem:

$$\underline{D}^{e\text{-ph}}(\vec{k},n)=\underline{D}^{b}(\vec{k},n)+m\vec{v}_{\vec{k}n}\vec{v}_{\vec{k}n}\ . \tag{1.5$'$}$$

This is the main result of this section.

This result violates the conventional view that the two deformation potentials are the same. However, the conventional view was already rejected in the authoritative review by Sham and Ziman.[8] They quoted a result somewhat different from (1.5′). The origin of this difference is hard to trace because they give no hint of how it was derived. A "proof" of the Sham-Ziman formula is given by Jones and March.[15] However, there seems to be an error in this proof, as is explained in the Appendix. As Sham and Ziman have pointed out, a common use of the "deformation-potential theorem" has been at band extrema in semiconductors. At these points, $\vec{v}_{kn}$ vanishes, and the conventional formula is correct. However, on the Fermi surface of a metal, the correction term $m\vec{v}\cdot\vec{v}$ is often very large, and the conventional formula is totally invalid.

C. Optic phonons

The algebra in parts A and B of this section permits a treatment of optic phonons by the simple expedient of abandoning relation (2.15), allowing the internal shifts $\vec{\delta}_a$ to remain finite as $\vec{Q}\rightarrow\vec{0}$, and requiring the strain $\underline{S}$ to vanish. This greatly simplifies the expressions for both energy shifts and electron-phonon matrix elements. Equation (2.13) can be written as

$$\delta\epsilon_{\vec{k}n}=\sum_a\vec{\delta}_a\cdot\vec{D}_a(\vec{k},n)\ , \tag{2.31}$$

$$\vec{D}_a(\vec{k},n)=-i\left\langle\vec{k},n\left|\sum_G\sum_i\vec{G}V_a(\vec{G})e^{i\vec{G}\cdot(\vec{r}-\vec{R}_{ia})}\right|\vec{k},n\right\rangle$$

$$=\langle\vec{k},n\,|\,\vec{\nabla}_{\vec{\tau}a}V_{\text{tot}}(r)\,|\,\vec{k},n\rangle\ . \tag{2.32}$$

For the case of an optic phonon of branch j, frequency ω_j, at $\vec{Q}=\vec{0}$, the displacement $\vec{u}_{ia}$ in Eq. (2.18) is just $\vec{\delta}_a(j)$ where

$$\vec{\delta}_a(j)=(\hbar/2M_aN\omega_j)^{1/2}\hat{\epsilon}^{a}_{j} \tag{2.33}$$

and $\hat{\epsilon}^a_j$ is a normalized eigenvector, obeying $\sum_a\hat{\epsilon}^a_j\cdot\hat{\epsilon}^a_{j'}=\delta_{jj'}$. Equation (2.23) can be written as

$$\langle\vec{k},n\,|\,\mathscr{H}_{e\text{-ph}}(j)\,|\,\vec{k},n\rangle=(\hbar/2M_aN\omega_j)^{1/2}\hat{\epsilon}^a_j\cdot\vec{D}_a(\vec{k},n)\ . \tag{2.34}$$

The same "optic deformation potentials" $\vec{D}_a(\vec{k},n)$ appear in (2.31) for the energy shift and (2.34) for the electron-phonon matrix element. Thus, all optic-phonon matrix elements can be constructed from calculations of electron energy shifts caused by sublattice displacements. The naive reasoning of Sec. I is correct for optic phonons; extra complexity occurs only for the acoustic case.

III. TRANSLATIONAL-INVARIANCE SUM RULE

In this section a proof is given of Eq. (1.6) for the electron-phonon deformation potential. After establishing the theorem, it is used in conjunction with Eq. (1.5′) to clarify the zero of energy relative to which $\underline{D}^b$ is defined. The basic idea is that in the presence of an acoustic wave, the electron-phonon interaction establishes an electronic current, which cancels the current of the moving ions, except for corrections which vanish at least as fast as Q when $\vec{Q}$ goes to zero. In other words, if all positive ions are moved slowly and uniformly, no dc electric current results. The potential felt by the electrons is given by (2.18) and (2.21), except that we want to recognize explicitly the (slow) time dependence of the ionic motion

$$\mathscr{H}_{e\text{-ph}}(\vec{Q},j;t)=-\sum_{i,a}\vec{\nabla}V_a(r-R_{ia})\cdot[\vec{u}(\vec{Q},j)+\vec{\delta}_a(\vec{Q},j)]\times e^{i(\vec{Q}\cdot\vec{R}_{ia}-\omega t)}\,. \tag{3.1}$$

The ions and the tightly bound core electrons have a net charge Ze, which gives a macroscopic electrical current

$$\vec{J}_{\text{ion}}(\vec{r},t)=ne\vec{v}(\vec{r},t)\,, \tag{3.2}$$

where $n=Z/\Omega_a$ is the number of valence electrons per atomic volume, and the ion velocity $\vec{v}$ is

$$\vec{v}(\vec{r},t)=-i\omega\vec{u}(\vec{Q},j)e^{i(\vec{Q}\cdot\vec{r}-\omega t)}\,. \tag{3.3}$$

In the small-Q limit, there is an exactly compensating electronic current:

$$J_{\text{el}}=-(e/N\Omega_a)\sum_{\vec{k},n}\vec{v}f(\vec{k},n)\,, \tag{3.4}$$

where $f(\vec{k},n)$ is the equilibrium Fermi-Dirac function. We now make a microscopic investigation of the sources of this electronic current.

There is a surprisingly simple prescription for calculating the intraband part of the current. Provided that ω is small, the electronic relaxation time τ is always short enough that $\omega\tau \ll 1$. A more stringent requirement is that the lattice wave should have a wavelength $2\pi/Q$ much longer than the electron mean free path l, or $Ql \ll 2\pi$, or $\omega\tau(v_F/v_s) \ll 2\pi$, where v_F and v_s are the Fermi and sound velocities. We shall assume that Q and ω are small enough that this is satisfied. Then the electrons reach a local equilibrium in which they move with the ions at the velocity $\vec{v}$ of the ions. In the stationary frame this corresponds to a shifted Fermi-Dirac distribution $f(\vec{k}-m\vec{v}/\hbar,n)$. This result does not seem very obvious to us for Bloch electrons, but it is a basic element of Pippard's theory, manifestly true for free electrons, and has been given a rigorous basis for Bloch electrons by Holstein.[16] The displaced equilibrium distribution carries a net current

$$\vec{J}_{\text{ra}}=-e\sum_{\vec{k},n}\vec{v}_{\vec{k},n}f(\vec{k}-m\vec{v}/\hbar,n)/\Omega$$

$$=-em\left(\frac{n}{m}\right)_{\text{eff}}\vec{v}(rt)\,, \tag{3.5}$$

$$\left(\frac{n}{m}\right)_{\text{eff}}\equiv\sum_{\vec{k},n}\vec{v}_{\vec{k}n}\vec{v}_{\vec{k}n}\left(-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right)\frac{1}{\Omega} \tag{3.6a}$$

$$=\sum_{\vec{k},n}\left(\frac{\partial^2\epsilon_{\vec{k}n}}{\partial\vec{k}\partial\vec{k}}\right)\frac{f(\vec{k},n)}{\hbar^2\Omega}\,, \tag{3.6b}$$

where (3.6b) follows from (3.6a) after integrating by parts. This fails by a factor $(1-m/m_{\text{eff}})$ to agree with (3.4) and cancel the ion current (3.2). The difference is made up by an interband current $\vec{J}_{\text{er}}$ as demonstrated by Holstein.[16] Holstein's proof will now be summarized, because we will later recalculate the intraband current $\vec{J}_{\text{ra}}$ copying Holstein's method.

To find $\vec{J}_{\text{er}}$, we calculate the current $j^{\text{er}}_{\vec{k}n}(\vec{Q},j)$ induced by interband transitions in the state $|\vec{k},n\rangle$ by the phonon perturbation $\mathscr{H}_{e\text{-ph}}$ [Eq. (3.1)], and sum over occupied states:

$$\vec{J}_{\text{er}}=\sum_{\vec{k},n}j^{\text{er}}_{\vec{k}n}(\vec{Q},j)f(\vec{k},n)e^{i\vec{Q}\cdot\vec{r}-\omega t}\,. \tag{3.7}$$

The state $|k,n\rangle$ acquires a small admixture $|\delta\psi_{\vec{k}n}\rangle$ of states $|\vec{k}+\vec{Q},n'\rangle$ in other bands $n'\neq n$ because of the phonon perturbation. When the velocity of the new state $|\vec{k},n\rangle+|\delta\psi_{\vec{k}n}\rangle$ is calculated, the cross terms contribute a current due to the interband matrix elements of the velocity operator $\vec{v}(\vec{Q})=(\vec{p}e^{-i\vec{Q}\cdot\vec{r}}+e^{-i\vec{Q}\cdot\vec{r}}\vec{p})/2m$. The interband contribution is polarized in the direction of the ion motion, and gives a macroscopic contribution when summed as in (3.7) over occupied states. From time-dependent perturbation theory we get

$$\left(-\frac{\Omega}{e}\right)\vec{j}^{\,\text{er}}_{\vec{k}n}(\vec{Q},j)=\sum_{n'(\neq n)}\frac{\langle\vec{k},n|\vec{v}(\vec{Q})|\vec{k}+\vec{Q},n'\rangle\langle\vec{k}+\vec{Q},n'|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k},n\rangle}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}+\vec{Q},n'}+\hbar\omega}+\sum_{n'(\neq n)}\frac{\langle\vec{k},n|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k}-\vec{Q},n'\rangle\langle\vec{k}-\vec{Q},n'|\vec{v}(\vec{Q})|\vec{k},n\rangle}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}-\vec{Q},n'}-\hbar\omega}\,. \tag{3.8}$$

This term when summed in (3.7) will be almost canceled by the current induced in the state $|-\vec{k},n\rangle$:

$$\left(-\frac{\Omega}{e}\right)\vec{j}^{\,\text{er}}_{-\vec{k}n}(\vec{Q},j)=-\sum_{n'(\neq n)}\frac{\langle\vec{k},n|\vec{v}(\vec{Q})|\vec{k}+\vec{Q},n'\rangle\langle\vec{k}+\vec{Q},n'|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k},n\rangle}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}+\vec{Q},n'}-\hbar\omega}-\sum_{n'(\neq n)}\frac{\langle\vec{k},n|\mathscr{H}_{e\text{-ph}}(\vec{Q},j)|\vec{k}-\vec{Q},n'\rangle\langle\vec{k}-\vec{Q},n'|\vec{v}(Q)|\vec{k},n\rangle}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}-\vec{Q},n'}+\hbar\omega}\,. \tag{3.9}$$

In writing (3.9) we have simply reversed the sign of $\vec{k}$ in (3.8) and then used the time-reversal symmetry $\psi_{-\vec{k}n}=\psi^*_{\vec{k}n}$, $\psi_{-\vec{k}-\vec{Q},n'}=\psi^*_{\vec{k}+\vec{Q},n'}$, $\epsilon_{-\vec{k}n}=\epsilon_{\vec{k}n}$, $\epsilon_{-\vec{k}-\vec{Q},n'}=\epsilon_{\vec{k}+\vec{Q},n'}$, and $\langle-\vec{k},n|\vec{v}|-\vec{k},n\rangle=-\langle\vec{k},n|\vec{v}|\vec{k},n\rangle$. The second term of (3.8) generates the first term of (3.9) and vice versa. Except for the fact that the sign of ω is reversed, (3.9) would completely cancel (3.8). We next add (3.8) and (3.9):

$$\vec{J}^{\,\mathrm{er}}_{\vec{k}n}(\vec{Q},j) \equiv \tfrac{1}{2}[\,\vec{j}^{\,\mathrm{er}}_{\vec{k}n}(\vec{Q},j)+\vec{j}^{\,\mathrm{er}}_{-\vec{k}n}(\vec{Q},j)] \tag{3.10}$$

$$= -\frac{e\hbar\omega}{\Omega}\sum_{n'\,(\neq n)}\{\,\langle\vec{k},n\,|\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k},n'\rangle\langle\vec{k},n'\,|\,\vec{v}(0)\,|\,\vec{k},n\rangle - \langle\vec{k},n\,|\,\vec{v}(0)\,|\,\vec{k},n'\rangle\langle\vec{k},n'\,|\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k},n\rangle\}/(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}n'})^2 \, . \tag{3.11}$$

In (3.11), the wave vector $\vec{Q}$ of the phonon has been set to zero everywhere except in the outside factor $\omega=v_s Q$, because we are interested only in the result which is lowest order in $\vec{Q}$. In this limit the internal strain $\vec{\delta}_a$ in (3.1) vanishes, and the electron-phonon perturbation is just a rigid shift of the whole lattice:

$$\mathcal{H}_{e\text{-ph}}(\vec{0},j) = -\vec{u}(\vec{0},j)\cdot\vec{\nabla}V(r) \, , \tag{3.12}$$

where $V(r)$ is the crystal potential of Eq. (2.1). Because $\vec{\nabla}V$ is $(i/\hbar)[\vec{p},\mathcal{H}]$, the matrix elements of $\mathcal{H}_{e\text{-ph}}(\vec{0},j)$ become

$$\langle\vec{k},n'\,|\mathcal{H}_{e\text{-ph}}(\vec{0},j)\,|\,\vec{k},n\rangle = (-i/\hbar)\langle\vec{k},n'\,|\,\vec{u}(\vec{0},j)\cdot\vec{p}\,|\,\vec{k},n\rangle(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}n'}) \, . \tag{3.13}$$

Also note that the operator $\vec{v}(0)$ is just $\vec{p}/m$. Therefore, we can rewrite (3.11) as

$$\vec{J}^{\,\mathrm{er}}_{\vec{k}n}(\vec{r},t) = -\frac{e}{\Omega}\left[\mathbb{1}-\left[\frac{m}{\underline{m}_{\mathrm{eff}}}\right]_{\vec{k}n}\right]\cdot\vec{v}(r,t) \, , \tag{3.14}$$

$$\left[\frac{m}{\underline{m}_{\mathrm{eff}}}\right]_{\vec{k}n} = 1+\frac{2}{m}\sum_{n'\,(\neq n)}\frac{\langle\vec{k},n\,|\,\vec{p}\,|\,\vec{k},n'\rangle\langle\vec{k},n'\,|\,\vec{p}\,|\,\vec{k},n\rangle}{(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}n'})} \tag{3.15a}$$

$$= \frac{\partial^2\epsilon_{\vec{k}n}}{\partial\vec{k}\,\partial\vec{k}}\frac{m}{\hbar^2} \, , \tag{3.15b}$$

where $\vec{v}(\vec{r},t)$ is given in Eq. (3.3). The identification of (3.15b) with (3.15a) is the well-known "effective-mass theorem."[17] When summed over occupied states as in (3.7), the resulting interband current is, using (3.6b),

$$\vec{J}_{\mathrm{er}} = -em\left[\frac{n}{m}\mathbb{1}-\left[\frac{n}{\underline{m}}\right]_{\mathrm{eff}}\right]\cdot\vec{v}(\vec{r},t) \, . \tag{3.16}$$

This is exactly sufficient to make up the missing part of $\vec{J}_{\mathrm{ra}}$ in Eq. (3.5) and yield zero net current:

$$\vec{J}_{\mathrm{ion}}+\vec{J}_{\mathrm{ra}}+\vec{J}_{\mathrm{er}}=\vec{0} \, . \tag{3.17}$$

This also provides confirming evidence that Eq. (3.5) for the intraband current is correct.

We now derive our sum rule by making a direct perturbative calculation of the intraband current $\vec{J}_{\mathrm{ra}}$ induced by the phonon perturbation (3.1) and comparing it with (3.5). We begin by denoting as $\vec{j}^{\,\mathrm{ra}}_{\vec{k}n}(\vec{Q},j)$ the missing $n'=n$ term from (3.8), and similarly for $\vec{j}^{\,\mathrm{ra}}_{-\vec{k}n}(\vec{Q},j)$ from (3.9). Next these two terms are averaged to give $\vec{J}^{\,\mathrm{ra}}_{kn}(\vec{Q},j)$ as in Eq. (3.10):

$$\vec{J}^{\,\mathrm{ra}}_{\vec{k}n}(\vec{Q},j) = \frac{e\hbar\omega}{\Omega}\frac{\langle\vec{k},n\,|\,\vec{v}(\vec{Q})\,|\,\vec{k}+\vec{Q},n\rangle\langle\vec{k}+\vec{Q},n\,|\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k},n\rangle}{(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}+\vec{Q}n})^2-(\hbar\omega)^2} - \frac{e\hbar\omega}{\Omega}\frac{\langle\vec{k},n\,|\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k}-\vec{Q},n\rangle\langle\vec{k}-\vec{Q},n\,|\,\vec{v}(\vec{Q})\,|\,\vec{k},n\rangle}{(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}-\vec{Q},n})^2-(\hbar\omega)^2} \, . \tag{3.18}$$

The denominators in (3.18) vanish as $\vec{Q}\rightarrow\vec{0}$ so we must be careful not to take Q to zero too early. Now sum over occupied states to get the total intraband current:

$$\vec{J}_{\rm ra}(\vec{Q},j)=\frac{e\hbar\omega}{\Omega}\sum_{\vec{k},n}(f_{\vec{k}n}-f_{\vec{k}+\vec{Q},n})\frac{\langle \vec{k},n\,|\,\vec{v}(\vec{Q})\,|\,\vec{k}+\vec{Q},n\rangle\langle\vec{k}+\vec{Q},n\,|\,\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k},n\rangle}{(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}+\vec{Q},n})^2-(\hbar\omega)^2}\ . \tag{3.19}$$

Here the second term of (3.18) has been rewritten by a shift of the dummy index of summation from $\vec{k}$ to $\vec{k}\,'=\vec{k}-\vec{Q}$, and a relabeling $\vec{k}\,'\rightarrow\vec{k}$. At this stage the $\vec{Q}\rightarrow\vec{0}$ limit is easily taken. The term $-(\hbar\omega)^2$ in the denominator can be dropped because $\omega=v_sQ$ is small compared with v_FQ. The matrix element $\langle\vec{k},n\,|\,\vec{v}(\vec{Q})\,|\,\vec{k}+\vec{Q},n\rangle$ can be approximated as $\vec{v}_{\vec{k}n}$. We have

$$\vec{J}_{\rm ra}(\vec{Q},j)=\frac{e\omega}{\Omega}\sum_{\vec{k},n}\left[\frac{f_{\vec{k}n}-f_{\vec{k}+\vec{Q},n}}{\epsilon_{\vec{k}+\vec{Q},n}-\epsilon_{\vec{k}n}}\right]\left[\frac{\vec{v}_{\vec{k}n}}{\vec{Q}\cdot\vec{v}_{\vec{k}n}}\right]\langle\vec{k}+\vec{Q},n\,|\,\mathcal{H}_{e\text{-ph}}(\vec{Q},j)\,|\,\vec{k},n\rangle\ . \tag{3.20}$$

For simplicity, let us now look only at the longitudinal part of the current $\vec{J}_{\rm ra}$

$$\vec{Q}\cdot\vec{J}_{\rm ra}(\vec{Q},j)=\frac{e\omega}{\Omega}\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]\langle\vec{k}+\vec{Q},n\,|\,\mathcal{H}_{e\text{-ph}}\,|\,\vec{k},n\rangle\ . \tag{3.21}$$

This should be compared with the longitudinal part of (3.5), using (3.3) for $\vec{v}(\vec{r}t)$:

$$\begin{aligned}\vec{Q}\cdot\vec{J}_{\rm ra}(\vec{Q},j)&=e\omega m\left[\frac{n}{m}\right]_{\text{eff},\alpha\beta}(iQ_\alpha u_\beta)\\&=\frac{e\omega}{\Omega}\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]mv_{\vec{k}n\alpha}v_{\vec{k}n\beta}S_{\alpha\beta}\ .\end{aligned} \tag{3.22}$$

Finally, we use the definition (1.2) of the electron-phonon deformation potential in (3.21), and by comparing (3.21) with (3.22) find, as given in Sec. I, the result

$$\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]D^{e\text{-ph}}_{\alpha\beta}(\vec{k},n)=\sum_{\vec{k},n}\left[-\frac{\partial f}{\partial\epsilon_{\vec{k}n}}\right]mv_{\vec{k}n\alpha}v_{\vec{k}n\beta}\ . \tag{1.6}$$

This is a new exact sum rule of surprising simplicity and power.

First, consider the free-electron limit. The Fermi surface is spherical and $D^{e\text{-ph}}_{\alpha\beta}$ is independent of the angular part of $\vec{k}$. Equation (1.6) then gives the familiar result[6] $D^{e\text{-ph}}_{\alpha\beta}=\frac{2}{3}\epsilon_F\delta_{\alpha\beta}$. For a cubic metal, the result is $\langle D^{e\text{-ph}}_{\alpha\beta}\rangle=\frac{2}{3}m\langle v^2\rangle\delta_{\alpha\beta}$. To our knowledge this is a new result. Under the 48-point-group operations in $\vec{k}$ space, a second-rank tensor $D_{\alpha\beta}(\vec{k},n)$ has a trace which transforms according to the identity representation Γ_1, and traceless components transforming as Γ_{12} and Γ'_{25}. Thus, it is clear that only the trace of $D_{\alpha\beta}(\vec{k},n)$ remains after averaging over states on the Fermi surface.

It is not clear to us whether Eq. (1.6) has any meaning in a semiconductor. At $T=0$ in a pure semiconductor there are no intraband currents, and (1.6) simply says $\vec{0}=\vec{0}$. In a pure semiconductor at high T, (1.6) implies that valence- and conduction-band deformation potentials have opposite signs, because the velocities on the right will be very small and the deformation potentials on the left must cancel.

In Sec. I it has already been shown that (1.6) and (1.5′) together imply that the reference energy of $\underline{D}^b$ in (1.5′) is the Fermi energy. Furthermore, we can speculate that (1.5′) may be a general result and not restricted to the rigid-ion model from which it was derived. Equation (1.6) tells us that if there are corrections, $\delta_{\alpha\beta}(\vec{k},n)$ to (1.5′) from non-rigid-ion effects, the correction must vanish when averaged over the Fermi surface.

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APPENDIX: RELATION TO DERIVATION BY JONES AND MARCH

Jones and March[15] provide a "derivation" of an equation which differs from (2.31), namely,

$$D^{e\text{-ph}}_{\alpha\beta}(k)=\bar{D}^{\,b}_{\alpha\beta}(k)+m\,(v_{s\alpha}-\hbar k_\alpha/m)v_{k\beta}\ , \tag{A1}$$

where $\vec{v}_s$ is the sound velocity. This is the result stated without proof by Sham and Ziman.[8] A careful inspection of the proof of Ref. 15 shows that their band deformation potential $\bar{D}^{\,b}$ is not defined as in (1.4) with the scaled wave vector $(\underline{1}-\underline{S})\vec{k}$, but instead with the unscaled wave vector. To convert back to a scaled wave vector is easy because quite generally

$$D^b_{\alpha\beta}(k)=\bar{D}^{\,b}_{\alpha\beta}(k)-\hbar k_\alpha v_{k\beta}\ . \tag{A2}$$

Thus (A1) becomes

$$D^{e\text{-ph}}_{\alpha\beta}(k)=D^b_{\alpha\beta}(k)+mv_{s\alpha}v_{k\beta}\ . \tag{A3}$$

We wish to emphasize that we believe (A1) and (A3) to be wrong, and (1.5′) to be right. The purpose of this appendix is to show where the "derivation" of Ref. 15 goes astray.

The method of proof parallels that of Sec. II of this paper, except that no rigid-ion model is made. Instead it is assumed quite generally that there exists a one-electron potential $V(\vec{r},\{\vec{R}\})$ where $\{R\}$ stands for the coordinates of all the atoms, not necessarily at their equilibrium positions. They derive a formula for the shift of a one-electron energy due to a strain $\underline{S}$,

$$E'(\vec{k}'n)-E(\vec{k}n)=S_{\alpha\beta}\left\langle \vec{k}n \left| \frac{-p_\alpha p_\beta}{m}+\sum_l (l_\alpha-r_\alpha)\frac{\partial V(\vec{r},\{\vec{R}\})}{\partial l_\beta} \right| kn \right\rangle , \tag{A4}$$

where $\vec{l}$ is the equilibrium coordinate of the lth atom. This derivation seems correct. Further, if we use the rigid-ion model (2.1) for $V(\vec{r},\{\vec{R}\})$, then after an integration by parts it is quite straightforward to show that (A4) simply reproduces the first three terms of Eq. (2.16). The fourth term, given in (2.17d), is missing from Ref. 15 because they have not considered the more complicated distortions which occur with more than one atom per cell.

Next, Jones and March calculate an electron-phonon matrix element. However, instead of considering an oscillatory distortion as in Eq. (2.18), they write the displacement of the lth atom as

$$u_{\vec{l}\alpha}=S_{\alpha\beta}(\vec{l})l_\beta . \tag{A5}$$

This equation is only valid for atoms at sites $\vec{l}$ which are much closer to the origin than the wavelength of the sound wave. At larger distances Eq. (A5) does not correctly describe the oscillatory displacements. Therefore, it is not possible for their derivation to give a correct $\vec{Q}$ dependence to the electron-phonon matrix element. Since the deformation potential $D_{\alpha\beta}^{e\text{-ph}}$ is the coefficient of the linear term in $\vec{Q}$ in the electron-phonon matrix element, there is no rigor whatsoever to their derivation.

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