

Mobility of an electron in a multimode polar lattice

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The interaction of a free electron with a polar lattice possessing more than one infrared-active optical-phonon mode is considered. From the full Lagrangian describing the electron-lattice system in the presence of an applied field we derive an effective electron-phonon coupling constant and an effective longitudinal optical-phonon frequency that we argue give accurate predictions when used in the extensive, existing polaron theories. We apply this formalism to the strongly coupled large polaron of $\text{Bi}_{12}\text{SiO}_{20}$, where the Boltzmann equation cannot apply. We calculate a theoretical prediction for the large polaron mobility as a function of temperature which gives good agreement with experiment. We determine the temperature dependence of Feynman's variational parameters v and w to assist in our predictions. [S0163-1829(99)01426-5]

I. INTRODUCTION

The small mobility of low-density electrons photoexcited into the conduction band of insulating, transparent, and strongly polar cubic n -type $\text{Bi}_{12}\text{SiO}_{20}$ (n -BSO) has been measured at temperatures from 300 to 480 K.¹ The magnitude of the mobility ($\sim 3 \text{ cm}^2/\text{V}^{-1} \text{ s}^{-1}$), its rate of decline with increasing temperature, and its independence of the particular crystal employed suggest that this mobility is intrinsic and dominated by interaction of the electron with longitudinal optical phonons.¹

If an independent-collision model were used to describe the observed electron drift and diffusion, the thermal mean free path ($\sim 0.2 \text{ nm}$) would be less than the de Broglie wavelength, and the collision rate times Planck's constant would be an order-of-magnitude larger than the electron's thermal energy; in this "strong coupling" regime, the Boltzmann equation cannot be expected to apply. In addition, all approaches suggest that the wavefunction of the conduction electron is delocalized over many tens of atoms. Such an electron with its accompanying cloud of virtual phonons has been called a "strongly-coupled large polaron" (in a polar crystal, an electron polarizes the lattice in its neighborhood).

A theory exists to treat this regime,^{2,3} but it assumes that the crystal lattice has only one polar longitudinal optical (LO) phonon branch which has no dispersion; i.e., it uses the much-studied "Fröhlich model" of the polaron.⁴ The starting point of this theory is the quantum-mechanical expression for the expected electron velocity in the presence of an externally applied spatially uniform electric field. The theory proceeds by a perturbation expansion about an unperturbed Hamiltonian (or Lagrangian) in which the electron is coupled to a second free particle rather than to the phonons. This two-particle unperturbed Hamiltonian, which exhibits much of the structure of the Fröhlich Hamiltonian, is exactly solvable for any values of the mass of the second particle and the strength of the electron's coupling to it. Feynman discovered a rigorous upper bound to the free energy of the Fröhlich

polaron that was a function of the (adjustable) second particle's mass and coupling.² Feynman *et al.* argued that the perturbation calculation of the expected velocity (and other properties) that they carried out would give a reasonable estimate in the strong-coupling regime of interest here, provided that one adjusted the two parameters in the unperturbed Hamiltonian to minimize the upper bound of the free energy.³

It is the purpose of this paper to adapt this theory to treat a material such as n -BSO, which has about a dozen distinct, strongly polar LO phonon branches. The problem becomes clearer if one considers Eqs. (46) and (47) predicted by this theory in Ref. 3 for the mobility μ of the "Fröhlich polaron." From there it follows (both in *esu* and in S.I.)

$$\frac{e}{\omega m^*} \mu^{-1} = \frac{\alpha}{3\sqrt{\pi}} \frac{\beta^{5/2}}{\sinh(\beta/2)} \frac{v^3}{w^3} K(a,b), \quad (1)$$

where ω is the (angular) LO phonon frequency, e is the magnitude of the electron charge, m^* is the effective mass of the electron in the conduction band when the nuclei are stationary at their average positions, $\beta \equiv \hbar\omega/k_B T$, and α is the dimensionless coupling constant for the electron-phonon interaction (in terms of which all theorists to date have expressed their results).

It will be most convenient for our purposes to use a Lagrangian formulation of our problem. In Sec. II we set up a complete Lagrangian for the multibranch lattice and then, in Sec. III, we develop two algorithms for determining appropriate effective values for ω and α for a multimode polar lattice. We find that they give the same values for ω and α to within a few percent, and give the same value for (1) to within less than 2%, when used to predict the mobility of n -BSO over the experimental range.

In addition $K(a,b)$ is determined by the two variational parameters v and w introduced by Feynman² when he proved that certain Lagrangian-path-integral expressions gave an upper bound to the ground-state polaron energy. This upper

bound has proven to be a significantly lower upper bound than has been found to date in conventional Hamiltonian quantum mechanics. In Eq. (1),

$$K(a,b) \equiv \int_0^\infty du [u^2 + a^2 - b \cos(vu)]^{-3/2} \cos(u), \quad (2)$$

where $a^2 \equiv (\beta/2)^2 + R\beta \coth(\beta v/2)$, $b \equiv R\beta/\sinh(b\beta v/2)$, and $R \equiv (v^2 - w^2)/(w^2 v)$.

In Sec. IV we evaluate the ‘‘best’’ v and w values using the extension by Osaka⁵ of Feynman’s upper bound for the ground-state energy to an upper bound for the free energy F at any temperature T .

In Sec. V we apply our models to the calculation of the large polaron mobility vs temperature in $\text{Bi}_{12}\text{SiO}_{20}$ and finally, in Sec. VI, we summarize the reasons we feel that our procedure is useful for calculating electron mobility (and other properties) in crystals with many polar lattice modes, especially when the assumption of independent electron-phonon collisions cannot apply.

II. ELECTRON AND EXTERNAL FIELDS IN A MULTIMODE POLAR LATTICE

In this section we will first review the physics of an electron in the conduction band of a polar lattice. To do this, we write a Lagrangian that describes a system consisting of one electron coupled to (1) a polar cubic lattice with many ‘‘infrared’’ (IR) modes of different frequencies and strengths, (2) bound electrons in fully occupied ‘‘ultraviolet’’ (UV) valence bands, (3) an applied homogeneous electric field, and (4) a transverse electromagnetic wave. In addition, the lattice dipoles and UV dipoles interact with each other via the longitudinal Coulomb interactions.

We use a description in which the atomic structure of the lattice is approximated by continuous field variables. From it we derive in a self-consistent way how the transverse polarization density affects the propagation of an electro-magnetic wave, and how the longitudinal polarization density responds to the field of the electron. In this way we demonstrate that we can extract the oscillator strengths and frequencies describing the polar lattice modes from, e.g., an infrared reflectivity spectrum of the material, and that we can use them to describe the interaction between the electron and the polar lattice. We will derive expressions for electron-phonon coupling in the presence of many polar vibrational branches, and introduce an effective longitudinal-optical frequency and an effective longitudinal-optical oscillator strength that we argue can be used with confidence in existing polaron theories that only consider one longitudinal-optical mode.

A. Statement of the problem

We study the behavior of an electron (of charge $-e$) moving near the bottom of a conduction band (with isotropic ‘‘band’’ mass m_0) under the influence of a uniform externally applied electric field $\vec{\mathcal{E}}^{\text{ext}}(t)$, while interacting with a polar lattice whose unit cell is so small (compared to the quantum wavelengths of the electron) that its polarization density $\vec{\mathcal{P}}(\vec{r}t)$ may be thought of as a continuous field variable. (Script symbols always denote real physical quantities, while the corresponding Roman letters denote their complex

transforms.) The electron’s position coordinate is $\vec{x}(t)$. The polarization density may be thought of as the sum of independent components $\vec{\mathcal{P}}_i(\vec{r}t)$ ($i=1,2,\dots,m;m+1,\dots,m+M$) at each position \vec{r} that corresponds to the m (infrared) polar lattice modes and the M bound-electron (ultraviolet) modes of the material:

$$\vec{\mathcal{P}}(\vec{r}t) = \sum_{i=1}^{m+M} \vec{\mathcal{P}}_i(\vec{r}t). \quad (3)$$

Each mode polarization density is assumed to be a quantum coordinate of the vibration responsible: when we do the quantum calculations by path integrals below, we will sum over all time trajectories $\vec{\mathcal{P}}_i(\vec{r}t)$. It will be useful sometimes to separate the polarization fields $\vec{\mathcal{P}}_i(\vec{r}t)$ into their transverse (divergenceless) part $\vec{\mathcal{P}}_i^{\text{Tr}}(\vec{r}t)$ and longitudinal (curl-free) part $\vec{\mathcal{P}}_i^{\text{L}}(\vec{r}t)$:

$$\vec{\mathcal{P}}_i(\vec{r}t) = \vec{\mathcal{P}}_i^{\text{Tr}}(\vec{r}t) + \vec{\mathcal{P}}_i^{\text{L}}(\vec{r}t). \quad (4)$$

B. Lagrangian and action functional

The Lagrangian for the path integral will have a term $(1/c)\vec{\mathcal{J}}(\vec{r}t) \cdot \vec{\mathcal{A}}(\vec{r}t)$, where $\vec{\mathcal{J}}(\vec{r}t)$ is the total electric current density and $\vec{\mathcal{A}}(\vec{r}t)$ is the total vector potential, which we assume to be a purely transverse field, i.e., have zero divergence (Coulomb gauge). The Lagrangian will also contain a pure Coulomb interaction potential that, in esu , is

$$\frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\vec{r}t)\rho(\vec{r}'t)}{|\vec{r}-\vec{r}'|}, \quad (5)$$

minus (divergent) self-potentials. Here $\rho(\vec{r}t)$ is the total charge density. In this problem

$$\rho(\vec{r}t) = -\text{div} \vec{\mathcal{P}}(\vec{r}t) - e \delta^3[\vec{r}-\vec{x}(t)], \quad (6)$$

and

$$\vec{\mathcal{J}}(\vec{r}t) = \partial \vec{\mathcal{P}}(\vec{r}t) / \partial t - e \dot{\vec{x}} \delta^3[\vec{r}-\vec{x}(t)], \quad (7)$$

which obviously obeys the charge-conservation condition

$$\partial \rho(\vec{r}t) / \partial t + \text{div} \vec{\mathcal{J}}(\vec{r}t) = 0. \quad (8)$$

The Lagrangian for our problem is

$$\begin{aligned} \mathcal{L} = \int d^3r \left\{ \sum_{i=1}^{M+m} \frac{2\pi}{w_i^2} [(\partial \vec{\mathcal{P}}_i / \partial t)^2 - \omega_i^2 \vec{\mathcal{P}}_i^2] + \vec{\mathcal{P}}^{\text{L}}(\vec{r}t) \cdot \vec{\mathcal{D}}^{\text{el}}(\vec{r}t) \right. \\ \left. + \frac{1}{8\pi} [(\partial \vec{\mathcal{A}}(\vec{r}t) / \partial t)^2 - (\text{rot} \vec{\mathcal{A}}(\vec{r}t))^2] \right. \\ \left. + \frac{1}{c} \vec{\mathcal{A}}(\vec{r}t) \cdot \partial \vec{\mathcal{P}}^{\text{Tr}}(\vec{r}t) / \partial t \right\} \\ + \frac{1}{2} \int d^3r \int d^3r' [\vec{\mathcal{P}}(\vec{r}t) \cdot \vec{\mathcal{G}}(\vec{r}-\vec{r}') \cdot \vec{\mathcal{P}}(\vec{r}'t)] \\ + \frac{m_0}{2} (\partial \vec{x}(t) / \partial t)^2 + e \vec{x}(t) \cdot \vec{\mathcal{E}}^{\text{ext}}(t), \quad (9) \end{aligned}$$

where

$$\vec{\mathcal{D}}^{el}(\vec{r}t) = \nabla \frac{e}{|\vec{r} - \vec{x}(t)|} \quad (10)$$

denotes the unshielded (longitudinal) Coulomb field of the electron, and we have explicitly substituted $\vec{\mathcal{P}}^L$ and $\vec{\mathcal{P}}^{Tr}$ when possible.

The first term in the Lagrangian describes kinetic and potential energy of the lattice modes, and the ω_i and w_i are the frequencies and oscillator strengths of the microscopic oscillators corresponding to each lattice mode when each oscillator is isolated.

The dipole-dipole kernel $\vec{\mathcal{G}}(\vec{r})$ is found, by substituting Eq. (6) into Eq. (5) and integrating by parts, to be $(-\nabla \nabla r^{-1})$. However, to avoid self-interaction and imitate the finite size of a unit cell, we use this result for $r > r_0$ ($r_0 \sim$ interatomic distance) and assume that $\vec{\mathcal{G}}(\vec{r})$ drops to zero for $r \leq r_0$ in some convenient manner; the final result will not be sensitive to the manner of this cutoff. In coordinate notation ($i, j = x, z, y$),

$$\mathcal{G}_{ij}(\vec{r}) = \begin{cases} \frac{3r_i r_j}{r^5} - \frac{\delta_{ij}}{r^3}, & r > r_0 \\ \text{falls to zero,} & r \leq r_0. \end{cases} \quad (11)$$

We note the absence of any coupling between the longitudinal and transverse parts of $\vec{\mathcal{P}}(\vec{r}t)$ in Eq. (9).

The behavior we want to study will be defined by quantum-mechanical unitary transformation matrices $U(t_1, t_2)$. They will be of the form of a sum-over-paths $\vec{\mathcal{P}}(\vec{r}t)$ and $\vec{x}(t)$ which we write

$$U(t_1, t_2) = \sum_{\vec{\mathcal{P}}(\vec{r}t), \vec{x}(t)} \exp\left(\frac{i}{\hbar} S\right). \quad (12)$$

Here the action functional is the time integral over our Lagrangian

$$S = \int_{t_1}^{t_2} \mathcal{L} dt. \quad (13)$$

Our next goal is to calculate the dielectric function $\epsilon(\nu)$ from Eq. (9). Comparing this expression with the experimental data for $\epsilon(\nu)$ will give the frequencies ω_i and the coupling strengths w_i of the polarization modes in our Lagrangian (9).

C. The action in frequency and wave-vector space

The action functional S of Eq. (13) is a quadratic functional of $\vec{\mathcal{P}}_i(\vec{r}t)$ and $\vec{A}(\vec{r}t)$, but these are not the ‘‘normal’’ coordinates since they are coupled to each other. In order to find the normal coordinates, it is very useful to rewrite Eq. (13) in terms of the transforms

$$\vec{P}_i^{Tr}(\vec{k}\nu) = \int dt \int d^3r \vec{\mathcal{P}}_i^{Tr}(\vec{r}t) \exp(i\nu t - i\vec{k} \cdot \vec{r}), \quad (14)$$

$$\vec{P}_i^L(\vec{k}\nu) = \int dt \int d^3r \vec{\mathcal{P}}_i^L(\vec{r}t) \exp(i\nu t - i\vec{k} \cdot \vec{r}), \quad (15)$$

$$\vec{A}(\vec{k}\nu) = \int dt \int d^3r \vec{\mathcal{A}}(\vec{r}t) \exp(i\nu t - i\vec{k} \cdot \vec{r}), \quad (16)$$

$$\vec{D}^{el}(\vec{k}\nu) = \int dt \int d^3r \vec{\mathcal{D}}^{el}(\vec{r}t) \exp(i\nu t - i\vec{k} \cdot \vec{r}), \quad (17)$$

$$G_{ij}(\vec{k}) = \int d^3r \mathcal{G}_{ij}(\vec{r}) \exp(-i\vec{k} \cdot \vec{r}), \quad (18)$$

and $\vec{P}(\vec{k}\nu) = \vec{P}^{Tr}(\vec{k}\nu) + \vec{P}^L(\vec{k}\nu)$. The transform (18) can be expanded in a Taylor series in powers of $(\vec{k}r_0)$. Since the electron wave function will contain only wavelengths much larger than the interatomic distance, we may keep only the lowest-order terms and write

$$G_{ij}(\vec{k}) = \begin{cases} \frac{4\pi}{3} (\delta_{ij} - 3k_i k_j / k^2), & k \ll r_0^{-1} \\ \text{falls to zero,} & \text{larger } k. \end{cases} \quad (19)$$

With Eqs. (14)–(18), and using Eq. (19) to separate the longitudinal and transverse components of the polarization, Eq. (13) can be rewritten (assuming terms with k not much smaller than r_0^{-1} are absent):

$$\begin{aligned} S = (2\pi)^{-4} \int d\nu \int d^3k & \left\{ \sum_{i=1}^{m+M} 2\pi [|\vec{P}_i^{Tr}(\vec{k}\nu)|^2 \right. \\ & + |\vec{P}_i^L(\vec{k}\nu)|^2] \frac{\nu^2 - \omega_i^2}{w_i^2} + \vec{P}^L(\vec{k}\nu) * \cdot \vec{D}^{el}(\vec{k}\nu) \\ & + \frac{1}{8\pi} |\vec{A}(\vec{k}\nu)|^2 \left(\frac{\nu^2}{c^2} - k^2 \right) + i \frac{\nu}{c} \vec{A}(\vec{k}\nu) * \cdot \vec{P}^{Tr}(\vec{k}\nu) \\ & \left. + \frac{2\pi}{3} [|\vec{P}^{Tr}(\vec{k}\nu)|^2 - 2|\vec{P}^L(\vec{k}\nu)|] \right\} + S^{el}[\vec{x}(t)]. \quad (20) \end{aligned}$$

Here the unperturbed electron action is abbreviated S^{el} and its form is seen in Eq. (9).

D. Transverse part of the polarization density

Because Eq. (20) is a quadratic form in $\vec{A}(\vec{k}\nu)$ and $\vec{P}_i^{Tr}(\vec{k}\nu)$, their quantum-expected values are related just as are their classical solutions. So we vary Eq. (20) to find that the following equations describe the classical solutions.

First, we find that the action (20) is stationary for small changes in $\vec{A}(\vec{k}\nu)$ about $\vec{A}_C(\vec{k}\nu)$ where

$$\frac{1}{4\pi} \vec{A}_C(\vec{k}\nu) \left(\frac{\nu^2}{c^2} - k^2 \right) - i \frac{\nu}{c} \vec{P}^{Tr}(\vec{k}\nu) = 0. \quad (21)$$

Next, the action S is stationary for small changes in the transverse part $\vec{P}_i^{Tr}(\vec{k}\nu)$ of $\vec{P}_i(\vec{k}\nu)$ about the classical solutions \vec{P}_{Ci}^{Tr} obeying

$$4\pi\vec{P}_{Ci}^{\text{Tr}}(\vec{k}\nu)\frac{\nu^2-\omega_i^2}{w_i^2}+\frac{4\pi}{3}\vec{P}_C^{\text{Tr}}(\vec{k}\nu)+i\frac{\nu}{c}\vec{A}(\vec{k}\nu)=0. \quad (22)$$

Since Eq. (22) is true for each ‘‘branch’’ i , we can sum these solutions to obtain an equation for the classical transverse polarization density $\vec{P}_C^{\text{Tr}}(\vec{k}\nu)\equiv\sum_i\vec{P}_{Ci}^{\text{Tr}}(\vec{k}\nu)$

$$\vec{P}_C^{\text{Tr}}(\vec{k}\nu)=-i\frac{\nu}{c}\vec{A}(\vec{k}\nu)\frac{\chi(\nu)}{1-(4\pi/3)\chi(\nu)}, \quad (23)$$

where

$$\chi(\nu)=\frac{1}{4\pi}\sum_{i=1}^{m+M}\frac{w_i^2}{\omega_i^2-\nu^2} \quad (24)$$

is the polarizability of an isolated unit cell. Here, the sum, as above, is taken over all infrared and ultraviolet branches i . Note that Eq. (23) agrees with the classical, linear relation of polarization density to electric field with the Lorentz local field correction.

Substituting Eq. (23) in Eq. (21), we find that the classical transverse (wave) solutions must all obey, for every \vec{k} ,

$$\left[\frac{1}{4\pi}\left(\frac{\nu^2}{c^2}-k^2\right)+\frac{\nu^2}{c^2}\frac{\chi(\nu)}{1-(4\pi/3)\chi(\nu)}\right]\vec{A}_C(\vec{k}\nu)=0. \quad (25)$$

Defining the refractive index $n(\nu)$ by $k=n(\nu)\nu/c$, and using the dielectric function $\epsilon(\nu)=n^2(\nu)$, we obtain from Eq. (25) the well-known Lorentz-Lorenz relation

$$\epsilon(\nu)=n^2(\nu)=\frac{1+(8\pi/3)\chi(\nu)}{1-(4\pi/3)\chi(\nu)}. \quad (26)$$

Of course, to fit Eqs. (26) and (24) to experimental data, we will need to include damping factors for the lattice and band oscillators, i.e., replace ν^2 by $\nu^2+i\nu\gamma$ everywhere. This damping arises mainly from small anharmonic coupling terms among oscillators, which affect the free energy and mobility negligibly, and which do not impede our determination of the set of values of w_i and ω_i to use in our Lagrangian (9) and action functional S Eq. (20). This determination is carried out for $\text{Bi}_{12}\text{SiO}_{20}$ in Appendix A and gives the values for the ‘‘infrared’’ (IR) lattice mode frequencies ω_i and coupling constants w_i in Table I.

E. Longitudinal part of the polarization density

For arbitrary electron motion, we find that the action (20) is stationary for small changes in the $\vec{P}_i^L(\vec{k}\nu)$ about the classical solutions $\vec{P}_{Ci}^L(\vec{k}\nu)$ which obey

$$4\pi\vec{P}_{Ci}^L(\vec{k}\nu)\frac{\nu^2-\omega_i^2}{w_i^2}-\frac{8\pi}{3}\vec{P}_C^L(\vec{k}\nu)+\vec{D}^{el}(\vec{k}\nu)=0. \quad (27)$$

Multiplying Eq. (27) by $w_i^2/(\omega_i^2-\nu^2)$ and summing over all branches i we obtain for the classical solution $\vec{P}_C^L(\vec{k}\nu)\equiv\sum_i\vec{P}_{Ci}^L(\vec{k}\nu)$

$$\vec{P}_C^L(\vec{k}\nu)=\chi(\nu)\left[\vec{D}^{el}(\vec{k}\nu)-\frac{8\pi}{3}\vec{P}_C^L(\vec{k}\nu)\right], \quad (28)$$

TABLE I. Frequencies, oscillator strengths, and damping coefficients in cm^{-1} used in Eq. (A1) to fit the experimental infrared reflectivity spectrum of $\text{Bi}_{12}\text{SiO}_{20}$.

ω_i	w_i	γ_i
105.50	164.19	226.6
159.897	193.27	61.1
178.027	371.21	94.0
206.247	172.17	72.0
250.058	472.30	111.8
360.088	1057.2	176.9
495.365	1100.0	131.3
540.467	1458.1	117.4
578.340	927.14	115.6
600.387	746.37	104.1
828.19	1110.4	116.4

which gives

$$\vec{P}_C^L(\vec{k}\nu)=\frac{\chi(\nu)}{1+(8\pi/3)\chi(\nu)}\vec{D}^{el}(\vec{k}\nu). \quad (29)$$

Comparing this with Eq. (26), we obtain

$$\vec{P}_C^L(\vec{k}\nu)=\frac{1}{4\pi}\left(1-\frac{1}{\epsilon(\nu)}\right)\vec{D}^{el}(\vec{k}\nu) \quad (30)$$

for the classical solution driven by the unshielded field $\vec{D}^{el}(\vec{k}\nu)$ of the conduction band electron.

F. Effective action for the electron-lattice interaction

To compare our results later to the existing Lagrangian-based theories, it will be useful at this point to calculate the part of the path integral (12) that is over all trajectories of the polarization coordinates $\mathcal{P}_i(\vec{r}t)$. This can be done exactly because the Lagrangian contains only terms that are independent of, or linear or quadratic in, the \mathcal{P}_i . The result is especially simple if we use the initial and final conditions on these paths that form the matrix element $\langle 0|U(t_1, t_2)|0\rangle$ of Eq. (12), where $|0\rangle$ represents the ground state of all unperturbed polarization oscillators. Then the result is $\sum_{\vec{x}(t)}\exp(iS'/\hbar)$, where S' is the previous action (20) in which \vec{P}_i^{Tr} and \vec{P}_i^L have been replaced by the classical solutions (23) and (29), with $\vec{A}(\vec{k}\nu)=0$. There is also an unimportant normalization term S'' in S' that does not contain $\vec{x}(t)$.⁶

The sum in the first term of Eq. (20) can be calculated using Eqs. (22) and (27). The two \vec{P}_C^{Tr} that appear in the first and in the last term of the integral in Eq. (20) cancel each other, and only a term $(1/2)P_C^L(\vec{k}\nu)*\vec{D}^{el}(\vec{k}\nu)$ remains in the effective action functional for the electron. S' can finally be written as

$$S'=S^{el}[\vec{x}(t)]+S^{\text{int}}+S''. \quad (31)$$

where S^{el} contains the terms describing the unperturbed electron, and

$$S^{\text{int}} = (2\pi)^{-4} \int d\nu \int d^3k \frac{1}{2} B(\nu) \vec{D}^{el}(\vec{k}\nu)^* \cdot \vec{D}^{el}(\vec{k}\nu), \quad (32)$$

where, from Eq. (30),

$$B(\nu) = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon(\nu)} \right) = \frac{\chi(\nu)}{1 + (8\pi/3)\chi(\nu)} \\ = \frac{\text{polynomial of degree } (m-1) \text{ in } \nu^2}{\text{polynomial of degree } m \text{ in } \nu^2} \quad (33)$$

can always be written in the form

$$B(\nu) = \frac{1}{4\pi} \sum_{i=1}^{m+M} \frac{W_i^2}{\Omega_i^2 - \nu^2}. \quad (34)$$

Each term in this sum, when it appears in the action functional (32), acts exactly as would an harmonic longitudinal lattice mode of frequency Ω_i and coupling constant W_i^2 coupled linearly to the conduction electron field \vec{D}^{el} .

The thermal speed of the conduction electron is such that its main frequency components are lower than the oscillator frequencies of the UV (optical) oscillators and are higher than the oscillator frequencies of the (infrared) longitudinal optical phonons (with a thermal speed of 10^5 m/s the electron moves by 1 nm in 10 fs). We, therefore, consider the Born-Oppenheimer approximation (assumed by Fröhlich and others) to be accurate for this problem. Thus, we assume the response speed of the bound electron clouds to be essentially instantaneous, and the electronic contribution to the dielectric polarization when the ions are kept immobile is practically given by the short-wavelength limit ϵ_∞ of the dielectric constant. On the other hand, the contribution related to the ionic displacements is assumed to be given by the strain-free dielectric constant ϵ_{dc} , i.e., that which does not include the effects of piezoelectricity or electrostriction. In contrast to the electronic clouds, the ions tend to remain in their position for picoseconds and follow the movements of the electron with a time delay. (It is this UV-dressed conduction electron accompanied by its local lattice deformation that has been called a ‘‘polaron.’’)

It follows that Eq. (34) can be separated into an infrared and an optical contribution, and that the latter can be represented by a constant, given by ϵ_∞

$$B(\nu) = \tilde{B}(\nu) + \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_\infty} \right), \quad (35)$$

with

$$\tilde{B}(\nu) = \frac{1}{4\pi} \sum_{i=1}^m \frac{W_i^2}{\Omega_i^2 - \nu^2}, \quad (36)$$

where m is, as in Eq. (3), the number of polar IR lattice branches. In Appendix A we fit the IR reflectivity spectrum of $\text{Bi}_{12}\text{SiO}_{20}$ very well with $m=11$ vibrational modes whose LO frequencies Ω_i and coupling parameters W_i are given in Table II. We note that the zero-frequency limit of Eq. (35) is $(4\pi)^{-1}(1 - 1/\epsilon_{dc})$, so that

TABLE II. LO frequencies and oscillator strengths, in cm^{-1} , obtained from Eqs. (26), (A1), and the parameters in Table I for $\text{Bi}_{12}\text{SiO}_{20}$. The sum of all W_i^2 is $38\,778 \text{ cm}^{-2}$. The sum of all numbers in the third column is 91.34 cm^{-1} .

Ω_i	W_i	$\frac{W_i^2}{\Omega_i} \coth(\hbar\Omega_i/2k_B T)$
106.23	8.86	2.92
160.51	9.50	1.51
180.33	20.85	5.83
206.69	10.05	1.05
252.76	27.00	5.26
369.64	61.78	14.40
501.71	52.87	6.63
553.60	86.18	15.35
585.36	75.41	10.90
607.29	98.15	17.59
834.53	89.36	9.90

$$\sum_{i=1}^m \frac{W_i^2}{\Omega_i^2} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_{dc}}. \quad (37)$$

We now drop the optical terms in Eq. (32), assuming that their effects are well summarized in ϵ_∞ and an effective mass m^* that replaces m_0 in the original Lagrangian (9). Therefore, in S^{int} we replace $B(\nu)$ with $\tilde{B}(\nu)$.

To make a direct comparison of Eq. (31) with the action functional for the electron used in Refs. 2 and 3, we perform the integrals over ν and \vec{k} in the action S^{int} of Eq. (32) to convert back to a space-time integral action.

The integral over the frequency ν in Eq. (32) corresponds to the Fourier transform of ‘‘harmonic oscillator’’ terms of the form $W_i^2/(\Omega_i^2 - \nu^2)$. Feynman showed⁶ that the correct quantum results for each harmonic oscillator represented in Eq. (36) are obtained by adding a small negative imaginary part to each oscillator frequency Ω_i , and using the resulting transform

$$\int \frac{d\nu}{2\pi} \frac{\exp(-i\nu t)}{\Omega_i^2 - \nu^2} = \frac{i}{2\Omega_i} \exp(-i\Omega_i|t|). \quad (38)$$

The transform $\vec{D}(\vec{k}\nu)$ in Eq. (32) can be calculated from Eq. (17) and is

$$\vec{D}^{el}(\vec{k}\nu) = 4\pi i e \frac{\vec{k}}{k^2} \int dt \exp(i\nu t) \exp[-i\vec{k} \cdot \vec{x}(t)]. \quad (39)$$

With this in mind, S^{int} becomes

$$S^{\text{int}} = (2\pi)^{-3} \int d^3k \frac{1}{2} \left| 4\pi i e \frac{\vec{k}}{k^2} \right|^2 \\ \times \int dt \int ds \exp(i\vec{k} \cdot [\vec{x}(t) - \vec{x}(s)]) \\ \times \sum_i \left[\frac{iW_i^2}{8\pi\Omega_i} \exp(-i\Omega_i|t-s|) \right]. \quad (40)$$

After performing the integral over \vec{k} we are left with

$$S^{\text{int}} = i \frac{e^2}{4} \int dt \int ds \frac{1}{|\vec{x}(t) - \vec{x}(s)|} \times \sum_i \left[\frac{W_i^2}{\Omega_i} \exp(-i\Omega_i|t-s|) \right]. \quad (41)$$

To complete our comparison of S^{int} with the literature we switch to the special ‘‘polaron’’ unit system in which frequencies are measured relative to a standard lattice frequency ω (to be chosen later for convenience), times are measured in units of ω^{-1} , energies are measured in units of $\hbar\omega$, lengths are measured in units of $\sqrt{\hbar/(m^*\omega)}$, electric fields are measured in units of $\sqrt{\hbar\omega^3 m^*/e}$, mobility is measured in units of $e/(m^*\omega)$, and temperature is measured in units of $\hbar\omega/k_B$. Rewriting Eq. (41) with these new units we find that Eq. (32) gives

$$\frac{i}{\hbar} (S' - S'') = i \int dt \left[\frac{1}{2} (\partial \vec{x}(t)/\partial t)^2 + \vec{x}(t) \cdot \vec{\mathcal{E}}^{\text{ext}}(t) \right] - 2^{-3/2} \int dt \int ds \frac{1}{|\vec{x}(t) - \vec{x}(s)|} \times \sum_{i=1}^m [\alpha_i \exp(-i\Omega_i|t-s|)], \quad (42)$$

where the dimensionless coupling constants α_i are defined by

$$\alpha_i = \frac{W_i^2}{\Omega_i \omega} \sqrt{\frac{m^* \text{Ry}}{m_e \hbar \omega}} \quad (43)$$

in terms of the free-electron mass m_e , the Rydberg of energy Ry ($\text{Ry} = m_e e^4 \hbar^{-2}/2$ in *esu*), the effective mass m^* of an electron in the unpolarized lattice, and the ‘‘standard’’ phonon energy $\hbar\omega$.

Comparing Eq. (42) with the expression (4) of Ref. 2 for an electron coupled to a single LO phonon branch of frequency ω shows that Eq. (42) is the same expression, except that it is summed over several phonon branches ($i = 1, 2, \dots, m$). If the lattice had only one phonon branch with frequency $\Omega = \omega$ and strength W , then our value (43) for its coupling would reduce to

$$\alpha = \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_{\text{dc}}} \right] \sqrt{\frac{m^* \text{Ry}}{m_e \hbar \omega}}, \quad (44)$$

where we used $W^2/\Omega^2 = 1/\epsilon_\infty - 1/\epsilon_{\text{dc}}$ from Eq. (37). The electron-phonon coupling constant (44) is the same as the one calculated by Fröhlich⁴ and used in Ref. 2.

We are now in a position to devise and compare two schemes for reducing the multiphonon-branch situation to a single-branch equivalent.

III. TWO WAYS TO OBTAIN A SINGLE LONGITUDINAL OPTICAL BRANCH MODEL

Our goal is to use the Lagrangian (9), or its electron-only form (42), to calculate the electron mobility and the full

frequency-dependent response of $\langle \vec{x}(t) \rangle$ to an arbitrary external electric field $\vec{\mathcal{E}}^{\text{ext}}$, and to be able to use in our calculation the extensive theoretical predictions for the special case when there is only a single term in the sum appearing in Eqs. (9) and (42).

In Ref. 3 the mobility calculation was carried out by using the $m=1$ form of Eq. (42) to calculate the density matrix at finite temperature for the electron. This density matrix was expressed as a double path integral [over two sets of trajectories $\vec{x}(t)$ and $\vec{x}'(t)$] in which the effective ‘‘Fröhlich’’ action functional $\Phi_F[\vec{x}(t), \vec{x}'(t)]$ of Eq. (14) of Ref. 3 has the same parameters as Eq. (42) with $m=1$ [or as Eq. (4) of Ref. 2] with the addition of the temperature T .

It is clear from a comparison of Eq. (14) of Ref. 3 with our Eq. (42) that, had those authors assumed m LO phonon branches instead of one, their interaction term Φ_F^{int} would have been simply converted to a sum over terms differing only in the phonon frequencies Ω_i and coupling constants α_i as follows:

$$\Phi_F^{\text{int}}[\vec{x}(t), \vec{x}'(t)] \rightarrow i 2^{-3/2} \int dt \int ds \sum_{i=1}^m \frac{H_i(t-s)}{|\vec{x}(t) - \vec{x}(s)|} + \text{similar terms containing } \vec{x}'(t). \quad (45)$$

Here

$$H_i(t) \equiv \alpha_i [\exp(-i\Omega_i|t|) + 2P(\beta_i) \cos(\Omega_i t)], \quad (46)$$

where $\beta_i \equiv \hbar\Omega_i/k_B T$ and $P(\beta) \equiv [\exp(\beta) - 1]^{-1}$.

Both of our schemes will reduce this expression to one term with one ‘‘effective’’ frequency Ω_e and one ‘‘effective’’ coupling constant W_e , or

$$\alpha_e = \frac{W_e^2}{\Omega_e \omega} \sqrt{\frac{m^* \text{Ry}}{m_e \hbar \omega}}. \quad (47)$$

Below, we will take the ‘‘standard frequency’’ ω to equal the effective frequency Ω_e in each case, so that we may use all the formulas in Refs. 2 and 3 directly.

A. First scheme

In our first scheme we choose Ω_e and W_e so as to make an effective time kernel H_e defined as in Eq. (46), but with a single effective frequency Ω_e and a single effective coupling coefficient W_e or α_e , to have the properties

$$H_e(0) = \sum_{i=1}^m H_i(0), \quad (48)$$

and

$$\partial H_e(t)/\partial t = \sum_{i=1}^m \partial H_i(t)/\partial t \quad \text{at } t=0. \quad (49)$$

We fulfill Eq. (48) by taking

$$\frac{W_e^2}{\Omega_e} \coth(\beta_e/2) = \sum_{i=1}^m \frac{W_i^2}{\Omega_i} \coth(\beta_i/2). \quad (50)$$

We fulfill Eq. (49) by taking

$$W_e^2 = \sum_{i=1}^m W_i^2. \quad (51)$$

Using the values for W_i and Ω_i listed in Table II [whose last column also gives the expressions on the right-hand side of Eq. (50)] for $\text{Bi}_{12}\text{SiO}_{20}$, and the conditions (50) and (51) at $T=295$ K, we obtain

$$W_e = 196.9 \text{ cm}^{-1}, \quad (52)$$

$$\Omega_e = 504 \text{ cm}^{-1}, \quad (53)$$

$$\alpha_e = 2.25 \sqrt{m^*/m_e}, \quad (54)$$

with $\omega = \Omega_e$ for the standard lattice frequency.

B. Second scheme

In our second scheme we choose Ω_e and W_e in a way suggested by Ref. 5, which gives an upper bound to the free energy of an electron coupled to a single branch. This has proven to be the lowest upper bound discovered to date. The ‘‘exact’’ Fröhlich action ‘‘S’’ of Eq. (1) in Ref. 5 resembles our Eq. (42), but with a double time integral that runs from 0 to $\beta = \hbar\Omega_1/k_B T$ and treats the Fröhlich model with a single phonon branch at frequency $\Omega_1 = \omega$ and coupling constant W_1 [giving α_1 , as in our Eq. (43)]. The time kernel $\tilde{H}_1(t)$ involved in Ref. 5 is

$$\tilde{H}_1(t) = \alpha_1 [\exp(-\Omega_1|t|) + 2P(\beta)\cosh(\Omega_1 t)] \quad (55)$$

which is a sort of ‘‘imaginary time’’ version of our Eq. (46).

In our second scheme we adjust the single effective frequency and coupling constants Ω_1 and W_1 so as to match

$$\int_0^{\beta_i} dt \tilde{H}_1(t) = \int_0^{\beta_i} dt \sum_{i=1}^m \tilde{H}_i(t), \quad (56)$$

and

$$\partial \tilde{H}_1(t) / \partial t = \sum_{i=1}^m \partial \tilde{H}_i(t) / \partial t \quad \text{at } t=0. \quad (57)$$

Here the \tilde{H}_i are defined as functions of α_i and Ω_i as in Eq. (55). We fulfill Eq. (56) by taking

$$\frac{W_1^2}{\Omega_1^2} = \sum_{i=1}^m \frac{W_i^2}{\Omega_i^2} \quad (58)$$

and fulfill Eq. (57) by taking

$$W_e^2 = \sum_{i=1}^m W_i^2. \quad (59)$$

Fortuitously, even though we based these results on matching the finite-temperature kernels (55), the temperature has canceled from both Eq. (58) and Eq. (59), the latter being identical with Eq. (51) of the first scheme.

From the values of W_i and Ω_i listed in Table II for $\text{Bi}_{12}\text{SiO}_{20}$, we obtain using Eq. (58) and (59)

$$W_e = 196.9 \text{ cm}^{-1}, \quad (60)$$

and

$$\Omega_e = 500 \text{ cm}^{-1}. \quad (61)$$

In the case of n -type $\text{Bi}_{12}\text{SiO}_{20}$ the prescription derived from Eqs. (50) and (51) gives the same results as Eqs. (58) and (59), to within a few percent. The change in the relation of β^{-1} to laboratory temperature counteracts the change in effective electron-phonon coupling constant when calculating the polaron mobility with Eq. (1) and the variational parameters v and w derived in the next section.

IV. TEMPERATURE DEPENDENCE OF THE FEYNMAN VARIATIONAL PARAMETERS

We determined the parameters v and w at every temperature by following the free energy minimization procedure described in Ref. 5. We rewrite here the upper bound F of the free energy of Ref. 5 in a slightly different form:

$$F = -(A + B + C) \quad (62a)$$

with

$$A = \frac{3}{\beta} \left[\ln\left(\frac{v}{w}\right) - \frac{1}{2} \ln(2\pi\beta) - \ln\left(\frac{\sinh(v\beta/2)}{\sinh(w\beta/2)}\right) \right] \quad (62b)$$

and

$$B = \frac{\alpha v}{\sqrt{\pi}[\exp(\beta) - 1]} \times \int_0^{\beta/2} dx \frac{\exp(\beta - x) + \exp(x)}{[w^2 x(1 - x/\beta) + Y(x)(v^2 - w^2)/v]^{1/2}}, \quad (62c)$$

where

$$Y(x) = \frac{1}{1 - \exp(-v\beta)} \{1 + \exp(-v\beta) - \exp(-vx) - \exp(v[x - \beta])\}, \quad (62d)$$

and

$$C = \frac{3}{4} \frac{v^2 - w^2}{v} \left(\coth(v\beta/2) - \frac{2}{v\beta} \right). \quad (62e)$$

The B and C terms are related to the expectation value of the action describing the electron in the polar crystal and of a trial action, respectively.^{2,5} Compared to Ref. 5 the integral in B has been rewritten in a symmetrized form which is more convenient for numerical computation.

At each temperature, the optimal values of the variational parameters v and w are obtained by numerically finding the minimum of Eq. (62a) as a function of v and w . The values of the variational parameters v and w as a function of temperature, as they were derived from the minimization of Eq. (62a), are shown in Table III.

Using these values in Eq. (2.4) of Ref. 9, we estimate a room-temperature polaron radius of approximately 0.6 nm for $\text{Bi}_{12}\text{SiO}_{20}$. The $\text{Bi}_{12}\text{SiO}_{20}$ unit cell is 1.0 nm large and

TABLE III. Variational parameters v and w for various coupling constants α and temperatures. $\beta = \hbar\omega/k_B T$.

β	$\alpha=1$		$\alpha=2$		$\alpha=3$		$\alpha=4$		$\alpha=5$	
	v	w	v	w	v	w	v	w	v	w
1.00	7.20	6.50	7.69	6.20	8.26	5.87	8.95	5.51	9.78	5.13
1.25	5.94	5.31	6.38	5.03	6.91	4.73	7.57	4.41	8.39	4.05
1.50	5.11	4.54	5.52	4.29	6.02	4.01	6.66	3.70	7.48	3.37
1.75	4.54	4.01	4.92	3.77	5.40	3.51	6.02	3.22	6.83	2.92
2.00	4.12	3.63	4.48	3.40	4.94	3.16	5.54	2.88	6.36	2.60
2.50	3.57	3.13	3.89	2.93	4.32	2.70	4.90	2.45	5.71	2.20
2.75	3.38	2.97	3.69	2.77	4.10	2.55	4.67	2.31	5.48	2.07
3.00	3.24	2.84	3.53	2.65	3.93	2.44	4.48	2.21	5.29	1.97

contains 66 atoms. The sphere defined by the polaron radius contains ~ 60 atoms. Therefore, the continuum approximation of Refs. 2,5,3 can be applied.

V. TEMPERATURE DEPENDENCE OF THE MOBILITY

The results derived above can be applied to the calculation of the large polaron mobility in $\text{Bi}_{12}\text{SiO}_{20}$ as a function of temperature.

The only unknown parameter in Eqs. (9) and (1) is the electron effective band mass m^* . The prediction of Eq. (1) at $T=300$ K corresponds to the room-temperature mobility value of $3.4 \text{ cm}^2/(\text{Vs})$ when setting $m^*=2.0m_e$.¹

From m^* , Eq. (1), and using the effective values of LO phonon frequency and coupling strengths derived above ($W_e=196.9 \text{ cm}^{-1}$ and $\Omega_e=504 \text{ cm}^{-1}$), we can predict the temperature dependence of the mobility. The results, given in Ref. 1, agreed very well with the experiment within the experimental error if $m^*=(2\pm 0.1)m_e$.

We find that putting $b=0$ in Eq. (1) makes less than 0.1% error throughout the temperature range in Ref. 1. This is useful because $K(a,0)=K_1(a)/a$, where K_1 is a modified Bessel function.⁷ We note that Eq. (1), where $K_1(a)/a$ can be substituted for $K(a,b)$, becomes equal to Eq. (24) in Ref. 8 in the limit of small a .

VI. CONCLUSIONS

We developed a theoretical description of an electron in the conduction band of a polar lattice characterized by more than one optical-phonon mode, and were able to derive in a self-consistent way both the polaron properties and the optical properties of the lattice, which can then be used to determine the electron-phonon coupling constant.

We discussed how the many phonon branches can be imitated by a single phonon branch, so that the extensive results of existing polaron theories can be applied to a crystal with many polar vibrational modes.

We calculated optimal values of the Feynman action describing the large polaron for all temperatures. From the resulting variational parameters v and w as a function of temperature we are able to predict the temperature dependence and absolute value of the large polaron mobility in a material with many polar longitudinal-optical branches.

We applied our theory to the case of $\text{Bi}_{12}\text{SiO}_{20}$ and obtained a very good agreement with the experimental value of

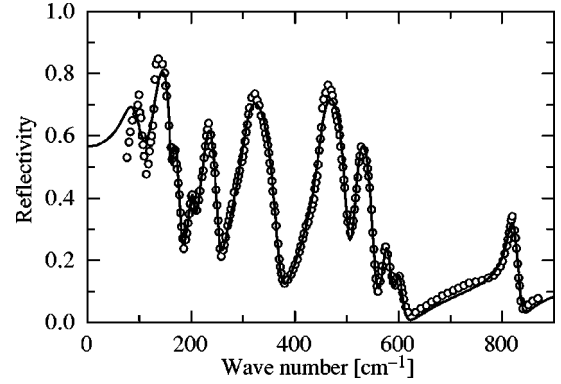


FIG. 1. The dots indicate the experimental room-temperature reflectivity spectrum of $\text{Bi}_{12}\text{SiO}_{20}$ (extracted from Ref. 10). The solid curve is the 11-oscillators approximation calculated from the parameters in Table I using Eqs. (26) and (A1).

the electron band mobility as a function of temperature published in Ref. 1.

APPENDIX A: DERIVATION OF THE BSO PARAMETERS

In the following we will adjust the microscopic oscillator parameters w_i and ω_i appearing in the Lagrangian (9) to fit the experimental data from the refractive index $n(\nu)$ of $\text{Bi}_{12}\text{SiO}_{20}$ throughout the infrared and visible range of frequencies ν . For the cubic crystal of interest here, $\epsilon(\nu) = n^2(\nu)$.

From this data, we will then derive the LO frequencies Ω_i and coupling strengths W_i appearing in Eq. (36). The frequencies Ω_i of the LO phonons are at the values of ν where the longitudinal polarization (29) diverges, i.e., the poles of Eq. (33). The frequencies of the transverse-optical (TO) phonons, on the other hand, correspond to the poles of the dielectric permittivity (26).

Instead of using Eqs. (26)–(24) to fit the index (or reflectivity) data of Ref. 10, we will, for reasons explained throughout Sec. II, use instead Eq. (26) and

$$\chi(\nu) = \frac{1}{4\pi} \sum_{i=1}^m \frac{w_i^2}{\omega_i^2 - \nu^2 - i\nu\gamma_i} + \frac{n_\infty^2 - 1}{n_\infty^2 + 2}. \quad (\text{A1})$$

For $\text{Bi}_{12}\text{SiO}_{20}$, $n_\infty = \sqrt{\epsilon_\infty} = 2.39$ is the refractive index at optical frequencies. The second term in Eq. (A1) takes care of providing the correct limiting value in the visible part of the electromagnetic spectrum.

The power reflectivity $R(\nu)$ for a set of values w_i , ω_i , and γ_i is obtained by substituting them into Eq. (A1) to calculate the refractive index $n(\nu)$ from Eq. (26), and then using the standard relation of Fresnel:

$$R(\nu) = \left| \frac{n(\nu) - 1}{n(\nu) + 1} \right|^2. \quad (\text{A2})$$

We obtain the data of Table I by a least-squares fit of Eq. (A2) with $m=11$ to the data of Ref. 10.

If we substitute the values of w_i , ω_i , and γ_i in Table I into Eq. (A1), and use Eqs. (26) and (A2), we obtain the solid curve in Fig. 1. The agreement with the data is excellent except at the low-frequency end where the experiments became difficult and did not approach the reflectivity appro-

priate for the known $\epsilon_{\text{dc}} = 50$. We, however, forced our fit to make $R(\nu)$ approach 56.6% as $\nu \rightarrow 0$.

We derived the constants W_i and Ω_i by comparing $B(\nu)$ of Eq. (35) with the expression for $[1 - 1/\epsilon(\nu)]/4\pi$ derived from Eqs. (26) and (A1) with all γ_j set to zero. The results are given in Table II.

APPENDIX B: THE SPECIAL CASE OF A SINGLE PHONON BRANCH

In order to better understand the relationships between our microscopic frequencies ω_i , the transverse-optical phonon frequencies and the longitudinal-optical phonon frequencies, it is interesting to rederive some useful expressions which are valid in the case of a single optical-phonon branch.

When there is only one effective infrared oscillator, Eqs. (50) and (51) and (59) and (58) are equivalent, and Ω_e , W_e are directly the oscillator frequency and oscillator strength of the longitudinal-optical mode.

In this case the TO and LO oscillator strengths and frequency are related by simple expressions.

Assuming one IR oscillator to describe the optical phonons and a constant UV contribution we can write, in place of Eq. (24), the microscopic polarizability $\chi(\nu)$ as

$$\chi(\nu) = \frac{1}{4\pi} \frac{w^2}{\omega^2 - \nu^2} + \chi_\infty, \quad (\text{B1})$$

where χ_∞ gives the polarizability at visible wavelengths.

The TO frequency corresponds to the pole of the dielectric permittivity (26) and is given by

$$\Omega_{\text{TO}}^2 = \omega^2 - \frac{1}{3} w^2 \frac{1}{1 - (4\pi/3)\chi_\infty}. \quad (\text{B2})$$

The LO frequency corresponds to the divergence of the longitudinal polarization (29), i.e., the pole of Eq. (33) or (34) [it also corresponds to the frequency where the dielectric permittivity (26) becomes equal to zero]. It is found to be

$$\Omega_e^2 = \omega^2 + \frac{2}{3} w^2 \frac{1}{1 + (8\pi/3)\chi_\infty}. \quad (\text{B3})$$

On the other hand, the dc (strain-free) dielectric permittivity as derived from Eqs. (B1) and (26) is

$$\epsilon_{\text{dc}} = \frac{\omega^2 [1 + (8\pi/3)\chi_\infty] + 2w^2/3}{\omega^2 [1 - (4\pi/3)\chi_\infty] - w^2/3}, \quad (\text{B4})$$

while the permittivity in the visible is

$$\epsilon_\infty = \frac{1 + (8\pi/3)\chi_\infty}{1 - (4\pi/3)\chi_\infty}. \quad (\text{B5})$$

From Eqs. (B2), (B3), (B4), and (B5) we obtain the well-known Lyddane-Sachs-Teller relation¹¹

$$\frac{\Omega_e^2}{\Omega_{\text{TO}}^2} = \frac{\epsilon_{\text{dc}}}{\epsilon_\infty}. \quad (\text{B6})$$

The LO frequency Ω_e also appears in Eqs. (34), (35), and (37). From Eqs. (37) and (B6) we see that the LO oscillator strength W_e is related to the LO-TO frequency splitting:

$$W_e = \frac{1}{\epsilon_\infty} (\Omega_e^2 - \Omega_{\text{TO}}^2). \quad (\text{B7})$$

¹I. Biaggio, R. W. Hellwarth, and J. P. Partanen, Phys. Rev. Lett. **78**, 891 (1997).

²R. P. Feynman, Phys. Rev. **97**, 660 (1955).

³R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Plazman, Phys. Rev. **127**, 1004 (1962).

⁴H. Fröhlich, Adv. Phys. **3**, 325 (1954).

⁵Y. Osaka, Prog. Theor. Phys. **22**, 437 (1959).

⁶R. P. Feynman, Phys. Rev. **80**, 440 (1950).

⁷M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).

⁸K. K. Thornber and R. P. Feynman, Phys. Rev. B **1**, 4099 (1970).

⁹T. D. Schultz, Phys. Rev. **116**, 526 (1959).

¹⁰W. Wojdowski, T. Lukasiewicz, W. Nazarewicz, and J. Zmlja, Phys. Status Solidi B **94**, 649 (1979).

¹¹R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).