PHYSICAL REVIEW VOLUME 139, NUMBER 5A 30 AUGUST 1965

Electron-Phonon Interaction for Indirect Interband Transitions in Germanium*

RALPH T. SHUEY†‡
The Johns Hopkins University, Baltimore, Maryland

(Received 5 April 1965)

Calculation of the interaction of electrons with short-wavelength phonons becomes tractable when the initial and final electronic wave vectors have high symmetry and a local-pseudopotential representation is used. After discussion of the general Bloch formulation for the electron-phonon interaction and of the pseudopotential method in band theory, we calculate as a specific example all allowed transitions in germanium between wave vectors Γ and L for electron states at the edge of the gap. Our result for the matrix element $\Gamma_{2'}+\mathrm{LA}\rightarrow L_1$ is nearly twice that deduced from optical absorption by McLean. The sensitivity of the results to the short-wavelength behavior of the pseudopotential is tested by use of two sets of pseudopotential parameters. Approximations are given for the case of wave vectors not exactly at the symmetry points. In the principal calculation, it is assumed that each nucleus rigidly carries a spherical pseudopotential. Since this is questionable in covalently bonded Ge, we also attempt, with partial success, to calculate by the deformable-ion method. This traditional alternative is ambiguous and unjustifiable, but it indicates the effect of using a different prescription in perturbing the crystal pseudopotential by a phonon. Resulting matrix elements are generally smaller.

I. INTRODUCTION

A THEORETICAL investigation of the interaction between electrons and phonons in real materials[1] does not proceed far in full generality. Progress from a formal to a quantitative description seems to require restriction to specific classes of materials, to specific branches of the vibration spectrum, and usually to long phonon wavelength; there is no universally applicable approximation scheme. Even when an explicit expression for the form and strength of a restricted part of the electron-phonon (E-P) interaction can be obtained, unambiguous experimental test is difficult, despite the broad range of phenomena qualitatively dependent on the E-P interaction. Directly observed quantities such as the variation of conductivity with temperature often depend on averages performed over a large part of the electron-phonon spectrum in an incompletely understood manner.

A relatively sensitive and specific probe of the E-P interaction may be afforded by electronic interband transition phenomena in an indirect-gap semiconductor such as germanium.[2–5] Initial and final states are highly localized in wave-vector space, and it is often possible to isolate from competing mechanisms the process going directly through the E-P interaction.

An interest in such effects[6] led the author to examine the possibility of calculating the relevant matrix elements. This would aid interpretation of the data and also test the theoretical principles used to make the calculation. These matrix elements are unusual in that they are virtual and involve quite short wavelengths. Apparently there has been no serious theoretical attack on them previously. Yet recent advances in the theory of band structure and the electron-phonon interaction[7] seem to make plausible numerical results possible.

This paper[8] analyzes the situation with specific application to interband transitions in Ge. This material was chosen because of the wealth of data and understanding already available. Section II briefly reviews the conception of an interacting electron-phonon system. The Bloch formula for the electron-phonon interaction in the one-electron approximation is presented and the arguments justifying it mentioned. Section III discusses the local-pseudopotential representation of Ge and its use in evaluating the Bloch formula. In Sec. IV, two slightly different sets of pseudopotential parameters are chosen and the electronic wave functions determined for wave vectors at the symmetry points Γ and L. Then, in Sec. V, we numerically evaluate the Bloch formula for all allowed transitions between Γ and L for the states at the edge of the gap. The result for the one matrix element available experimentally is about a factor of 2 too high. The approximation of rigid spherical pseudo-ions is used. As a possible alternative, we attempt, with partial success, in Sec. VI, to use the deformable-ion approximation. Finally, in Sec. VII, we discuss wave vectors away from symmetry points and calculate effects linear in phonon wave vector.

We anticipate that the procedures introduced in this

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* Based on a Ph.D. thesis submitted to the Johns Hopkins University.

† National Science Foundation Cooperative Graduate Fellow, 1964–65.

‡ Address after July 1, 1965; General Electric Research Laboratory, Schenectady, New York.

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paper will work equally well for intervalley scattering and for semiconductors other than Ge. An electronic computer should be used for any extensive calculations.

II. ELECTRON-PHONON INTERACTION

This section outlines notation and the conception of electrons, phonons, and their interaction, to be used in this paper. The discussion is general and without specific reference to Ge. We suppose a mathematical model of a quasi-infinite crystal with the symmetry of some space group. There is a complete set of crystal states specified in an electron-phonon number representation. The individual phonon modes are described by a dynamical matrix[9] which is a triply periodic function of wave vector $\mathbf{q}$. The eigenvector $\mathbf{e}_b(\mathbf{q},p)$ for the branch p gives the relative displacements of the nuclei at positions b in a unit cell; the corresponding eigenvalue $\omega^2(\mathbf{q},p)$ is the square of the classical mode frequency or essentially of the phonon-energy quantum. The classical nuclear displacement in the lth cell is

$$\mathbf{u}_{lb}\propto (m_b)^{-\frac{1}{2}}\mathbf{e}_b(\mathbf{q},p)e^{i\mathbf{q}\cdot\mathbf{r}_l}, \tag{2.1}$$

with m_b the mass. The entire configuration of nuclei so displaced transforms as some representation of the group of the wave vector $\mathbf{q}$. (This comprises all elements of the space group which result in a configuration of the same or equivalent wave vector.)

Exact knowledge of the dynamical matrix throughout the Brillouin zone would determine its expansion in a Fourier series, and the Fourier coefficients could be interpreted as force constants between individual nuclei. The experimental $\omega(\mathbf{q},p)$ curves[10] available for many materials (including Ge) with $\mathbf{q}$ along a symmetry axis show that such a force system must, in general, be long range but do not suffice to determine the form of the force with any precision. Therefore, we regard the wave-vector language as fundamental.

Similarly, the one-electron states are described by one-electron energies and wave functions which are triply periodic, multibranched functions of wave vector $\mathbf{k}$ in a repeated zone scheme. Each spinor wave-function branch transforms as some representation of the double group of the wave vector. We assume with Bloch[11] that the states are eigenstates of an effective Hamiltonian which is independent of energy and wave vector. An effective Hamiltonian determined by refined *a priori* band calculation may not satisfy this condition. This would happen, for example, if the Hartree-Fock equations were used without making an approximation such as Slater's[12] for the exchange term. Nevertheless, the assumption is generally made in formal band theory.[13]

These electron-phonon states so specified are supposed to be nearly but not exactly stationary states of the entire crystal. By means of packets and an ensemble formalism, one can refer to local occupation probabilities in this electron-phonon number representation and develop a transport theory. These states have the physical significance that external influences such as a magnetic field, light, or electrical contacts are properly regarded as coupling to these states and changing occupation numbers. The one-phonon and one-electron energies are what such an external probe would see if there were no coupling between microscopic excitations, such as anharmonicity and the electron-phonon interaction. Thus these energies do not include such contributions as anharmonic broadening and electron self-energy in the phonon field.

Suppose also that an effective one-electron Hamiltonian can be obtained when the nuclei are not in a perfect lattice. A general arrangement can be described by values for the complex normal coordinates[14]

$$Q_{\mathbf{q}p}=(N)^{-1/2}\sum\nolimits_{lb}(m_b)^{1/2}\mathbf{u}_{lb}\cdot\mathbf{e}_b^*(\mathbf{q}p)e^{-i\mathbf{q}\cdot\mathbf{r}_l}, \tag{2.2}$$

where N is the number of cells in an arbitrary large phonon normalization volume. Presumably for only slightly perturbed configurations, the electron Hamiltonian can be expanded in powers of the $Q_{\mathbf{q}p}$.

Now the electron-phonon (E-P) interaction operator can be described: Obviously it conserves electron number and total crystal momentum (modulo reciprocal lattice vector). As long as we are able to calculate with only one-electron wave functions, the interaction must be taken as changing the state of only one electron. Plausibly the interaction can be expanded in powers of the phonon creation and annihilation operators[15]; only the linear terms (one-phonon vertex) will be important at temperatures well below the melting point. This linear part of the E-P interaction scatters an electron from wave vector $\mathbf{k}$ to wave vector $\mathbf{k}'$ and simultaneously creates a phonon of wave vector equivalent to $\mathbf{k}$-$\mathbf{k}'$ or annihilates one with wave vector equivalent to $\mathbf{k}'$-$\mathbf{k}$. We postulate that the E-P matrix element is equal to the matrix element between one-electron wave functions of the linear change in the one-electron Hamiltonian H resulting when each nucleus undergoes a displacement equal to the matrix element of its position operator between phonon states. The nuclear position operator

$$\mathbf{u}_{lb}=\sum\nolimits_{\mathbf{q}p}(\hbar/2m_b\omega_{\mathbf{q}p}N)^{1/2}(e^{i\mathbf{q}\cdot\mathbf{r}_l}\mathbf{e}_b a+e^{-i\mathbf{q}\cdot\mathbf{r}_l}\mathbf{e}_b^* a^\dagger) \tag{2.3}$$

has matrix element

$$\langle\mathbf{u}_{lb}\rangle=(n\hbar/2m_b\omega_{\mathbf{q}p}N)^{1/2}e^{i\mathbf{q}\cdot\mathbf{r}_l}\mathbf{e}_b(\mathbf{q}p) \tag{2.4}$$

for annihilation of a phonon of wave vector $\mathbf{q}$ and

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[9] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 11.

[10] B. N. Brockhouse, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin, Inc., New York, 1964), p. 221.

[11] F. Bloch, Z. Physik **52**, 555 (1928).

[12] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[13] E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1962), Vol. 13, pp. 305, 347.

[14] Maradudin *et al.*, Ref. 9, p. 30.

[15] C. Herring, in *Proceedings of the International Conference on Semiconductor Physics Prague, 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 62.

branch p. The corresponding E-P matrix element is

$$M_{\mathrm{E-P}}=(n\hbar/2\omega_{\mathbf{q}p})^{1/2}\langle\mathbf{k}_2 j_2|\,\partial H/\partial Q_{\mathbf{q}p}|\mathbf{k}_1 j_1\rangle. \quad (2.5)$$

The E-P matrix element for the conjugate process, in which an electron is scattered from $\mathbf{k}_2 j_2$ to $\mathbf{k}_1 j_1$ with creation of a phonon in mode $\mathbf{q}p$, is simply the complex conjugate

$$M_{\mathrm{E-P}}{}^*=(n\hbar/2\omega_{\mathbf{q}p})^{1/2}\langle\mathbf{k}_1 j_1|\,\partial H/\partial Q_{\mathbf{q}p}|\mathbf{k}_2 j_2\rangle. \quad (2.6)$$

Here j_1 and j_2 indicate the electron bands, n is the occupation of the $\mathbf{q}p$ mode when the electron is in $\mathbf{k}_1 j_1$, and the wave vectors satisfy

$$\mathbf{k}_2=\mathbf{k}_1+\mathbf{q}+\mathbf{G}, \quad (2.7)$$

with $\mathbf{G}$ a reciprocal lattice vector.

This form of E-P interaction is in essence that proposed by Bloch[16] in 1928. Bloch used the deformable ion prescription for $\partial H/\partial Q$, and he considered only real transitions. Subsequently, several other treatments have been proposed[1] for the effective electron wave functions and the linear change of the effective electron Hamiltonian needed for the Bloch formula (2.5). In 1950, Frölich[17] introduced the consideration of virtual matrix elements, in connection with superconductivity. Since then several attempts have been made at a rigorous, first-principles treatment of the E-P interaction. But every approach, when reduced to a form susceptible to detailed realistic calculation, seems to lead back toward the Bloch formula (2.5). There are formal manipulations[7] which purport to show that at least for real transitions it is in essential agreement with other approaches, such as the Born-Oppenheimer separation,[18,19] the Nakajima-Bardeen-Pines canonical transformation,[18] and the deformation transformation.[20]

III. PSEUDOPOTENTIAL THEORY

Evaluation of the Bloch formula (2.5) for the E-P interaction requires an electron Hamiltonian whose eigenfunctions may be readily determined, and a prescription for the derivative of that Hamiltonian with respect to the phonon normal coordinate. The Hamiltonian ought also to meet the test that its eigenvalues reasonably represent the experimental band structure over the range of energy and wave vector encompassed by the E-P matrix elements to be computed.

There is available a simple local potential which reproduces the Ge band structure within 0.3 eV over the 10-eV range reached by ultraviolet-reflection measurements.[21] This crudeness is not necessarily serious, since a small change in the potential produces a significant change in energy levels but a surprisingly small change in wave functions. Furthermore, the total electron Hamiltonian should include, in addition to this local potential, a spin-orbit term; and the spin-orbit splittings in Ge are of order 0.3 eV.

This potential is a pseudopotential in that it has no bands representing the core levels; its lowest eigenvalue corresponds to the bottom of the valence band. But it is not so weak that the electrons become "nearly free." For nearly free electrons, the eigenfunctions at wave vectors of high symmetry can be well approximated by a single plane wave symmetrized to give the appropriate representation of the group of the wave vector; and the eigenvalue can be well approximated by the kinetic energy of the plane waves plus the expectation of the potential in the symmetrized combination. The energy gap at $\mathbf{k}=0$ in Ge is between the lowest valence states of $\Gamma_{25'}$ and $\Gamma_{2'}$ symmetry. For the $\Gamma_{25'}$ and $\Gamma_{2'}$ symmetrized plane waves (SCPW) of lowest kinetic energy, the diagonal matrix element of the pseudopotential happens to vanish, while the matrix element connecting to the next lowest SCPW is, in each case, greater than the kinetic energy difference.

In the diamond structure there are "forbidden" Fourier components of potential which vanish for a potential having full cubic instead of only tetrahedral symmetry about each nuclear site. The forbidden components of one-electron potential should be small, despite the tetrahedral distortion associated with covalent bonding, because the corresponding components of charge density are small. The (222) forbidden component of charge density is actually large enough to be measurable by x rays in C and Si, but in Ge any asphericity of the valence-electron charge density is masked by the larger core contribution.[22] The pseudopotential for Ge referred to above has no forbidden components. Hence it can be decomposed into identical spherical units, each centered at a nuclear site. This suggests that the pseudopotential for the lattice distored by a phonon could be found by rigidly moving each spherical unit with its nucleus.

Such a "rigid ion" prescription is plausible for a complete (including core states) theory, because in the various schemes for constructing a crystal potential, the contributions of the individual Hartree or Hartree-Fock ions are, in general, just so superposed. The effect of the other valence electrons on the long-range part of the bare ion potential is accounted for by some process of cellular truncation or dielectric response analysis. Since this process in practice has spherical symmetry, the potential associated rigidly and independently with each nucleus is spherically symmetric.

It has been argued[7] that a rigid-ion prescription ought to be equally valid in a pseudopotential represen-

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[20] L. J. Sham and J. M. Ziman, Ref. 7, p. 241.

[21] D. Brust, Phys. Rev. **134**, A1337 (1964).

[22] J. J. DeMarco and R. J. Weiss, Phys. Rev. **137**, A1869 (1965); S. Göttlicher and E. Wölfel, Z. Electrochem. **63**, 891 (1959).

tation. The kernel of the argument is the "general pseudopotential scattering theorem,"[23,24] which is: Let the (possibly nonlocal) complete potential rigidly carried by individual nuclei be nonoverlapping even as seen by an electron incident at a valence-band energy, and consider only E-P transitions conserving electron (not total) energy.

For each bound state of the individual potential unit, there will be a band of zero width. To pass to a pseudopotential representation, add to the complete Hamiltonian H a repulsive term $V_R=(E-H)P$, where P is the projection operator onto the core bands, and E is the valence electronic energy at which the transition occurs. This V_R will almost surely be nonlocal, even if the original potential was local. The eigenfunctions for eigenvalue E of the pseudo-Hamiltonian $H_p=H+V_R$ comprise all the pseudo-wave functions, that is, "smooth" functions whose projections orthogonal to the core bands are eigenfunctions of the true Hamiltonian H at eigenvalue E. The theorem states that instead of using the true eigenfunctions and $\partial H/\partial Q$ to calculate the E-P interaction, we may equally well use any corresponding pseudo-wave functions and $\partial H_p/\partial Q$.

There are other pseudo-Hamiltonians which will include some of the pseudo-wave functions among their eigenfunctions. In general, these operators are not Hermitian and do not give quite the correct phonon scattering. The situation is analyzed in Ref. 24.

While this "theorem" leaves open the question of what happens in other than the ubiquitous "good metal" and for general transitions, it does support the rigid-ion prescription in a pseudopotential representation, with the proviso that the change of electronic energy should be small compared to the difference between either level and the highest core level. As mentioned above, Ge is not exactly a free-electron metal, even in the pseudopotential representation. If we accept the great computational convenience of neglecting tetrahedral and cubic distortion in the pseudopotential assigned to each core, we still have spheres of influence that are definitely overlapping. It is the interference pattern of the core potentials arranged in the diamond structure that causes the pileup of valence electrons at the tetrahedral bonding sites.

IV. DETERMINATION OF THE PSEUDOPOTENTIAL BAND STRUCTURE

Use of a local pseudopotential to represent all but the spin-orbit coupling term in the electron Hamiltonian greatly simplifies calculations, and the subject of electron-phonon interaction is murky enough that there is no certainty that a more complicated approach would give a better answer.

Treatment of the spin-orbit (s-o) coupling is standard.[25,26] It is important only near symmetry points where there are degeneracies in the nonrelativistic band structure that may be split. At $\Gamma_{25'}$, for example, the six spinors formed from the three orbitals are arranged into $\Gamma_7{}^+$ and $\Gamma_8{}^+$ representations of the double group. These are spinor eigenfunctions of the total one-electron Hamiltonian, neglecting the off-diagonal s-o matrix element connecting them to $\Gamma_7{}^+$ and $\Gamma_8{}^+$ functions higher up in the band structure. This is a very good approximation, because the s-o matrix elements in Ge are of order $\sim$0.1 eV, while the smallest energy denominator here is about 11 eV. The s-o matrix elements cannot be calculated just from the pseudo wavefunctions and the known form of the s-o operator, because in Ge the matrix elements depend almost completely on the core part of the true wave functions.[26] Instead, the diagonal matrix elements are taken from the experimental band splittings.

We now discuss in detail the pseudopotential representation of the Ge band structure mentioned in the preceding section. Choose the origin at an inversion center and align a Cartesian coordinate system with the crystallographic axes. The two atoms in the unit cell at the origin ($\mathbf{r}_l=0$) are at

$$\mathbf{r}_{0b}=\pm\tfrac{1}{2}\boldsymbol{\tau}=\pm(111)a/8. \tag{4.1}$$

The Ge lattice constant is designated by a. The pseudopotential can be given as a Fourier series

$$V(\mathbf{r})=\textstyle\sum_{\mathbf{G}}V(\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{r}}, \tag{4.2}$$

where $\mathbf{G}$ is a reciprocal lattice vector. In order that the entire protential be invariant under the diamond space group $O_h{}^7$, certain $V(\mathbf{G})$ must be zero and all $V(\mathbf{G})$ of equal $|\mathbf{G}|$ must have equal magnitude and a certain relative sign. If we take $V(\mathbf{r})$ as a superposition of identical spherical units,

$$V(\mathbf{r})=\textstyle\sum_{lb}U(\mathbf{r}-\mathbf{r}_{lb}), \tag{4.3}$$

then the Fourier coefficients $V(\mathbf{G})$ may be written as the product of a form factor and a structure factor, *viz*,

$$V(\mathbf{G})=U(\mathbf{G})\cos\mathbf{G}\cdot\tfrac{1}{2}\boldsymbol{\tau}. \tag{4.4}$$

The form factor is the Fourier transform

$$U(\mathbf{K})=U(|\mathbf{K}|)=(\tfrac{1}{2}\Omega)^{-1}\int d^3r e^{-i\mathbf{K}\cdot\mathbf{r}}U(\mathbf{r}), \tag{4.5}$$

where $\frac{1}{2}\Omega$ is the volume per atom and the integration is over all space.

Thus a potential $V(\mathbf{r})$, which is completely general except that it lacks the forbidden components, may be specified by giving the values of the function $U(|\mathbf{K}|)$ for the discrete set $|\mathbf{K}|=|\mathbf{G}|$, where

$$|\mathbf{G}|^2=3,8,11,16,24,\cdots \tag{4.6}$$

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[23] L. J. Sham, Proc. Phys. Soc. (London) **78**, 895 (1961).

[24] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

[25] E. O. Kane, J. Phys. Chem. Solids **1**, 83 (1956).

[26] L. Liu, Phys. Rev. **126**, 1317 (1962).

in units of $(2\pi/a)^2$. The approximate magnitude of these $U(K)$ can be guessed *a priori:* If it means anything to say crudely that the projection of a pseudo-wave function orthogonal to some core states is a true wave function, then these $U(K)$ ought to lie roughly along the "universal orthogonalized-plane-wave (OPW) form factor" curve discussed by Harrison.[27] Indeed, Harrison has computed a curve[28] for Si which gives Brust's[21] empirical points to within 25%.

Since the remaining variability of $U(|\mathbf{G}|)$ can correspond to a rather large variability in electronic energy levels, a fine adjustment of $U(|\mathbf{G}|)$ can be performed by requiring that it give a good account of the experimental band structure. The "experimental" structure should be for the pure crystal at zero temperature, with spin-orbit effects subtracted. Thus the direct gap $\Gamma_{2'}-\Gamma_{25'}$ should be more like 1.00 eV than 0.80 eV. At this point, however, it is sobering to take note of a calculation by Herman[29] indicating that the relativistic terms invariant under the single group contribute -0.84 eV to the direct gap in Ge.

Some decision must be made on how to treat the $U(|\mathbf{G}|)$ for $|\mathbf{G}|^2>11$. Phillips[30] took them all equal to $U(11)$, while Brust[21] took them all equal to zero. Since the proposed calculation may be delicate, something more plausible should be done. Four-parameter functional forms to bring the $U(K)$ curve smoothly back to zero at large K have been suggested by Bassani and Brust,[31] and by Falicov and Golin.[32] There is no apparent reason not to have it again become negative, as happens with some of Harrison's OPW form factor curves.[33] However, this would be expected to happen at around $K=4K_F$, which is too short a wavelength to have much effect at the energy levels of interest. (By K_F is meant the radius of the Fermi sphere of a noninteracting fermion gas, equal in average density to the Ge valence electrons.)

TABLE I. Pseudopotential form factors in rydbergs. The points listed in the upper part of the table determine the band structure. The other points are needed for a rigid-ion calculation of E-P matrix elements between Γ and L.

$(Ka/2\pi)^2$	K/K_F	$U_A(K)$	$U_B(K)$
3	1.11	-0.230	-0.230
8	1.81	0	0
11	2.12	$+0.060$	$+0.050$
16	2.56	$+0.085$	$+0.060$
19	2.78	$+0.070$	$+0.040$
24	3.13	$+0.025$	$+0.015$
$\frac{3}{4}$	0.55	-0.49	-0.49
$2\frac{3}{4}$	1.06	-0.255	-0.255
$4\frac{3}{4}$	1.39	-0.125	-0.125
$6\frac{3}{4}$	1.66	-0.038	-0.038
$8\frac{3}{4}$	1.89	$+0.018$	$+0.018$
$10\frac{3}{4}$	2.10	$+0.055$	$+0.045$
$12\frac{3}{4}$	2.28	$+0.080$	$+0.065$
$14\frac{3}{4}$	2.45	$+0.088$	$+0.065$
$16\frac{3}{4}$	2.62	$+0.082$	$+0.055$

TABLE II. Electronic energy levels in electron volts. In all three cases, the average pseudopotential was arbitrarily chosen zero. It is expected that the exact eigenvalues for the potentials given in Table I are 0.05-0.10 eV lower than those shown here. Also shown for reference are the experimental relative energy levels at zero temperature, with the spin-orbit splitting of $\Gamma_{25'}$ and $L_{3'}$ deducted. (The zero level is arbitrarily taken at $\Gamma_{2'}$.)

	No potential	Potential A	Potential B	Relative "experimental"
$\Gamma_{2'}$	14.15	10.43	10.29	0
L_1	13.07	10.33	10.29	-0.15
$\Gamma_{25'}$	14.15	9.32	9.63	-1.00
$L_{3'}$	13.07	8.24	8.51	-2.35

Since the eigenvectors from previous pseudopotential calculations of the Ge band structure were not immediately available, it was decided to start afresh and to pay closer attention to short wavelengths. Two plausible $U(K)$ curves were used. Table I gives pertinent values of both; a sketch of $U_B(K)$ has appeared in Ref. 8. Potential A is an interpolation and extrapolation through Brust's[21] values, while potential B has a slightly weaker repulsive core.

By considering only wave vectors of high symmetry, calculations could be carried out by hand. Symmetrized combinations of plane waves[34] and secular determinants for the electronic energy levels were found. The determinants were truncated at about 50 plane waves (from 4 to 9 symmetrized plane waves), and the eigenvalues (Table II) and eigenvectors (Table III) found for both edges of the gap at Γ and L. It appears that potential A gives a somewhat better representation of the relative energy levels. The momentum matrix element $\langle S|p_x|X\rangle$ across the direct gap at Γ is 1.04 h/a for both sets of normalized pseudo-wave functions. The experimental value is about 1.18 h/a; an error of this direction and magnitude is to be expected in a pseudopotential representation.[35]

By the standard formulas of $\mathbf{k}\cdot\mathbf{p}$ perturbation theory,[25] the electronic wave functions near a symmetry point in the Brillouin zone can be expressed in terms of those at the symmetry point. Since a manageable theory of interband transitions would take into account the mixing-in only of the states immediately across the gap, consideration of only the four states indicated in Tables II and III should be adequate.

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[32] L. M. Falicov and S. Golin, Phys. Rev. **137**, A871 (1965).

[33] W. A. Harrison, Phys. Rev. **129**, 2512 (1963); **136**, A1107 (1964).

[34] The chosen symmetrized plane waves are given in the author's Ph.D. thesis, Johns Hopkins University, 1965 (unpublished).

[35] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).

TABLE III. Coefficients of normalized symmetrized plane waves in the expansion of normalized electron eigenfunctions. The SCPW are labeled by the squared length of the wave vector in units of $(2\pi/a)^2$.

	$\Gamma_{2'}$			$\Gamma_{25'}$	
K^2	A	B	K^2	A	B
3	0.854	0.853	3	0.804	0.814
4	0.518	0.543	4	0.579	0.562
11	0.061	0.024	8	0.108	0.120
12	0.043	0.017	11^a	0.088	0.078
			11^b	0.028	0.034
			12	−0.051	−0.045

	L_1			$L_{3'}$	
K^2	A	B	K^2	A	B
$\frac{3}{4}$	−0.407	−0.419			
$2\frac{3}{4}$	+0.856	+0.856	$2\frac{3}{4}$	0.954	0.956
$4\frac{3}{4}$	−0.282	−0.274	$4\frac{3}{4}$	0.210	0.211
$6\frac{3}{4}(2)$	+0.098	+0.084	$6\frac{3}{4}$	−0.175	−0.168
$6\frac{3}{4}(6)$	−0.049	−0.064	$8\frac{3}{4}^a$	0.075	0.069
$8\frac{3}{4}$	−0.010	+0.007	$8\frac{3}{4}^b$	0.070	0.069
$10\frac{3}{4}$	+0.010	+0.026	$10\frac{3}{4}$	−0.060	−0.059
$12\frac{3}{4}$	+0.056	+0.044	$12\frac{3}{4}$	−0.010	−0.012
$12\frac{3}{4}$	+0.010	+0.009	$12\frac{3}{4}$	−0.002	−0.002

V. MATRIX ELEMENTS BETWEEN Γ AND L

Consider a process in which a phonon of wave vector $\mathbf{q}$ and branch p is absorbed. In the approximation of rigid spheres of influence, the potential associated with the phonon is

$$\partial V/\partial Q_{\mathbf{q}p}=\delta V=-(2/\rho V)^{1/2}\sum_{lb}e^{i\mathbf{q}\cdot\mathbf{r}_l}\mathbf{e}_b(\mathbf{q}p)\times\nabla U(\mathbf{r}-\mathbf{r}_{lb}). \quad (5.1)$$

Here $\mathbf{r}_l$ is the position of the inversion center in the lth cell, $\mathbf{r}_{lb}$ are the positions of the two atoms in the lth cell, ρ is the crystal density, and V is the arbitrary phonon normalization volume. The phonon potential may be expanded in a Fourier series:

$$\delta V(\mathbf{r})=\sum_{\mathbf{G}}\delta V(\mathbf{q}+\mathbf{G})e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}, \quad (5.2)$$

$$\delta V(\mathbf{q}+\mathbf{G})=-\left(\frac{2}{\rho V}\right)^{1/2}\int_{-\infty}^{+\infty}d^3r\,\Omega^{-1}e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\sum_b\mathbf{e}_b\cdot\nabla U(\mathbf{r}-\mathbf{r}_{0b}). \quad (5.3)$$

The gradient operator in (5.3) is transferred to the exponential by partial integration. A plausible asymptotic form for $U(\mathbf{r})$ would be a charge of +4 screened by the Ge dielectric constant of 16. Since there is no surface integral contribution, even if $U(\mathbf{r})$ does fall off as slowly as $1/r$, we have

$$\delta V(\mathbf{q}+\mathbf{G})=-i(2/\rho V)^{1/2}U(|\mathbf{q}+\mathbf{G}|)(\mathbf{q}+\mathbf{G})\cdot\tfrac{1}{2}\sum_b\mathbf{e}_b e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_{0b}}. \quad (5.4)$$

TABLE IV. Phonon eigenvectors.

Component		TOI	LO	LA	TAI
$-\frac{1}{2}\boldsymbol{\tau}$	e_x	$i/2$	$1/\sqrt{6}$	$i/\sqrt{6}$	1/2
	e_y	$-i/2$	$1/\sqrt{6}$	$i/\sqrt{6}$	−1/2
	e_z	0	$1/\sqrt{6}$	$i/\sqrt{6}$	0
$+\frac{1}{2}\boldsymbol{\tau}$	e_x	$i/2$	$-1/\sqrt{6}$	$i/\sqrt{6}$	−1/2
	e_y	$-i/2$	$-1/\sqrt{6}$	$i/\sqrt{6}$	1/2
	e_z	0	$-1/\sqrt{6}$	$i/\sqrt{6}$	0

In this section, we consider only the special case of electron states exactly at the band extrema. A phonon connecting such states has L symmetry, which greatly simplifies the determination of the phonon potential. Because of the cubic symmetry, it is sufficient to consider only one of the four inequivalent L points in the Brillouin zone; we choose $\mathbf{q}=(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$. The possible $\mathbf{e}_b(\mathbf{q}p)$ are completely determined by symmetry: Both nuclear displacements must be precisely along or transverse to the wave vector $\mathbf{q}$, and the relative phase must be 0 or π. The only question is whether the $\mathbf{e}_b(\mathbf{q}p)$ of a given parity belongs to the acoustical or optical branch. After comparison of the experimental phonon dispersion curves[36] with the general force-constant expansion of the dynamical matrix,[37] there is no question that the transverse optical (TO) is odd ($L_{3'}$) and the transverse acoustical (TA) is even (L_3). Definite parity assignment to the longitudinal branches cannot be made by force constant arguments[37]; but from the interband transition experiments, it is clear[38] that the acoustic (LA) is odd ($L_{2'}$), and the optic (LO) even (L_1).

The phase of the phonon eigenvector $\mathbf{e}_b(\mathbf{q}p)$ and of the electronic wave function $e^{i\mathbf{k}\cdot\mathbf{r}}u_j(\mathbf{k},\mathbf{r})$ is arbitrary. In a material such as Ge with inversion symmetry, it is possible to use a gauge

$$\mathbf{e}_b^*=-\mathbf{e}_{-b} \quad \text{and} \quad u^*(\mathbf{r})=u(-\mathbf{r})$$

in which the E-P matrix element is real. Eigenvectors chosen accordingly are shown in Table IV. Only one polarization of the transverse phonon is indicated.

In order to evaluate (5.4) for any plane wave, the values of $U(|\mathbf{q}+\mathbf{G}|)$ in the lower part of Table I are needed. Except for $U(\frac{3}{4})$, these represent an interpolation between points fairly well fixed by the band structure. The value $U(\frac{3}{4})=-0.49Ry$ is needed only for the longitudinal phonons; this is a remnant of the ancient rule that only longitudinal phonons interact with electrons. The extrapolation is fairly unambiguous because the curvature of $U(K)$ is nearly zero in the region between $K^2=3$ and $K^2=\frac{3}{4}$. Furthermore, the $U(K)$ for Ge should be fairly close to the universal "good metal"[27] curve, even for a wave vector as short as $K^2=\frac{3}{4}$, because at this point the wave vector dependent dielectric constant $\epsilon(K)$ suggested for Ge by Penn[39] is only about 15% less than either the Thomas-Fermi or free-electron Hartree formulas for $\epsilon(K)$ appropriate to "good metals." In other words, for

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[36] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[37] F. Herman, J. Phys. Chem. Solids **8**, 405 (1959).

[38] M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961); J. J. Tiemann (private communication).

[39] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

TABLE V. Coefficients in plane-wave expansion of $\partial V/\partial Q$ for the two potentials, A and B. The units are rydbergs times $(\rho V)^{-1/2}(2\pi/a)$.

Plane wave	TOI		LO		LA		TAI	
	A	B	A	B	A	B	A	B
$\frac{1}{2}(111)$			−0.390		−0.162			
$\frac{1}{2}(3\bar{1}\bar{1})$	−0.334		−0.028		−0.068		−0.138	
$\frac{1}{2}(\bar{1}33)$	−0.068		−0.167		+0.069		+0.162	
$\frac{1}{2}(333)$			+0.038		+0.092			
$\frac{1}{2}(511)$	+0.050		−0.030		+0.071		−0.021	
$\frac{1}{2}(5\bar{3}1)$	+0.020		+0.028		+0.011		+0.048	
$\frac{1}{2}(\bar{5}33)$	−0.144	−0.117	+0.006	+0.006	+0.014	+0.011	−0.059	−0.048
$\frac{1}{2}(155)$	+0.044	+0.035	−0.235	−0.191	−0.098	−0.079	+0.105	+0.085
$\frac{1}{2}(7\bar{1}\bar{1})$	−0.086	−0.071	+0.106	+0.086	−0.044	−0.035	+0.209	+0.170
$\frac{1}{2}(7\bar{1}3)$	−0.249	−0.170	−0.176	−0.130	−0.425	−0.311	−0.096	−0.071
$\frac{1}{2}(\bar{3}55)$	+0.231	+0.170	+0.068	+0.051	−0.164	−0.122	−0.095	−0.071
$\frac{1}{2}(733)$	+0.044	+0.030	−0.285	−0.191	+0.119	+0.079	−0.108	−0.072

reasonably short wavelength disturbances, such as an L phonon, the energy gap does not drastically affect the screening capability of the valence electrons. For very long wavelength disturbances in insulators, the model of independently screened spherical pseudo-ions must be examined more closely.[40]

For each of the four phonons in Table IV, the coefficients (5.4) determine the expansion of the phonon potential $\partial V/\partial Q_{\mathbf{q}p}$ in the SCPW[34] with the symmetry of the phonon. Table V gives the coefficient of one member of each SCPW.

It is perhaps not completely trivial to remark that these expansions would be the same if $\mathbf{q}$ had been taken as $-(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$, or any other wave vector equivalent to $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$, instead of $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$; a phonon is the same thing regardless of which of a set of equivalent wave vectors is used to label it.

It is necessary to choose a specific basis for each degenerate electron and phonon state involved in the calculation. For the electrons at $\Gamma_{25'}$, we make the usual choice of functions transforming like X, Y, and Z. (More precisely but less concisely, the $\Gamma_{25'}$ functions transform as YZ, XZ, and XY.) For $L_{3'}$ electrons and L_3, $L_{3'}$ phonons, we define basis functions $|\mathrm{II}\rangle$ and $|\mathrm{I}\rangle$ polarized within and perpendicular to, respectively, the $1\bar{1}0$ reflection plane:

$$\rho_{x\bar{y}}|\mathrm{I}\rangle = -|\mathrm{I}\rangle, \tag{5.5}$$

$$\rho_{x\bar{y}}|\mathrm{II}\rangle = +|\mathrm{II}\rangle, \tag{5.6}$$

$$\langle \mathrm{I}|\delta_{3xyz}|\mathrm{II}\rangle = +\tfrac{1}{2}\sqrt{3}. \tag{5.7}$$

We use the standard notation of ρ for a reflection operator, δ for a rotation operator. Under the C_{3v} subgroup Λ of the D_3 group at L, I transforms like $(X-Y)/\sqrt{2}$ and II like $(2Z-X-Y)/\sqrt{6}$. We denote the one-dimensional representations $\Gamma_{2'}$ by S, L_1 and $L_{2'}$ by L.

Now that SCPW expansions have been obtained for the phonon potential (Table V) and the electron eigenfunctions (Table III), calculation of the Bloch E-P matrix element (2.5) is straightforward. For the electron states, SCPW coefficients become small after the first two or three, but this is not the case for the phonon potential. Therefore, it is necessary to consider in $\partial V/\partial Q$ wave vectors as long as the sum of two wave vectors appearing with large coefficients in the SCPW expansion of the electronic eigenfunctions; this includes about 70 waves. At the outer (long-wave-vector) part of this region, the coefficients (Table V) are relatively large this reflects principally the positive peak in $U(K)$, representing the "repulsive core" of the atomic pseudopotential. The importance of these wave vectors in the phonon potential is illustrated in Fig. 1 by the significant change between 52 and 70 plane waves.

In practice, the calculation was carried no further than the 76 waves indicated in Table V. Table VI gives a complete, nonredundant selection of matrix elements for all allowed processes between the band edges. By comparison with Table II, it is seen that the matrix elements are less sensitive than relative energy levels to the choice of pseudopotential. A feel for the numerical work suggests that the uncertainty due to truncation of the electron and phonon SCPW expansions is comparable to the uncertainty due to choice of pseudo-

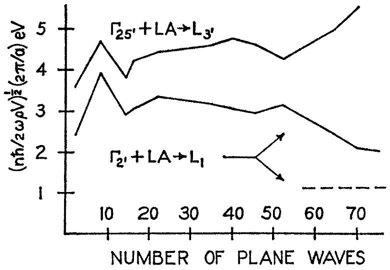

FIG. 1. Convergence of the E–P matrix element with number of $\partial V/\partial Q$ plane waves for the LA transitions in potential B. Shown dashed in McLean's value for $\Gamma_{2'}$+LA → L_1. Number of waves in the electron eigenfunctions is held constant at ∼50, but the calculation is insensitive beyond ∼20. Rapidity of apparent convergence was comparable for the $\Gamma_{25'} \rightarrow L_1$ transitions, worse for $\Gamma_{2'}$+TA → $L_{3'}$, better for all components of $\Gamma_{25'}$+TO → $L_{3'}$.

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[40] L. Kleinman, Phys. Rev. **130**, 2283 (1963).

TABLE VI. Electron-phonon matrix elements between Γ and L in units of $(n\hbar/2\omega\rho V)^{1/2}(2\pi/a)$ times electron volts.

Process	Specific matrix elements	Potential A	B
$\Gamma_{2'}+\mathrm{LA}\rightarrow L_1$	$\langle L\|L\|S\rangle$	2.0	2.0
$\Gamma_{25'}+\mathrm{TA}\rightarrow L_1$	$\langle L\|\mathrm{I}\|(X-Y)/\sqrt{2}\rangle$	1.9	1.7
$\Gamma_{25'}+\mathrm{LO}\rightarrow L_1$	$\langle L\|L\|(X+Y+Z)/\sqrt{3}\rangle$	−4.0	−4.4
$\Gamma_{25'}+\mathrm{LA}\rightarrow L_{3'}$	$\langle \mathrm{I}\|L\|(X-Y)/\sqrt{2}\rangle$	5.9	5.5
$\Gamma_{2'}+\mathrm{TA}\rightarrow L_{3'}$	$\langle \mathrm{I}\|\mathrm{I}\|S\rangle$	0.8	1.0
$\Gamma_{25'}+\mathrm{TO}\rightarrow L_{3'}$	$\langle \mathrm{I}\|\mathrm{II}\|(X-Y)/\sqrt{2}\rangle$	13.5	13.3
	$\langle \mathrm{I}\|\mathrm{I}\|(X+Y)/\sqrt{2}\rangle$	−2.4	−2.2
	$\langle \mathrm{I}\|\mathrm{I}\|Z\rangle$	+8.6	8.1

potential, which is indicated in Table VI by the last two columns.

Data from interband transition experiments have already been successfully reduced to an E-P matrix element apparently only for the transition $\Gamma_{2'}+\mathrm{LA}\rightarrow L_1$. McLean[41] deduced from optical absorption an equivalent deformation potential of 1.3 eV. Since $|\mathbf{q}|=\frac{1}{2}\sqrt{3}(2\pi/a)$, the matrix element is 1.1, in the units of Table VI. Since one would like to believe the error in the experimental value to be less than 50%, the value of 2.0 in Table VI is definitely high. Furthermore, that value was obtained with normalized pseudo-wave functions. If we normalized, instead, the projection of the pseudo-wave functions orthogonal to a space of core states, the theoretical value would be increased by 15–20%. Of course, the values in Table VI are already at least that uncertain anyway. At this point, we might bring up the remark of McLean[41] that it one attempts to estimate the $\Gamma_{2'}+\mathrm{LA}\rightarrow L_1$ E-P matrix element by an extrapolation of deformation potential theory, using the experimental deformation potentials, one comes out an order of magnitude above experiment.

We hope to return in the future to the question of obtaining from past or future interband transition experiments more information on the E-P matrix elements involved.

VI. DEFORMABLE ION

Because the approximation of rigid spheres of influence is especially questionable for the covalently bonded diamond structure, it would be of interest to obtain some estimate of the sensitivity of the E-P matrix element to the prescription used in computing $\partial V/\partial Q$. An alternative is offered by the original prescription of Bloch,[16] the "deformable ion." To apply this, it is necessary to interpolate "smoothly" between the displacements at the nuclear sites. The method is purely intuitive and not derivable from more general principles, so that no precise criterion is offered for making this interpolation. However, at or near wave vectors of high symmetry, such as the center of the zone or the center of a face, the restrictions of symmetry on the interpolation are so great that it is possible to get answers without being too arbitrary. We now parallel the work of the preceding section, using the deformable ion.

The phonon potential is

$$\partial V/\partial Q=\delta V(\mathbf{r})=-(2/\rho V)^{1/2}\nabla V(\mathbf{r})\cdot\delta\mathbf{x}(\mathbf{r})\,, \qquad (6.1)$$

where $\delta\mathbf{x}$ is to equal $\mathbf{e}_b$ at the nuclear sites, and the entire potential is to have the same symmetry as the phonon under the group of L. Therefore, $\delta\mathbf{x}(\mathbf{r})$ must be everywhere transverse or everywhere longitudinal, and the interpolation need be performed only on its algebraic magnitude. This magnitude is to be of L_1 symmetry for the odd modes LA, TO, and of $L_{2'}$ symmetry for the even modes LO, TA. The most general such function can be expanded in the appropriate SCPW. The "smoothness" criterion then could be interpreted as meaning that only one or a few of the SCPW of shortest wave vector be used. Once the Fourier expansion of $\delta\mathbf{x}(\mathbf{r})$ is chosen, it can be folded into the expansion of the crystal potential $V(\mathbf{r})$ to give the plane-wave coefficients of $\partial V/\partial Q$. In this model, we need only the $U(K)$ pertaining to the band structure, and the lower part of Table I is not used.

For the even modes, we used just the longest wavelength $L_{2'}$ SCPW; normalized to $(2)^{-1/2}$ at $\mathbf{r}=-\frac{1}{2}\boldsymbol{\tau}$, this is

$$-0.766\,\sin\pi a^{-1}(x+y+z)\,.$$

For TA, the resulting phonon potential coefficient closely resembled the rigid-ion values shown in Table V. For the $\Gamma_{25'}+\mathrm{TA}\rightarrow L_1$ transition, this was reflected in the E-P matrix elements, which were 2.0 and 1.4 for potentials A and B, respectively. It was noted in the caption to Fig. 1 that $\Gamma_{2'}+\mathrm{TA}\rightarrow L_{3'}$ showed the poorest convergence; this effect was magnified for the deformable ion, so that from as far as the calculation was carried, it was difficult to say more than that the matrix element was small.

For LO, the potential components again bore some resemblance to those in Table V. However, the calculation of $\Gamma_{25'}+\mathrm{LO}\rightarrow L_1$ showed poorer convergence, greater dependence on pseudopotential choice, and smaller result (by half an order of magnitude), compared to the corresponding calculation in Sec. V.

For the odd modes, a deformable ion calculation was first performed using just the longest wavelength L_1 SCPW. Normalized to $i/\sqrt{2}$ at $\mathbf{r}=\pm\frac{1}{2}\boldsymbol{\tau}$, this is 1.85 $i\cos\pi a^{-1}(x+y+z)$. This is a rather implausible interpolation in that the peak displacement is 2.61 times the displacement at the nuclear sites. For LA, a typical plane-wave coefficient was twice as large and of opposite sign compared to the rigid case. The situation was similar for the resulting E-P matrix elements. For TO, there did not seem to be much relation at all, beyond comparable magnitude.

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[41] T. P. McLean, Ref. 2, pp. 53, 86.

TABLE VII. Matrix elements between electronic wave functions of derivative with respect to wave vector in the (111) direction of $e^{-i(\mathbf{q}-\mathbf{q}_0)\cdot\mathbf{r}}\partial V/\partial Q_{\mathbf{q}p}$, in units of $(\rho V)^{-1/2}$ eV, for potential A only. Polarizations chosen are the same as in Table VI. Values are less certain than those of Table VI, as discussed in the text.

Forbidden process	Derivative matrix element
$\Gamma_{2'}+\mathrm{LO}\rightarrow L_1$	8.8
$\Gamma_{25'}+\mathrm{TO}\rightarrow L_1$	4.0
$\Gamma_{25'}+\mathrm{LA}\rightarrow L_1$	15
$\Gamma_{25'}+\mathrm{LO}\rightarrow L_{3'}$	36
$\Gamma_{2'}+\mathrm{TO}\rightarrow L_{3'}$	0.6
$\Gamma_{25'}+\mathrm{TA}\rightarrow L_{3'}$	1.8; 4.4; 4.3

The interpolated displacement, using only the L_1 SCPW of next-to-longest wavelength, is

$$0.255i[\cos\pi a^{-1}(3x-y-z)+\cos\pi a^{-1}(3y-z-x)+\cos\pi a^{-1}(3z-x-y)].$$

Here the ratio of peak to nuclear displacements is 1.08, as was the case with the longest wavelength SCPW for the even modes. For LA, the plane-wave coefficients were smaller but generally of the same sign, compared to Table V. The calculation for $\Gamma_{2'}+\mathrm{LA}\rightarrow L_1$ followed that of Sec. V fairly well, with the results 0.8 and 1.1 for potentials A and B, respectively. Notice that the latter happens to be exactly the experimental result quoted in the preceding section.

For $\Gamma_{25'}+\mathrm{LA}\rightarrow L_{3'}$, there again was poor convergence and sensitivity to the potential. The short wavelength contributions tended to cancel the long-wavelength contributions, in contrast with Fig. 1, so that the result seemed to be nearly an order of magnitude smaller. For TO, the plane-wave coefficients themselves were much smaller than in Table V, but otherwise unrelated.

VII. PHONONS ALONG Λ

For interband transitions with inhomogeneous geometry, such as in tunnel junctions or the Franz-Keldysh effect, and for "forbidden" transitions, it is essential to consider wave vectors away from the symmetry points. As mentioned in Sec. IV, the cell-periodic part $u_j(\mathbf{k},\mathbf{r})$ of an electronic wave function near a symmetry point $\mathbf{k}_0$ is easily expressed to a good approximation in terms of the $u_i(\mathbf{k}_0,r)$ at the symmetry point. Unfortunately, there seems to be no similar simple relation for the cell-periodic part $e^{-i\mathbf{q}\cdot\mathbf{r}}\partial V/\partial Q_{\mathbf{q}p}=u_p(\mathbf{q},\mathbf{r})$ of the phonon potential.

By means of a force-system analysis of neutron-scattering results, one should be able to obtain good expressions for the polarizations $\mathbf{e}_b(\mathbf{q}p)$ near a $\mathbf{q}_0$ where they are determined by symmetry. In our case, $\mathbf{q}_0=(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$. Then $\partial V/\partial Q$ can be calculated as in Sec. V or Sec. VI. The matrix elements

$$\langle\mathbf{k}_0 j'|e^{-i(\mathbf{q}-\mathbf{q}_0)\cdot\mathbf{r}}\partial V/\partial Q_{\mathbf{q}p}|\mathbf{0}j\rangle$$

will suffice to determine the general Bloch E-P matrix element.

Because by far the largest electronic effective mass involved in interband transitions in Ge is the longitudinal mass at L_1, the most important $\delta\mathbf{q}=\mathbf{q}-\mathbf{q}_0$ will be parallel to $\mathbf{q}_0$. Fortunately, this is the easiest to handle, because the $\mathbf{e}_b$ do not change direction. The wave vector $\mathbf{q}$ remains on the symmetry line Λ and its group merely loses the inversion operation. We consider here only this special case.

An exact description of all $\mathbf{e}_b(\mathbf{q}p)$ along Λ requires only two real parameters, which we take as ϕ_t and ϕ_l, the phase of the nuclear displacement at $+\frac{1}{2}\boldsymbol{\tau}$ for the transverse and longitudinal modes, respectively, relative to the phase with wave vector $\mathbf{q}_0$. The phase at $-\frac{1}{2}\boldsymbol{\tau}$ is determined by the condition $\mathbf{e}_b{}^*=-\mathbf{e}_{-b}$ introduced in Sec. V. The parameters ϕ_t and ϕ_l are functions of δq, the algebraic magnitude of the displacement of $\mathbf{q}$ in a (111) direction. (For $\delta q>0$, $\mathbf{q}$ is outside the first Brillouin zone and is equivalent to a wave vector just inside $-\mathbf{q}_0$.) We now specialize to effects linear in δq, which should be sufficient for interband transitions. It would be of definite theoretical interest to consider large δq and perform an interpolation to the deformation potential regime in E-P interaction, but we have not done so.

In general, $e^{-i(\mathbf{q}-\mathbf{q}_0)\cdot\mathbf{r}}\partial V/\partial Q_{\mathbf{q}p}$ does not have definite parity, but the term of zero order in δq does have parity, and the linear term, in fact, has the opposite parity. We shall find the plane wave coefficients of this linear term and then its matrix element between electronic wave functions.

Consider first the method of rigid spherical pseudo ions, in which the plane wave coefficients of $\partial V/\partial Q$ are given by formula (5.4). There are three comparable contributions to the linear change in the coefficient as $\mathbf{q}$ moves away from $\mathbf{q}_0$: the change in $U(|\mathbf{q}+\mathbf{G}|)$, the change in the projection of $\mathbf{q}+\mathbf{G}$ on the direction of polarization (zero for transverse modes), and the change in phase of $\mathbf{e}_b e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_{0b}}$.

For $b=+\frac{1}{2}\boldsymbol{\tau}$, the rate of change of this phase is

$$(\partial\phi/\partial q)-(\sqrt{3}a/8).$$

Consider first the transverse phonons: Since parity changes between Γ and L, the average $\partial\phi_t/\partial q$ over a reciprocal lattice vector is $(a/2\sqrt{3})$. For the two force constant models of Herman[37] fitting the Ge phonons, the $\partial\phi_t/\partial q$ at q_0 are 0.82 and 0.85 of this average.[42] We take the higher value, which gives $(\partial\phi_t/\partial q)-(\sqrt{3}a/8)=0.030a$, with an uncertainty of at least 30%. The final results, in Table VII, are not necessarily this bad, since for the transverse phonons the $e_b e^{-(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_{0b}}$ term is generally the smaller contribution to the linear change in plane wave coefficient.

Secondly, consider the longitudinal phonons: Since the parity does not change between Γ and L, the aver-

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[42] These are for the models labeled ii and iii. For the other models, i and iv, which have the wrong longitudinal parity at L, the values are 1.06 and 0.87.

age $\partial\phi_l/\partial q$ is zero, and at $\mathbf{q}_0$ it should be large and negative. The two Herman[37] values are -2.1 and -1.2 times $\sqrt{3}a/8$. We take the total $(\partial\phi_t/\partial q)-(\sqrt{3}a/8)$ to be $-2.5\sqrt{3}a/8=-0.54a$, again with at least 30% uncertainty. All three effects contribute comparably to the linear change of plane-wave coefficient, so this uncertainty carries over in large measure to the final results in Table VII. Furthermore, the linear approximation itself should be used only with caution in an interband transition calculation, because of the proximity of the branch point connecting LA and LO.

The convergence and general behavior of the calculation was, on the average, the same as for the work of Sec. V. Calculations were made of the quantities in Table VII for the deformable ion case by assuming that no new plane waves were mixed into the interpolating function. General behavior of the calculation was as bad as in Sec. VI; in fact, the algebra is essentially identical. Moreover, the prefactor to the result includes $(\partial\phi/\partial q)-(\sqrt{3}a/8)$, which as discussed above, is rather uncertain.

ACKNOWLEDGMENTS

The author wishes to thank Professor John C. Ward for guidance throughout the course of this work. He also thanks Dr. J. J. Tiemann for introducing this problem to him and Dr. F. S. Ham, Dr. W. A. Harrison, and Dr. G. D. Mahan for helpful discussion.

PHYSICAL REVIEW VOLUME 139, NUMBER 5A 30 AUGUST 1965

Trapping of a Resonant Phonon by a Pair of Paramagnetic Ions*

D. L. Huber
Department of Physics, University of Wisconsin, Madison, Wisconsin

(Received 5 April 1965)

The trapping of a resonant phonon by a pair of paramagnetic ions is studied in the limit of zero temperature with the aid of the Heitler damping formalism. The probability amplitudes of the states (spin 1 up, spin 2 down, no phonon), (spin 1 down, spin 2 up, no phonon), and (spin 1 down, spin 2 down, one phonon) are computed. Provided coherence is maintained between the two spins, the transfer of energy to the crystal lattice takes place in the time $T_{10}(1-\sin k_0r_{12}/k_0r_{12})^{-1}$. Here T_{10} is the spin-lattice relaxation time for an isolated ion at zero degrees, k_0 is the wave vector of the resonant phonon, and r_{12} is the distance between the spins. The relation of this result to the general problem of spin-lattice relaxation at low temperature is discussed.

I. INTRODUCTION

In the standard treatment of the spin-lattice relaxation of a two-level paramagnetic spin system it is assumed that the ensemble of spins can be characterized by a temperature.[1,2] Loosely speaking, a description in terms of a spin temperature different from the lattice temperature is valid whenever the spin-spin relaxation time T_2 is less than the spin-lattice relaxation time T_1.[3] In this paper we will discuss the transfer of energy from the spin system to the lattice for a situation where the opposite condition holds, namely $T_1 \ll T_2$.

At zero degrees an isolated spin in the excited level has a lifetime T_{10}, where T_{10} is the spin-lattice relaxation time evaluated at $T=0$. We will show that the presence of a neighboring spin may greatly enhance this lifetime, provided coherence is maintained between the two spins for intervals greater than T_{10}. We identify this enhancement with the coherent trapping of the resonant phonon. Although the situation studied is somewhat artificial there is reason to believe that the results of the calculation indicate the conditions under which an analogous trapping may be present in a crystal with a large number of spins.

II. THEORY

In order to discuss this effect in detail we start with the Hamiltonian of the two-spin system ($S=\frac{1}{2}$),

$$\mathcal{H}=\omega_0(S_z^1+S_z^2)+\sum_{\mathbf{k}}\omega_k a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+S_x^1\sum_{\mathbf{k}}A_k e^{i\mathbf{k}\cdot\mathbf{r}_1}\times(a_{\mathbf{k}}^\dagger+a_{-\mathbf{k}})+S_x^2\sum_{\mathbf{k}}A_k e^{i\mathbf{k}\cdot\mathbf{r}_2}(a_{\mathbf{k}}^\dagger+a_{-\mathbf{k}}). \quad (1)$$

The first term in (1) is the Zeeman interaction ($\hbar=1$), the second is the phonon Hamiltonian ($a_{\mathbf{k}}$ and $a_{\mathbf{k}}^\dagger$ are the phonon annihilation and creation operators), while the third and fourth terms couple the spins to the lattice. In the interaction terms, $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the locations of the two spins and $\mathbf{k}$ is the phonon wave vector. The x components of the spins are denoted by S_x^1 and S_x^2, and A_k is a coupling constant inversely proportional to the square root of the volume of the crystal. We will assume for simplicity that $\omega_k=vk$ where v is the velocity of sound, and that A_k depends only on the magnitude of $\mathbf{k}$. Since we are interested in the limit $T_1 \ll T_2$ we have omitted the dipolar coupling. The

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* Work supported in part by the Wisconsin Alumni Research Foundation.

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