

Structural Phase Transitions Induced by a Pseudo-Jahn-Teller Effect*

B. Halperin†

Institut für Theoretische Physik, Universität Frankfurt, 6 Frankfurt/M., Germany

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A theory is presented for the structural phase transitions occurring in crystals in which the ionic constituents are pseudo-Jahn-Teller ions with nearly twofold electronic degeneracy. We consider the case of a strong Jahn-Teller coupling and study the dynamic properties by means of a time-dependent density matrix which takes into account the correlation between the electronic and vibrational motions of a single ion. The results are compared with those obtained in a recent theory of Pytte and Stevens, in which single-ion terms are treated in a decoupling approximation.

The increasing attention being recently given to the problem of structural phase transitions in rare-earth compounds,¹ especially in DyVO₄, makes the cooperative pseudo-Jahn-Teller effect (PJTE) of conceptual interest. As the simplest prototype of such systems we consider a crystal containing complex ions (one per unit cell) the lowest electronic states of which are *only nearly* two-fold degenerate and well separated from the higher-lying ones. The nearly degenerate ground doublet $\psi_{1,l}$, $\psi_{2,l}$ at lattice site l is coupled to a single local normal coordinate Q_l which, in turn, interacts lattice dynamically with other coordinates $Q_{l'}$, belonging to lattice sites $l' \neq l$. Q_l represents a mode of distortion of the complex made up of the PJT ion and the ligands around it, all belonging to lattice cell l . It transforms according to a one-dimensional representation (not the totally symmetric one) of the point group of the lattice cell.

With $\sqrt{\frac{1}{2}}(\psi_{1,l} \pm \psi_{2,l})$ taken as basis functions, the matrix Hamiltonian we consider is

$$H = \hbar\Omega \sum_l \left(\frac{1}{2} p_l^2 + \frac{1}{2} q_l^2 + \lambda q_l \sigma_{x,l} + \epsilon \sigma_{x,l} - \frac{1}{2} \sum_{l'} v_{ll'} q_l q_{l'} \right). \quad (1)$$

Here $\sigma_{l,i}$ are the Pauli spin matrices operating within the function space of the ion at lattice site l . The local normal coordinate q_l has been written in dimensionless form, i.e., $q_l = (M\Omega/\hbar)^{1/2} Q_l$ with Ω the Einstein frequency and M the effective mass of the local vibration, while p_l is the dimensionless momentum conjugate to q_l . λ , ϵ , and $v_{ll'}$ are, respectively, the JT coupling coefficient, half the splitting of the ground electronic energy level, and the mutual interaction of ions at different sites, all in units of $\hbar\Omega$.

From this Hamiltonian the following equations of motion are obtained for the nonequilibrium thermal expectation values (denoted by $\langle \dots \rangle_{ne}$) of the electronic and vibrational operators at lattice site l :

$$\Omega^{-1} \frac{\partial}{\partial t} \langle \sigma_{x,l} \rangle_{ne} = -2\lambda \langle q_l \sigma_{y,l} \rangle_{ne},$$

$$\Omega^{-1} \frac{\partial}{\partial t} \langle \sigma_{y,l} \rangle_{ne} = 2\lambda \langle q_l \sigma_{x,l} \rangle_{ne} - 2\epsilon \langle \sigma_{x,l} \rangle_{ne},$$

$$\Omega^{-1} \frac{\partial}{\partial t} \langle \sigma_{z,l} \rangle_{ne} = 2\epsilon \langle \sigma_{y,l} \rangle_{ne},$$

$$\Omega^{-2} \frac{\partial^2}{\partial t^2} \langle q_l \rangle_{ne} = -\langle q_l \rangle_{ne} - \lambda \langle \sigma_{x,l} \rangle_{ne} + \sum_{l'} v_{ll'} \langle q_{l'} \rangle_{ne}. \quad (2)$$

The simplest decoupling procedure in order to calculate the collective mixed-mode frequencies from the equations of motion is that in which a random-phase approximation (RPA) is used. Such a treatment amounts to (i) replacing thermal averages of products of operators such as, for instance $\langle q_l \sigma_{x,l} \rangle_{ne}$ by the product of their thermal averages, $\langle q_l \rangle_{ne} \langle \sigma_{x,l} \rangle_{ne}$, and (ii) linearizing the expressions thus obtained with respect to the fluctuations about the equilibrium mean-field values. The first stage of this decoupling scheme treats the electronic and vibrational coordinates as if they were independent degrees of freedom, ignoring the intrinsic JT coupling within each ion. Solutions for the frequencies obtained in this way appear in a recent paper of Pytte and Stevens.² Their work, however, primarily concerns the coupling to the elastic strain, which we do not consider. If, in addition, a corresponding decoupling is introduced into the equilibrium density matrix, i.e., if the term $q_l \sigma_{x,l}$ which appears in $e^{-H/kT}$ is replaced by $q_l \langle \sigma_{x,l} \rangle$ + $\langle q_l \rangle \sigma_{x,l} - \langle q_l \rangle \langle \sigma_{x,l} \rangle$, where $\langle \dots \rangle$ denotes an equilibrium average, the density matrix becomes separable in the electronic and vibrational coordinates. Using a molecular-field approximation (MFA) for the interionic interaction, the equilibrium averages can now easily be calculated and shown to satisfy the static parts of the RPA-decoupled equations of motion. An immediate shortcoming associated with such a decoupling scheme emerges from the expression thus obtained for $\langle q \rangle$, which for a "ferrodistortive"³ order is given by

$$\langle q \rangle = (1 - v_0)^{-1} W^{-1} \lambda^2 \langle q \rangle \tanh(\beta \hbar \Omega W), \quad (3)$$

where $W = (\lambda^2 \langle q \rangle^2 + \epsilon^2)^{1/2}$, $\beta = 1/kT$, and v_0 is the zeroth Fourier component of $v_{ll'}$. (In our units $v_0 < 1$.) Equation (3) predicts a spurious phase transition at a temperature T_t given by $\lambda^2 \epsilon (1 - v_0) = \tanh(\beta_t \hbar \Omega \epsilon)$ even if the interionic interaction $v_{ll'}$,

vanishes.

Elliott *et al.*¹ have overcome this last difficulty first by transforming the Hamiltonian into displaced oscillators, which eliminates the JT term and leaves an effective Ising interaction of the form $-\frac{1}{2}\sum_{ll'}J_{ll'}\sigma_{\mathbf{r},l}\sigma_{\mathbf{r},l'}$. Their crucial step is the subtraction of the terms with $l=l'$, which correspond to the JT energy of single ions and give no contribution to the ordering. The resulting coupling is $-\sum_{\mathbf{r}}J_{\mathbf{r}}\sigma_{\mathbf{r}}(k)\sigma_{\mathbf{r}}(-k)$, where, in our notation,

$$J_{\mathbf{r}} = \lambda^2 \hbar \Omega \left((1 - v_{\mathbf{r}})^{-1/2} - \frac{1}{N} \sum_{\mathbf{r}'} (1 - v_{\mathbf{r}'})^{-1/2} \right),$$

which cancels when $v_{\mathbf{r}} = 0$. However, the fact that the displaced-phonon operators explicitly depend on $\sigma_{\mathbf{r}}$ and do not commute with the term $\hbar \Omega \epsilon \sigma_{\mathbf{r}}$ in the Hamiltonian has not been taken into account in the calculation of the equilibrium averages $\langle \hat{\sigma}_i \rangle$ in Ref. 1.

The aim of this comment is to present a method which avoids the difficulties associated with the RPA by directly calculating thermal averages using a time-dependent density matrix which, though approximate, still takes into account correlations between single-ion operators.

The static properties are calculated by means of

a molecular-field density matrix $\rho_{\text{MFA}} = \prod_i \rho_i$, with

$$\rho_i = z_i^{-1} \exp \left\{ -\beta \hbar \Omega \left[\frac{1}{2} p_i^2 + \frac{1}{2} (q_i - q_{0,i})^2 + \lambda q_i \sigma_{\mathbf{r},i} + \epsilon \sigma_{\mathbf{r},i} \right] \right\}. \quad (4)$$

Here $q_{0,i} \equiv \sum_{l'} v_{ll'} \langle q_l \rangle$ is the molecular field acting on the coordinate q_i due to its interaction with the other ions, and $z_i = \text{Tr}_i \exp \{ \dots \}$, where $\{ \dots \}$ stands for the expression inside the curly brackets in (4).

The condition for the existence of a double-minima potential in the single-ion Hamiltonian in (1), and hence for a PJTE to occur, is $\epsilon < \lambda^2$. The PJT stabilization energy (the depth of the minima) is then $E_{\text{PJT}} = \frac{1}{2} \hbar \Omega \lambda^2 (1 - \epsilon/\lambda^2)^2$. Contrary to the case in DyVO_4 , this comment considers a strong JT coupling, namely, $\epsilon \hbar \Omega, \hbar \Omega \ll E_{\text{PJT}}$ or $\epsilon, 1 \ll \lambda^2$. Restricting the treatment to the temperature range $kT \gg \hbar \Omega$, the thermal average of an observable A_i may be approximated by an integral over phase space $\Gamma_i = \{ \tilde{p}_i, \tilde{q}_i \}$ (\tilde{p}_i and \tilde{q}_i denoting classical variables) and a trace over the electronic states. Having performed the integration over \tilde{p}_i , we are left with

$$\langle A_i \rangle = \text{Tr}_{\text{el}} \int \rho_c(\tilde{q}_i) A_i d\tilde{q}_i,$$

with ρ_c , the probability density in configuration space, given by

$$\rho_c = z_c^{-1} \exp \left\{ -\beta \hbar \Omega \left[\frac{1}{2} (q - q_0)^2 + \lambda q \sigma_{\mathbf{r}} + \epsilon \sigma_{\mathbf{r}} \right] \right\} \left\{ 1 - \frac{1}{12} (\beta \hbar \Omega)^2 + \frac{1}{24} (\beta \hbar \Omega)^3 [(q - q_0)^2 + 2(q - q_0)\lambda \sigma_{\mathbf{r}} + \lambda^2] \right\}. \quad (5)$$

The factor in curly brackets in Eq. (5) is the correction to the classical expression,⁴ here taken to order $(\beta \hbar \Omega)^3$. The normalization factor z_c is determined from $\text{Tr}_{\text{el}} \int \rho_c dq = 1$.

The self-consistency equation which determines $\langle q_i \rangle$ is therefore

$$\begin{aligned} \langle q_i \rangle = z_c^{-1} \int_{-\infty}^{\infty} dq 2q \exp \left\{ -\frac{1}{2} \beta \hbar \Omega (q - q_{0,i})^2 \right\} & \left\{ \left[1 - \frac{1}{12} (\beta \hbar \Omega)^2 \right] \cosh \beta \hbar \Omega W' + \frac{1}{24} (\beta \hbar \Omega)^3 \right. \\ & \times \left. \left\{ [(q - q_{0,i})^2 + \lambda^2] \cosh \beta \hbar \Omega W' - 2(q - q_{0,i}) \lambda^2 q W'^{-1} \sinh \beta \hbar \Omega W' \right\} \right\}, \quad (6) \end{aligned}$$

where $W' = (\lambda^2 q^2 + \epsilon^2)^{1/2}$.

It is instructive to point out that the equilibrium averages obtained by means of ρ_c satisfy the static parts of the uncoupled equations of motion. For instance, in accordance with the second equation in (2) we find $\epsilon \langle \sigma_{\mathbf{r}} \rangle = \lambda \langle q \sigma_{\mathbf{r}} \rangle \neq \lambda \langle q \rangle \langle \sigma_{\mathbf{r}} \rangle$.

In order to study the linear response of the system, we conceive the molecular field $q_{0,i}$ to contain an additional external field F_i^{ext} which couples to q_i via a term $-F_i^{\text{ext}} q_i$ in the Hamiltonian. The static single-particle susceptibilities $\chi_{\text{or}}(T)$ and $\chi_{\text{dis}}(T)$ in the ordered and disordered phases are then obtained by linearizing Eq. (6) with respect to F_i^{ext} about $q_{0,i} = \sum_{l'} v_{ll'} \langle q_l \rangle$ or about $q_{0,i} = 0$, respectively. If we assume that the maximum value of the Fourier transform of $v_{ll'}$ occurs for $k=0$, the disordered phase will become unstable with respect to a ferrodistorptive ordering at a stability

limit T_t which is determined by³ $v_0 \chi_{\text{dis}}(T_t) = 1$. For $\epsilon \ll \lambda^2 v_0$ we find

$$kT_t = \frac{\hbar \Omega \lambda^2 v_0}{1 - v_0} \left(1 - \frac{1}{2} \frac{\epsilon^2}{\lambda^4} \frac{(1 - v_0)}{v_0} [f(v_0) - 1] \right), \quad (7)$$

where the function f is defined by

$$\begin{aligned} f(u) = [2\pi(1-u)u]^{-1/2} e^{(1-u^{-1})/2} \\ \times \int_{-\infty}^{\infty} x^{-1} \sinh[x(u^{-1} - 1)^{1/2}] e^{-x^2/2} dx. \quad (8) \end{aligned}$$

The stability limit of the ordered phase is found to coalesce with T_t , and $\langle q \rangle^2 = \alpha(T_t - T)/T_t$ for $T \leq T_t$, as is the case in a second-order transition. The proportionality factor is

$$\begin{aligned} \alpha = 3\lambda^2(1 - v_0)^{-2} \\ \times \{ 1 + [3(1 - 2v_0) - (1 - 4v_0)f(v_0)]\epsilon^2/(4\lambda^4 v_0) \}. \end{aligned}$$

Inspection of Eq. (8) in the interval of physical interest $0 \leq v_0 \leq 1$ shows that $f(v_0) \geq 1$, with the equality sign holding true at the boundaries. Also, $f_{\max} \sim 1.64$ at $v_0 \sim 0.27$. It thus appears that the transition temperature of the PJT system is always lower than that of the corresponding pure JT system. This is a direct consequence of the presence of the term $\epsilon \sigma_x$ in (1), which induces tunneling between the otherwise uncoupled, doubly degenerate sets of vibronic states which are localized at the two potential wells of each ion.

In order to study the dynamic behavior we construct an approximate nonequilibrium density matrix by allowing the coefficients of the operators $\tilde{\sigma}$ and q in (4) to become time dependent. In other words, we take $\rho_i(t)$ and $\rho_c(t)$ of the same form as in Eqs. (4) and (5) but now⁵ with $q_{0,i}(t) = q_0 + \Lambda_{x,i}(t)$ and with three more additional terms appearing in the exponential, which are $-\beta \hbar \Omega [\Lambda_{x,i}(t) \sigma_{x,i} + \Lambda_{y,i}(t) \sigma_{y,i} + \Lambda_{z,i}(t) \sigma_{z,i}]$. Clearly, this particular choice for $\rho(t)$, which excludes time-dependent coefficients of products of operators, implicitly introduces a truncation in the number of equations of motion. At the equilibrium state, the vector $\tilde{\Lambda}(t) \equiv [\Lambda_x, \Lambda_y, \Lambda_z, \Lambda_q]$ vanishes by definition. For linear deviations from equilibrium, the thermal averages in Eq. (2) are directly calculated by means of $\rho_c(t)$, which we expand near $\tilde{\Lambda}_i = 0$, retaining only terms linear in $\Lambda_{j,i}$ ($j = x, y, z$, and q). Setting $\langle \sigma_{x,i} \rangle_{ne} = \langle \sigma_x \rangle + \delta \langle \sigma_{x,i} \rangle$, etc., we then have a linear transformation relating the components of the vector $\tilde{\delta}_i(t) \equiv (\delta \langle \sigma_{x,i} \rangle, \dots, \delta \langle q_i \rangle)$ to those of $\tilde{\Lambda}_i(t)$:

$$\tilde{\delta}'_i(t) = \tilde{M} \tilde{\Lambda}'_i(t), \quad (9)$$

where the primed symbols denote column vectors. Similarly, the time-dependent parts $\delta \langle q_i \sigma_{y,i} \rangle$, etc., of the thermal averages which appear in the right-hand sides of Eqs. (2) may also be expressed in terms of $\Lambda_{j,i}$ (and $\Lambda_{j,i'}$). Having Fourier transformed the resulting equations of motion we obtain another linear transformation, denoted by $\tilde{S}(v_k)$, for the k th Fourier components:

$$\Omega^{-1} \begin{bmatrix} \tilde{\delta} \langle \sigma_{x,k} \rangle \\ \tilde{\delta} \langle \sigma_{y,k} \rangle \\ \tilde{\delta} \langle \sigma_{z,k} \rangle \\ \Omega^{-1} \tilde{\delta} \langle q_k \rangle \end{bmatrix} = \tilde{S}(v_k) \begin{bmatrix} \Lambda_{x,k} \\ \Lambda_{y,k} \\ \Lambda_{z,k} \\ \Lambda_{q,k} \end{bmatrix}. \quad (10)$$

The equations of motion will have nontrivial solutions provided that the following condition is met:

$$\det[\tilde{U}(\omega_k) \cdot \tilde{M} - \tilde{S}(v_k)] = 0, \quad (11)$$

where the matrix elements $U_{nm}(\omega_k)$ are given by $i\omega_k \Omega^{-1} \delta_{nm}$ for $n=1, 2, 3$ and by $-\omega_k^2 \Omega^{-2} \delta_{nm}$ for $n=4$. Equation (11) has one single root $\omega_1 = 0$ which above T_t corresponds to σ_x while below T_t it corresponds to a mixed mode which involves the motion of σ_x and q as well. For $k=0$, $\epsilon \ll 1$, and $T \geq T_t$ we find for the remaining two double roots

$$\omega_{0,2}^2 \approx 4\Omega^2 \epsilon^2 v_0 f(v_0) \Delta, \quad (12)$$

$$\omega_{0,3}^2 \approx \Omega^2 \{1 - v_0 + 4\epsilon^2 f(v_0) + 2\epsilon^2 \Delta v_0^{-1} [(1 - 2v_0)f(v_0) - 1]\},$$

where $\Delta \equiv |T - T_t|/T_t \ll 1$. The eigenmodes are represented in terms of the relative amplitudes of σ_x , σ_y , σ_z , q , and p when each mode oscillates separately in the system. The dominant terms in these ratios are found to be

$$0 : \pm i[v_0 f(v_0) \Delta]^{1/2} : 1 : -\frac{\lambda}{1-v_0} : \mp \frac{2i\epsilon\lambda}{1-v_0} [v_0 f(v_0) \Delta]^{1/2}$$

and

$$0 : \pm 2i\epsilon(1-v_0)^{1/2} f(v_0) : 4\epsilon^2 f(v_0) : \lambda : \pm i\lambda(1-v_0)^{1/2},$$

corresponding to $\omega_{0,2}$ and $\omega_{0,3}$, respectively. Equation (12) shows $\omega_{0,2}$ to be the frequency of the soft mode associated with the transition, which vanishes in a Cochran-type behavior as $T \rightarrow T_t$. For $T \lesssim T_t$ we find $\omega_{0,2} = 2\lambda \langle q \rangle \Omega f^{-1}(v_0) \times [1 - 2\epsilon^2 f(v_0)/(1-v_0)]$, where the dominant term, which is $2\sqrt{3}\lambda^2 \Delta^{1/2} \Omega [(1-v_0)f(v_0)]^{-1}$, exhibits a much steeper rise of $\omega_{0,2}$ versus Δ than that above T_t .

It is interesting to compare these results with those obtained from the RPA theory of Ref. 2, where single-ion terms are treated in a decoupling approximation. In addition to a single root $\omega_1 = 0$ one finds for $T \geq T_t$, $\epsilon \ll 1$, and $k=0$ two RPA double roots, which are $\omega_{0,2}^2 = 4\Omega^2 \epsilon^2 \Delta$ and $\omega_{0,3}^2 = \Omega^2 \times [1 - v_0 + 4\epsilon^2(1-\Delta)]$, with the corresponding relative amplitudes given by

$$0 : \pm i\Delta^{1/2} : 1 : -\lambda/(1-v_0) : \mp 2i\epsilon\lambda\Delta^{1/2}/(1-v_0)$$

and

$$0 : \pm 2i\epsilon(1-v_0)^{1/2} : 4\epsilon^2 : \lambda : \pm i\lambda(1-v_0)^{1/2}.$$

For $T \lesssim T_t$, the RPA solution gives $\omega_{0,2} = 2\lambda \langle q \rangle \Omega \times [1 - 2\epsilon^2/(1-v_0)]$. Bearing in mind that $1 \leq f(v_0) \leq 1.64$, it thus appears that at least for the considered range of parameters the RPA expressions for the mixed-mode frequencies and amplitudes are numerically rather similar to those of our theory, except when v_0 becomes small compared to unity. In the limit $T \rightarrow \infty$ the results of the two theories coincide, giving $\omega_2 = 2\epsilon\Omega$ and $\omega_3 = (1-v_k)^{1/2}\Omega$, which are, respectively, the unperturbed electronic excitation and phonon energies.

To conclude, we should point out that our theory considers the case where the dominant driving mechanism for the phase transition is the coupling of the electronic states of the PJT ion to a $k=0$ optical-phonon mode, and disregards couplings to acoustic-phonon modes and elastic strain. The structure of the ferrodistorive phase corresponds to a "freezing" of this optical mode, without changing the dimensions of the unit cell.

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[†]Present address: Soreq Nuclear Research Centre, Yavne, Israel.

¹R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. Roy. Soc. (London) A328, 217 (1972), and references cited therein.

²E. Pytte and K. W. H. Stevens, Phys. Rev. Lett. 27, 862

(1971).

³See, for example, H. Thomas, in *Structural Phase Transitions and Soft Modes*, Geilo, 1971, edited by E. J. Samuelsen, E. Andersen, and J. Feder (Universitetsforlaget, Oslo, 1971), p. 15.

⁴L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1959), § 33.

⁵We assume a ferrodistoritive ordering and omit the site index l from the equilibrium averages.

Separate Contributions of Longitudinal and Transverse Phonons towards the Thermal Conductivity of Ge in the Ziman Limit

G. P. Srivastava and G. S. Verma

Physics Department, Banaras Hindu University, Varanasi-5, India

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A variational treatment is used to calculate the contributions of longitudinal and transverse phonons towards the phonon conductivity of Ge in the Ziman limit. The matrix elements occurring in the formula for thermal conductivity are evaluated using the corrected expressions of three-phonon scattering strengths.

In this short paper we present the results of calculation of the phonon conductivity due to three-phonon scattering processes for the different polarization branches. The calculations are performed in the Ziman limit,¹ the first and the lowest term of a sequence of the bounds² approaching the thermal transport coefficient κ . We take the variational trial function Φ_s^3 as

$$\Phi_s^3 = -a_s \vec{q} \cdot \nabla T / T,$$

where a_s is the variational parameter for the polarization S . This leads to the following expressions for the separate contributions of longitudinal and transverse phonons:

$$(\kappa_0^L)_L = \frac{k_0}{N_0 \Omega} \left(\frac{X_1^L X_1^L P_{11}^{TT} - 2 X_1^L X_1^T P_{11}^{TL}}{P_{11}^{LL} P_{11}^{TT} - P_{11}^{TL} P_{11}^{LT}} \right),$$

$$(\kappa_0^L)_T = \frac{k_0}{N_0 \Omega} \left(\frac{2 X_1^T X_1^T P_{11}^{LL} - X_1^T X_1^L P_{11}^{LT}}{P_{11}^{LL} P_{11}^{TT} - P_{11}^{TL} P_{11}^{LT}} \right)$$

in the notations of Hamilton and Parrott.³ The matrix elements are evaluated with the modified expressions for three-phonon scattering strengths, which are given elsewhere.⁴

The separate contributions of longitudinal and transverse phonons, $(\kappa_0^L)_L$ and $(\kappa_0^L)_T$, respectively, are shown in Table I. It may be noted that the contribution of transverse phonons is as high as 74% of the total conductivity $\kappa_0^L = (\kappa_0^L)_L + (\kappa_0^L)_T$. The total conductivity κ_0^L (Ziman limit) is also given in the third column of Table I. It can be seen that the

calculated values are nearly equal to or somewhat higher than the experimental values at low temperatures (say, 140 °K). This is due to neglect of mass-defect scattering. At higher temperatures (say, 300 °K) the calculated values are lower than the experimental values. As a matter of fact, if one includes mass-defect scattering also, the calculated values will lie below the experimental ones⁵ (shown in the fourth column of Table I) at all temperatures. This is evident because the Ziman limit κ_0^L gives the lowest bound of a sequence of transport coefficients all of which bound the exact transport coefficient κ from below. The next higher bounds, viz., κ_1^L , κ_2^L , etc., may give results nearer to the exact coefficient κ .

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TABLE I. Contributions of longitudinal and transverse phonons towards the thermal conductivity of Ge.

Temp. (°K)	$(\kappa_0^L)_L$ (W cm ⁻¹ °K ⁻¹)	$(\kappa_0^L)_T$ (W cm ⁻¹ °K ⁻¹)	κ_0^L (W cm ⁻¹ °K ⁻¹)	κ^a Expt. (W cm ⁻¹ °K ⁻¹)
140	0.3301	0.9158	1.246	1.5
180	0.3263	0.7623	1.089	1.1
220	0.3031	0.6452	0.9483	0.82
260	0.2786	0.2592	0.5378	0.66
300	0.2552	0.1029	0.3581	0.58

^aReference 5.