

Soft-Mode Superconductivity in SrTiO_{3-x}

J. APPEL

Gulf General Atomic Incorporated, San Diego, California 92112

(Received 19 January 1968; revised manuscript received 14 November 1968)

The transition temperature T_c of SrTiO_{3-x} is calculated as a function of the electron concentration. The effective electron-electron interaction has an attractive part caused by the intravalley exchange of soft optical phonons that have been observed in the tetragonal phase with Raman scattering and neutron diffraction. The Coulomb part is determined by the longitudinal dielectric constant for a degenerate polar semiconductor. The deformation potential for the interaction between electrons and soft phonons of symmetry A_{1g} is used as an adjustable parameter to fit T_c at one experimental point.

I. INTRODUCTION

SUPERCONDUCTIVITY has been observed in a number of degenerate semiconductors such as GeTe ,¹ SnTe ,² InTe ,³ SrTiO_{3-x} ,⁴ and $\text{Sr}_{1-y}\text{Ba}_y\text{TiO}_{3-x}$.⁵ These substances have very special dielectric properties. They are highly polar compounds which are almost ferroelectric.⁶ Their static dielectric constant ϵ_0 is of the order of 10^2 to 10^4 , whereas their high-frequency dielectric constant ϵ_∞ is only of the order 10. In Fig. 1, the longitudinal dielectric constant is plotted which determines the Coulomb interaction between two excess electrons in an insulator (see also Sec. III). The screening of the bare Coulomb interaction is due to the ion deformations and the ion displacements, both induced by the excess electrons. In a degenerate semiconductor, the conduction electrons cause additional screening,⁷ beyond that provided by the ion lattice. However, the qualitative picture of Fig. 1 remains valid in that at low frequencies the Coulomb repulsion is almost absent, whereas at higher frequencies the anomalous dispersion occurs. For large electron concentrations, with the Fermi energy E_F much greater than the LO-phonon energy ω_l , the anomalous dispersion can lead to a net attractive interaction resulting in superconductivity.^{8,9}

In SrTiO_{3-x} , superconductivity is observed for electron concentrations n such that $E_F \lesssim \omega_l$. Although the dielectric properties favor superconductivity, they are to be complemented by an attractive mechanism

which outweighs the Coulomb repulsion near the Fermi surface (FS). Since n and $N(0)$ are small, the BCS parameter $N(0)V$ for intravalley scattering of electrons by acoustic phonons is smaller than in metals. This observation led Cohen¹⁰ to his theory of superconductivity in many-valley superconductors, in which the attractive interaction arising from the exchange of intravalley phonons can be larger than the Coulomb repulsion. Koonce, Cohen, Schooley, Hosler, and Pfeiffer¹¹ have applied this theory to SrTiO_{3-x} to explain the n dependence of T_c . Their work is based on the many-valley structure of the cubic phase found by Kahn and Leyendecker.¹² Recently, Unoki and Sakudo¹³ have

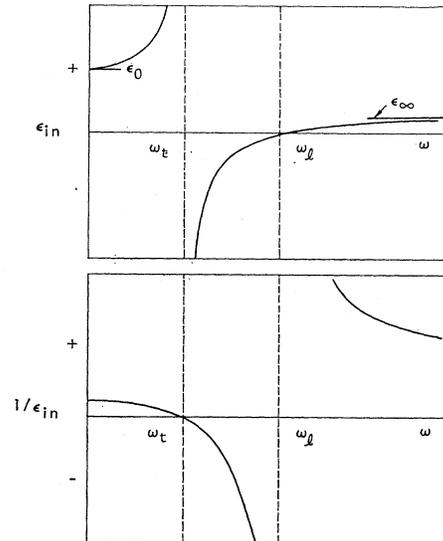


FIG. 1. Longitudinal dielectric constant of an insulator and its reciprocal. The dielectric constant for $q=0$ is given by

$$\frac{1}{\epsilon_{in}} = \frac{1}{\epsilon_0} + \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{\omega_l^2}{\omega^2 - \omega_l^2}$$

where ϵ_0 and ϵ_∞ are the static and the high-frequency dielectric constant, respectively. Here ω_l is equal to the unrenormalized frequency of the LO phonons, ω_l .

¹⁰ M. L. Cohen, Phys. Rev. **134**, A511 (1964).

¹¹ C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. **163**, 380 (1967).

¹² A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A132 (1964).

¹³ H. Unoki and T. Sakudo, J. Phys. Soc. Japan **23**, 546 (1967).

¹ R. A. Hein, J. W. Gibson, R. Mazelsky, R. C. Miller, and J. K. Hulm, Phys. Rev. Letters **12**, 320 (1964).

² R. A. Hein, J. W. Gibson, R. S. Allgaier, B. B. Houston, Jr., R. Mazelsky, and R. C. Miller, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 604; J. K. Hulm, C. K. Jones, D. W. Deiss, H. A. Fairbank, and P. A. Lawless, Phys. Rev. **169**, 388 (1967).

³ S. Geller and G. W. Hull, Phys. Rev. Letters **13**, 127 (1964).

⁴ J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Letters **12**, 474 (1964); J. R. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, M. L. Cohen, and C. Koonce, *ibid.* **14**, 305 (1965).

⁵ J. F. Schooley, H. P. R. Frederikse, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. **159**, 301 (1967).

⁶ W. Cochran, in *Ferroelectricity*, edited by E. F. Weller (Elsevier Publishing Co., Inc., Amsterdam, 1967).

⁷ H. Ehrenreich, J. Phys. Chem. Solids **8**, 130 (1959).

⁸ V. L. Gurevich, A. I. Larkin, and Yu. A. Firsov, Fiz. Tverd. Tela **4**, 185 (1962) [English transl.: Soviet Phys.—Solid State **4**, 131 (1962)].

⁹ L. V. Keldysh, Usp. Fiz. Nauk SSSR **86**, 327 (1965) [English transl.: Soviet Phys.—Usp. **8**, 496 (1965)].

established a phase transition from cubic (O_h^1) to tetragonal (D_{4h}^{18}) at 110°K, with the help of ESR measurements. The tetragonal unit cell is shown in Fig. 2, together with the cubic unit cell. The phase transition has been observed on reduced strontium titanate, too, for electron concentrations as high as $3.6 \times 10^{20} \text{ cm}^{-3}$.¹⁴ The transition cubic \rightarrow tetragonal reduces the symmetry of the first Brillouin zone. Therefore, it is not certain that a many-valley structure similar to that for the cubic phase does also exist in the tetragonal phase. The experimental results on transport phenomena do not give a unique picture. Magnetoresistance¹⁵ and Schubnikov-de Haas measurements¹⁶ can be explained with a many-valley structure. Measurements of the piezoresistance¹⁷ and of the I - V tunneling characteristics¹⁸ lead to a direct-gap structure with the conduction-band minimum at the center of the Brillouin zone. The different experimental results can be reconciled with the reasonable assumption that both zone center and edges are occupied at concentrations $n \gtrsim 10^{18} \text{ cm}^{-3}$.¹⁹

Of crucial importance for our discussion is the effect of the phase transition cubic \rightarrow tetragonal on the phonon spectrum and on the electron-phonon interaction. Above the phase transition (cubic symmetry) there is only one soft-phonon branch at $q=0$. It consists of a doubly degenerate TO branch whose frequency changes as $[\epsilon_0(T)]^{-1/2}$.²⁰ This "ferroelectric mode" has odd-symmetry character and it is neither Raman-active nor does it scatter conduction electrons.²¹⁻²³ As a result of the phase transition cubic \rightarrow tetragonal and the increase of the unit cell, additional phonon branches are introduced in the first Brillouin zone. Thereby, the frequencies of those $q=0$ phonons present before the transition are not much affected, and also the dielectric properties remain almost unchanged.²⁴ Below the phase transition (tetragonal symmetry), two *new* soft phonons with *even*-symmetry character have independently been

observed in Raman scattering²⁵ and in inelastic neutron diffraction.²⁶ One of these modes has a $q=0$ displacement field that transforms according to the identity representation of the tetragonal point group. Therefore, the corresponding electron-phonon matrix element is finite, *independent of the symmetry character of the electron states*. The matrix element is weakly screened by other electrons because the optical modes are associated with relative displacements of the ions in a unit cell, and the corresponding short-range electron-phonon interaction is not sensitive to screening effects.

It is the purpose of this paper to present a theory of superconductivity in SrTiO_{3-x} based on the intravalley exchange of soft phonons between conduction electrons. For small energy transfers, these electrons experience a weak Coulomb interaction, in virtue of the pseudoferroelectric properties of strontium titanate. In other words, in the important low-frequency range where soft pho-

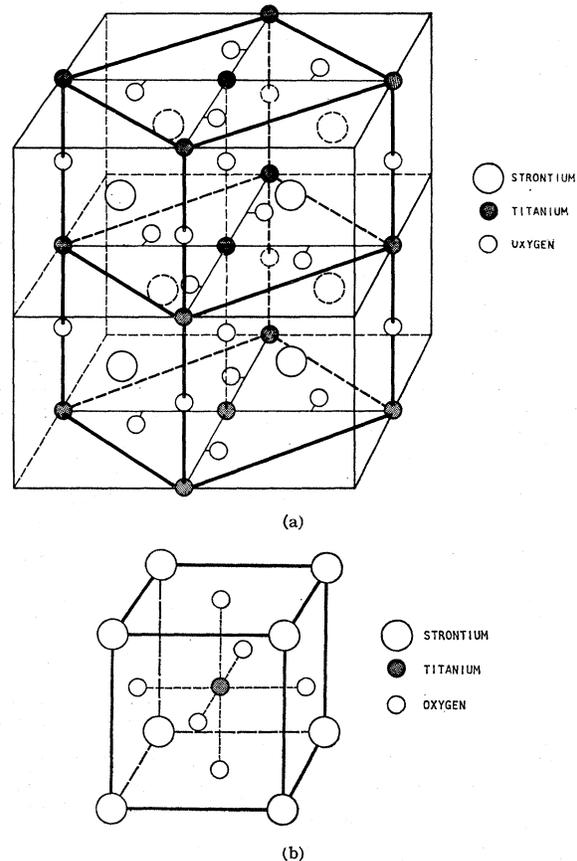


Fig. 2. (a) Unit cell for the tetragonal structure D_{4h}^{18} of SrTiO_3 according to Unoki and Sakudo (Ref. 13). The cell contains four molecular units and its dimensions are \sqrt{a} , \sqrt{a} , c , where a and c correspond to the tetragonal one molecular unit. The ratio $c/a = 1.00062$ at 4.2°K. (b) Unit cell for the cubic structure O_h^1 of SrTiO_3 .

¹⁴ C. K. Jones and D. K. Hulm, Phys. Letters **26A**, 182 (1968).

¹⁵ H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. **143**, 648 (1966).

¹⁶ H. P. R. Frederikse, W. R. Thurber, W. R. Hosler, J. Babiskin, and P. Siebenmann, Phys. Rev. **158**, 775 (1967).

¹⁷ O. N. Tufte and E. L. Stelzer, Phys. Rev. **141**, 675 (1966).

¹⁸ S. Shapiro, Phys. Rev. **140**, A169 (1965).

¹⁹ In the cubic phase, the FS may have the same shape as in BaTiO_{3-x} , where it consists of three mutually orthogonal cigars oriented along the three main directions and intersecting near the zone center. See C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967).

²⁰ A. S. Barker, Phys. Rev. **145**, 391 (1966).

²¹ E. Burstein, in *1966 Tokyo Summer Lectures in Theoretical Physics*, edited by R. Kubo (W. A. Benjamin, Inc., New York, 1966).

²² J. M. Worlock and P. A. Fleury [Phys. Rev. Letters **19**, 1176 (1967)] observe, however, electric-field-induced Raman scattering by the ferroelectric mode.

²³ S. H. Wemple, A. Jayaraman, and M. DiDomenico, Jr., [Phys. Rev. Letters **17**, 142 (1966)] find that the deformation of the cubic crystal under pressure leads to scattering of conduction electrons by the ferroelectric mode. In the undeformed cubic crystal, however, the matrix element for the interaction between electrons and the $q=0$ ferroelectric mode vanishes.

²⁴ R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

²⁵ P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters **21**, 16 (1968).

²⁶ G. Shirane and Y. Yamada (to be published).

nons provide an attractive interaction, the lattice polarization can follow a conduction electron.²⁷

This paper does not aim, however, for a rigorous mathematical theory of superconductivity in a compound as complex as SrTiO_{3-x}. In order to find the physical origin of superconductivity in this substance, we use a simple electron-phonon model and make justified approximations in describing the effective electron-electron interaction. Since the interaction between electrons and soft phonons of the tetragonal phase is important for our discussion, a careful proof for the existence of a finite matrix element is given in Appendix B.

II. ENERGY GAP AND TRANSITION TEMPERATURE

The observable parameter is the transition temperature T_c as a function of the electron concentration n . Energy gap and transition temperature are related by the BCS formula $2\Delta_0 = 3.5k_B T_c$. The gap is found by employing the analytic method of Bogoliubov^{28,29} in solving the integral equation given by

$$\Delta(k) = \frac{1}{4\pi^2} \int_0^\infty V(k, k') \frac{\Delta' k'^2 dk'}{(\Delta'^2 + \epsilon'^2)^{1/2}}, \quad (1)$$

where $\epsilon' = \epsilon(k') = (k'^2 - k_F^2)/2m_b$. Here m_b is the band effective mass and $\Delta_0 = \Delta(k_F)$; k_F is the Fermi momentum. The interaction kernel is of the form derived by Eliashberg³⁰ and by Liu³¹; k and k' play the role of convenient energy variables.

For metals, the validity of the Eliashberg kernel is based on the generalization of Migdal's theorem from the normal state to the pairing interaction in the superconducting state.³² For degenerate semiconductors there exists no general proof of Migdal's theorem. For the interaction between electrons and acoustic phonons, the electron self-energy can be calculated to an accuracy of order u/v_F , where u is the sound velocity and v_F is the Fermi velocity, if vertex corrections are ignored.³³ It will be assumed that for the electron concentrations of

²⁷ The favorable dielectric properties of SrTiO_{3-x} for superconductivity have been pointed out in earlier communications by J. Appel, Phys. Rev. Letters **17**, 1045 (1966); W. Klose and H. Schuster, Solid State Commun. **6**, 89 (1968). However, to find T_c versus n , the attractive interaction was attributed to intravalley exchange of acoustic phonons using the electron-phonon coupling constant derived by P. Morel and P. W. Anderson [Phys. Rev. **125**, 1263 (1962)] for metals. It is shown in Appendix A that this coupling constant, found from the jellium model, is larger than that derived from the deformation-potential model.

²⁸ N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. **34**, 58 (1958) [English transl.: Soviet Phys.—JETP **7**, 41 (1958)].

²⁹ N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *New Method in the Theory of Superconductivity* (Consultants Bureau Enterprises, Inc., New York, 1958), p. 85.

³⁰ G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].

³¹ S. H. Liu, Phys. Rev. **125**, 1244 (1962).

³² J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), p. 164.

³³ J. Appel (unpublished).

interest here, $n \geq 10^{19} \text{ cm}^{-3}$, Migdal's theorem also holds for the interaction between electrons and optical phonons.³⁴

For the calculation of Δ_0 from Eq. (1), it is taken into account that the pair condensation amplitude has a narrow peak at E_F , so that it is useful to rewrite this equation in the form

$$\Delta(k) = K(k, k_F) \int_0^\infty \frac{\Delta_0 dk'}{(\epsilon'^2 + \Delta'^2)^{1/2}} + \int_0^\infty [K(k, k')\Delta' - K(k, k_F)\Delta_0] \frac{dk'}{(\epsilon'^2 + \Delta'^2)^{1/2}}, \quad (2)$$

where $K(k, k') = V(k, k')k'^2/4\pi^2$. In the second term, the integrand vanishes at $k' = k_F$ and, therefore, Δ' under the square root may be set equal to zero if $\Delta_0 \ll E_F$. After some integrations, one arrives at a linear inhomogeneous equation given by

$$\Delta(k) = V(k, k_F) \frac{k_F m}{2\pi^2} \Delta_0 \ln \frac{4\sqrt{3}E_F}{\Delta_0} - \int_0^\infty \frac{d}{dk'} \left([K(k, k')\Delta'] \frac{k' - k_F}{|\epsilon'|} \right) \ln \left(2 \frac{|k' - k_F|}{k_F} \right). \quad (3)$$

This equation can be transformed into an integral equation for the function $\Delta(k) \ln(\Delta_0/4\sqrt{3}E_F)/\Delta_0$.²⁹ The first iteration yields the solution in BCS form

$$\Delta_0 = \tilde{\omega} e^{-1/N(0)V}, \quad (4)$$

where

$$\tilde{\omega} = 4\sqrt{3}E_F \exp \left[-\frac{1}{2} \int_0^\infty \frac{d}{dk'} \times \left(\frac{V(k_F, k')V(k', k_F)}{V^2} \frac{k'^2}{m_b k_F} \frac{k' - k_F}{|\epsilon'|} \right) \times \ln \left(2 \frac{|k' - k_F|}{k_F} \right) \right] dk' \quad (5)$$

and

$$V = V(k_F, k_F), \quad N(0) = k_F m_b / 2\pi^2. \quad (6)$$

The energy gap is given in terms of three parameters: the effective electron-electron interaction V at the FS, the density of states $N(0)$ at the FS, and the frequency factor $\tilde{\omega}$. All three parameters depend on n . With the help of Eq. (4) and the BCS relation between Δ_0 and T_c , we shall discuss $T_c(n)$. Equation (4) presents the asymptotic solution of Eq. (1) for small $N(0)V$; for SrTiO_{3-x}, one has $N(0)V < 0.2$.

³⁴ On the other hand, in the *one-electron* problem for polar crystals, vertex corrections must be taken into account in calculating the electron self-energy: J. Appel, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1968), Vol. 21, p. 231.

III. INTERACTION KERNEL $V(k, k')$

The evaluation of Δ_0 requires the effective interaction $V(k, k')$ as a function of energy and momentum transfer. An accurate evaluation of $V(k, k')$ is a difficult task for several reasons. The validity of mathematical approximation such as the random-phase approximation for the electron-phonon system and, in particular, the neglect of electron-phonon vertex corrections has not been studied for polar semiconductors. Furthermore, the parameters that enter the coupled electron-phonon system, e.g., matrix elements, are not well known.

Because of these difficulties, a simple model will be chosen to describe the electron-phonon system in SrTiO_{3-x} . In particular, the deformation-potential constant for the interaction between electrons and phonons of symmetry A_{1g} is taken as an adjustable parameter, to fit T_c versus x at one point. We shall find, however, that this semiempirical deformation potential has the correct magnitude, to be expected from the tetragonal distortion of the cubic lattice.

The effective interaction is divided into two parts:

$$V(k, k') = V_1(k, k') + V_2(k, k'). \quad (7)$$

The first part accounts for the Coulomb interaction between two electrons and depends on the longitudinal dielectric constant. The second part is due to the exchange of soft phonons. A third part, namely, the exchange of acoustic phonons, plays no significant roles here as is shown in Appendix A.

Because $n \lesssim 5 \times 10^{20} \text{ cm}^{-3}$, the FS is so small that umklapp processes can be ignored.³⁵

Let us first determine the Coulomb part $V_1(k, k')$. To find the Coulomb interaction in a degenerate semiconductor, we begin with the Coulomb interaction between two excess electrons in the conduction band of an insulator. This interaction is determined by the longitudinal dielectric constant $\epsilon_{\text{in}}(\omega, q)$ shown in Fig. 1 for $q=0$. At low frequencies, $\omega < \omega_t$, ϵ_{in} is large, corresponding to a weak repulsion. At higher frequencies, $\omega_t < \omega < \omega_l$, the anomalous dispersion occurs; ϵ_{in} is negative and favors an attraction. Finally, at $\omega > \omega_l$, the displacement polarization can no longer follow an electron; ϵ_{in} becomes positive again. In Fig. 1, the transverse frequency ω_t occurs as the parameter $(\epsilon_{\infty}/\epsilon_0)\omega_l$. The electrons do not interact with the transverse phonons. The form of the dielectric constant shown in Fig. 1 presumes only one group of optical branches (one longitudinal and two degenerate transverse branches), corresponding to two ions per unit cell. This model can also be applied to SrTiO_3 , where the dielectric constant changes from its "static" value $\sim 2 \times 10^4$ to a value of the order 8 (which is close to $\epsilon_{\infty} = 5.2$) after going through the first dispersion. The dielectric constant is assumed to be real. Phonon damping introduces an imaginary part centered at ω_t ; this part is usually small.

³⁵ P. E. Seiden, Phys. Rev. **168**, 403 (1968).

In degenerate semiconductors, the Coulomb interaction is also screened by conduction electrons. For our simple phonon model, the dielectric constant $\epsilon_{ds}(\omega, q)$ has been derived by Gurevich, Larkin, and Firsov³⁶ and by Appel.³⁷ The final result for the Coulomb interaction between two electrons can be written

$$\begin{aligned} \mathcal{U}_1(\omega, q) &= \frac{v(q)}{\epsilon_{ds}(\omega, q)} \\ &= v(q) \left[\frac{1}{\epsilon_{\infty}(\omega, q)} - \left(\frac{1}{\epsilon_{\infty}(\omega, q)} - \frac{1}{\epsilon_0(\omega, q)} \right) \frac{\omega_l^2}{\omega^2 - \omega_l^2} \right]. \quad (8) \end{aligned}$$

Here $v(q) = 4\pi e^2/q^2$ and $\epsilon_{\infty}(\omega, q) = \epsilon_{\infty} + v(q)\pi(\omega, q)$, where $\pi(\omega, q)$ is the electron polarizability in the random-phase approximation (RPA). From here on, the frequency ω_l is the renormalized phonon frequency. The Eliashberg kernel $V_1(k, k')$ corresponding to $\mathcal{U}_1(\omega, q)$ is given by

$$\begin{aligned} V_1(k, k') &= \frac{1}{2} \int_0^{\theta_m} \sin\theta \, d\theta \, v(q) \\ &\times \left[\left(\frac{1}{\epsilon_{\infty}(\omega, q)} - \frac{1}{\epsilon_0(\omega, q)} \right) Q_1(k', k) - \frac{1}{\epsilon_{\infty}(\omega, q)} \right], \quad (9) \end{aligned}$$

where $\omega = |\epsilon - \epsilon'|$ and $q = |\mathbf{k}' - \mathbf{k}|$ are energy and momentum transfer, respectively, and where

$$Q_1(k', k) = \frac{1}{2} \left(\frac{\omega_l}{\omega_l + |\epsilon| + |\epsilon'|} + \frac{\omega_l}{\omega_l - |\epsilon| + |\epsilon'|} \right). \quad (10)$$

The maximum scattering angle θ_m is for nonumklapp scattering given by

$$\cos\theta_m = \begin{cases} -1, & k' \leq q_m - k \\ (k^2 + k'^2 - q_m^2)/2kk', & q_m - k < k' < q_m + k \\ +1, & q_m + k \leq k' \end{cases} \quad (11)$$

where q_m is the value of the maximum phonon wave vector. The Coulomb kernel, Eq. (9), consists of two parts: (a) the optical-phonon-induced interaction caused by the screened longitudinal displacement polarization (first term), and (b) the direct interaction screened by the conduction electrons and by the lattice of polarizable ions (second term). This definition of the Coulomb kernel follows from the definition of the dielectric constant for a polar substance. The integration over θ in Eq. (9) is readily carried out if one uses the Thomas-Fermi approximation $v(q)\pi(\omega, q)/\epsilon_{\infty} = k_{\text{TF}}^2/q^2$, where $k_{\text{TF}} = [4\pi e^2 N^*(0)/\epsilon_{\infty}]^{1/2}$; here $N^*(0) = 2(m^*/m_b)N(0)$ is the specific-heat density of states. For electron concentrations $10^{19} \lesssim n \lesssim 10^{21} \text{ cm}^{-3}$, this approximation is well justified since the plasma fre-

³⁶ V. L. Gurevich, A. I. Larkin, and Yu. A. Firsov, Fiz. Tverd. Tela **4**, 185 (1962) [English transl.: Soviet Phys.—Solid State **4**, 131 (1962)].

³⁷ J. Appel, Phys. Rev. Letters **17**, 1045 (1966).

quency $\omega_p \gg \omega_l$. The result of the integration is given by

$$V_1(k, k') = \frac{m_b/m^*}{2N(0)} \left\{ \left[a^2 \ln \left(1 + \frac{1}{a^2} \right) - \frac{\epsilon_\infty}{\epsilon_0} a^2 \ln \left(1 + \frac{\epsilon_0}{\epsilon_\infty} \frac{1}{a^2} \right) \right] Q_1(k, k') - a^2 \ln \left(1 + \frac{1}{a^2} \right) \right\}, \quad (12)$$

where $a^2 = k_{TF}^2/4k_F^2$. In evaluating the coupling constant in front of $Q_1(k', k)$, we assume that both initial and final state are on the Fermi surface.

The second part of the interaction kernel, $V_2(k, k')$, accounts for the attractive interaction between two electrons that is caused by the exchange of virtual soft phonons. It is crucial for our discussion that one of the two soft optical phonons observed in Raman and neutron scattering interacts with the conduction electrons. At $q=0$, the symmetry character of this phonon is A_{1g} , corresponding to a displacement field that transforms according to the identity representation of the tetragonal point group. It is shown in Appendix B that at $q=0$ a finite electron-phonon matrix element exists, independent of the electronic structure. For simplicity, we assume a parabolic energy band.

In terms of the deformation-potential constant \mathcal{E} for soft phonons, the bare matrix element is given by (Appendix B)

$$g^{(0)}(q) = i[1/2MN\omega_s(q)]^{1/2}K\mathcal{E}, \quad q \ll K \quad (13)$$

where M is the ionic mass per unit cell, N is the number of unit cells per unit volume, and K is 2π times a vector of the reciprocal lattice. The screening of $g^{(0)}(q)$ by conduction electrons is described by the static Hartree-Fock approximation ($\omega_p \gg \omega_s$):

$$g(q) = g^{(0)}(q)/(1 + k_{TF}^2/K^2). \quad (14)$$

In the denominator occurs K , and not q , since we are dealing with a *short-range* interaction. The soft zone-center phonon of the tetragonal phase arises from a $\langle 111 \rangle$ zone-boundary phonon of the cubic phase.

The electron-electron interaction due to phonon exchange can be written

$$V_2(\omega, q) = |g(q)|^2 2\omega_s(q)/[\omega^2 - \omega_s^2(q)]. \quad (15)$$

The corresponding Eliashberg kernel is given by

$$V_2(k', k) = \frac{1}{2} \int_0^{\theta_m} \sin \theta \, d\theta \frac{2|g(q)|^2}{\omega_s(q)} Q_2(\mathbf{k}, \mathbf{k}'), \quad (16)$$

where $q = |\mathbf{k}' - \mathbf{k}|$ and

$$Q_2(\mathbf{k}, \mathbf{k}') = \frac{1}{2} \left(\frac{\omega_s(q)}{\omega_s(q) + |\epsilon| + |\epsilon'|} + \frac{\omega_s(q)}{\omega_s(q) - |\epsilon| + |\epsilon'|} \right), \quad (17)$$

with $\epsilon = \epsilon(k)$. At this point we make an approximation and replace the coupling parameter $2|g(q)|^2/\omega_s(q)$ by

its angular average over the FS. The matrix element $g(q)$ is given by Eq. (14) and the dispersion has the form $\omega_s(q) = \omega_s(0) + b_s q^2$. Then one finds

$$\left\langle \frac{2|g(q)|^2}{\omega_s(q)} \right\rangle_{\text{FS}} = \frac{1}{MN\omega_s(0)\omega_s(2k_F)} \left(\frac{K\mathcal{E}}{1 + k_{TF}^2/K^2} \right)^2, \quad (18)$$

taking into account

$$\frac{1}{2k_F^2} \int_0^{2k_F} \frac{q dq}{\omega_s^2(q)} = \frac{1}{\omega_s(0)\omega_s(2k_F)}. \quad (19)$$

The average given by Eq. (18) plays the role of BCS coupling parameter. The interaction kernel is now given by

$$V_2(k, k') = \left\langle \frac{|g(q)|^2}{\omega_s(q)} \right\rangle_{\text{FS}} \int_0^{\theta_m} \sin \theta \, d\theta Q_2(\mathbf{k}, \mathbf{k}'). \quad (20)$$

With the effective electron-electron interaction consisting of the Coulomb part, Eq. (12), and the attractive part due to the exchange of soft phonons, Eq. (20), the transition temperature will be calculated in Sec. IV.

IV. TRANSITION TEMPERATURE $T_c(n)$

According to Eq. (4) for the energy gap Δ_0 and the BCS relation between Δ_0 and T_c , the transition temperature is

$$T_c = 0.57 \tilde{\omega} e^{-1/N(0)(V_1 + V_2)}. \quad (21)$$

The frequency $\tilde{\omega}$ is given by Eqs. (5), (12), and (20); V_1 and V_2 are the values of the interaction kernels at the FS. All three parameters $\tilde{\omega}$, V_1 , and V_2 depend on the electron concentration n .

The BCS formula (21) will be used to discuss the concentration dependence of T_c . In this formula, renormalization effects are apparently neglected. Let us keep in mind, however, that the deformation-potential constant \mathcal{E} is an adjustable parameter. A value will be taken for \mathcal{E} that gives a T_c near the experimental T_c for a given concentration.

The values of V_1 and V_2 are found from Eqs. (12) and (20) in the form

$$N(0)V_1 = -\frac{1}{2} \frac{m_b}{m^*} \frac{\epsilon_\infty a^2}{\epsilon_0(k_F)} \ln \left(1 + \frac{\epsilon_0(k_F)}{\epsilon_\infty a^2} \right) \quad (22)$$

for the Coulomb interaction, and

$$N(0)V_2 = \frac{N(0)}{MN\omega_s(0)\omega_s(2k_F)} \left(\frac{K\mathcal{E}}{1 + k_s^2/K^2} \right)^2 \quad (23)$$

for the attractive interaction. Let us discuss the parameters occurring in Eqs. (22) and (23).

(a) *Density of states $N(0)$.* The band density of states for one spin direction, $N(0) = k_F m_b / 2\pi^2$, is not known for the tetragonal phase. The screening density of states is proportional to m^* ; specific-heat measurements yield

$m^* = 5.2m_b$.³⁸ We assume $m^* = m_b$ to determine the deformation-potential constant \mathcal{E} . Thereby, electron-phonon renormalization effects are neglected and it is assumed that the FS is connected. If a many-valley model applies, then $m_b = m^*/\nu^{2/3}$ and $k_F = 3.1(n/\nu)^{1/3} \text{ cm}^{-1}$, where ν is the number of valleys. In this case \mathcal{E} increases by a factor $\nu^{1/2}$. Since \mathcal{E} is an adjustable parameter, the shape T_c versus n curve is almost independent of the electronic structure.

(b) *Coulomb interaction*: ϵ_∞ , $\epsilon_0(q)$, ω_l , $\omega_t(q)$. The high-frequency dielectric constant is $\epsilon_\infty = 5.2$ and the low-frequency dielectric constant is $\epsilon_0(q=0) = 2 \times 10^4$.³⁹ In the Coulomb interaction occurs also the longitudinal frequency $\omega_l = 5.45 \times 10^{12} \text{ cps}$.⁴⁰ The frequency of the transverse "ferroelectric mode," $\omega_t(q)$ turns away sharply from $q=0$ (see Fig. 3). Therefore, the static dielectric constant depends on q . In the cubic phase, this dependence has near $q=0$ the form

$$\frac{\epsilon_0(q)}{\epsilon_\infty} = \frac{\omega_l^2}{\omega_l^2(q)} \prod_{j=2}^4 \frac{\omega_{lj}^2}{\omega_{lj}^2}, \quad (24)$$

where ω_{lj} and ω_{lj} are the frequencies of the higher optical branches at the zone center. For $q=0$, Eq. (24) goes into the Lyddane-Sachs-Teller relation for SrTiO_3 .²⁰ For small q , it presents a good approximation for $\epsilon_0(q)$ and accounts for the rapid decrease of lattice screening as q increases from zero. This effect is taken into account in the Coulomb interaction at the FS by writing $\epsilon_0 = \epsilon_0(k_F)$ in Eq. (12). The dispersion of the "ferroelectric mode" $\omega_t(q) = \omega_t(0) + 4.2 \times 10^{-3} q^2 \text{ cps}$ is found from the neutron diffraction measurements of Cowley,⁴⁰ using $\omega_t(0) = 1.9 \times 10^{11} \text{ cps}$. This value of $\omega_t(0)$ is obtained from the Lyddane-Sachs-Teller relation with the static dielectric constant $\epsilon_0(0) = 2 \times 10^4$.

(c) *Attractive interaction*: $\omega_s(q)$, K , \mathcal{E} . The dispersion of the soft mode has the form $\omega_s(q) = \omega_s(0) + b_s q^2$; this dispersion has not yet been measured. We take $b_s = 1.1 \times 10^{-3}$ in order to fit the shape of the experimental $T_c(n)$ curve. A pertinent parameter is $\omega_s(0)$ in Eq. (23). The value for $\omega_s(0) = 1.38 \times 10^{12} \text{ cps}$ (or 0.0057 eV) is accurately known from Raman and neutron scattering.^{25,26} For \mathbf{K} we take the corner R of the cubic Brillouin zone, $K_x = K_y = K_z = \pi/a$, where $a = 3.9 \times 10^{-8} \text{ cm}$. The soft $q=0$ phonons of the tetragonal phase result from the condensation of a triply degenerate phonon of odd symmetry at R . At the transition temperature T_a ($= 110^\circ \text{K}$ for SrTiO_3), the R -phonon symmetry Γ_{25} is broken and two new $q=0$ phonons of even symmetry, A_{1g} and E_g , arise. Below the transition temperature, R becomes a lattice point in wave-vector space. The deformation potential for the A_{1g} phonon is taken as $\mathcal{E} = 0.99 \text{ eV}$, so that T_c becomes 0.275°K at $n = 10^{20} \text{ cm}^{-3}$.

³⁸ E. Ambler, J. H. Colwell, W. R. Hosler, and J. F. Schooley, *Phys. Rev.* **148**, 220 (1966).

³⁹ H. E. Weaver, *J. Phys. Chem. Solids* **11**, 274 (1959).

⁴⁰ R. A. Cowley, *Phys. Rev.* **134**, A981 (1964).

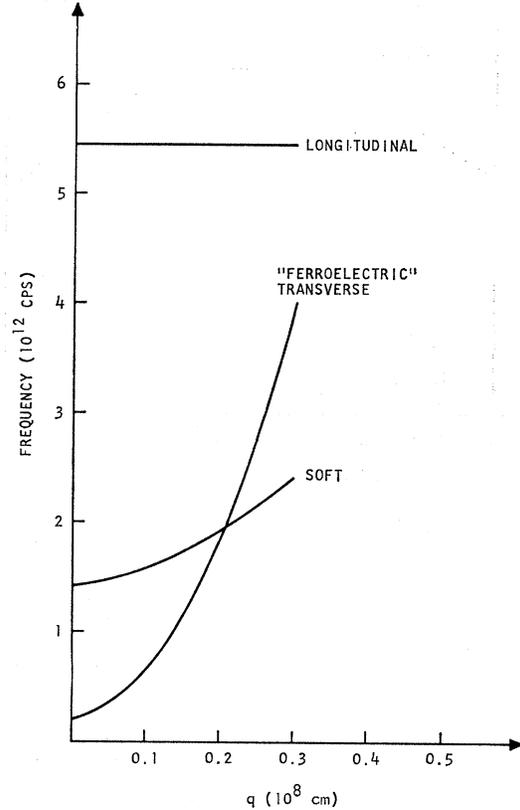


FIG. 3. Dispersion of the optical-phonon frequencies characterizing the effective electron-electron interaction; ω_l is the LO phonon frequency, $\omega_t(q)$ is the TO phonon frequency, and $\omega_s(q)$ is the soft-phonon frequency. Parameter values characterizing the dispersion curves are given in Sec. IV.

Under (a)–(c) are clearly stated the values of the parameters used to determine the effective electron-electron interaction. Two of these parameters— \mathcal{E} and the dispersion term $b_s q^2$ of the A_{1g} phonon—are not known from either theory or experiment. We find, however, that the experimental $T_c(n)$ curve is obtained with a reasonable choice of both parameters. The dispersion of the soft phonon must be characterized by $b_s > 0$. Furthermore, our value $b_s = 1.1 \times 10^{-3}$ is of a magnitude comparable with those found from Cowley's curves for the soft-phonon branches (see Fig. 8 of Ref. 40). Our deformation-potential constant is small, $\mathcal{E} = 0.99 \text{ eV}$, for the following reason: Above the temperature T_a the electron-phonon matrix element for the R corner (Γ_{25}) vanishes. Below T_a the matrix element for the zone-center phonon (A_{1g}) is given by

$$g(0) = \int_{\text{crystal}} |\psi_{\mathbf{k}}(\mathbf{r})|^2 \delta V(\mathbf{r}, A_{1g}) d\mathbf{r} = \text{const } \varphi, \quad (25)$$

where $\varphi \propto (T_a - T)^{1/2}$ is the order parameter for the second-order phase transition⁴¹; at $T=0$, $\varphi \approx 0.037$.

⁴¹ H. Thomas and K. A. Müller, *Phys. Rev. Letters* **21**, 1256 (1960).

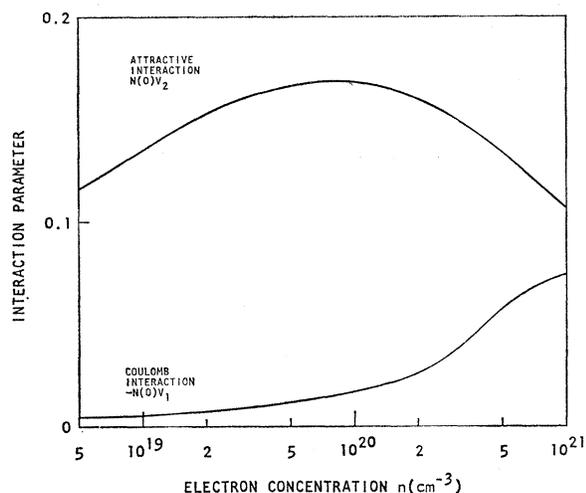


FIG. 4. Electron-concentration dependence of the coupling parameters $N(0)V_1$ and $N(0)V_2$ which determine the Coulomb interaction and the attractive interaction, respectively.

Therefore, we expect our deformation potential to be smaller by a factor of the order φ than ordinary deformation potentials for optical phonons in polar crystals.

The Coulomb interaction and the attractive interaction are shown in Fig. 4 as a function of n . The Coulomb interaction increases with n because the decrease of lattice screening outweighs the increase of electron screening in this concentration range. The attractive interaction first increases due to $N(0)$. After reaching a maximum, it decreases, since in Eq. (23) the change of $\omega_s(2k_F)$ and of the screening function become dominant.

Finally, the frequency factor $\tilde{\omega}$ must be known as a function of n . For metals, $\tilde{\omega} = 2\omega_{\text{Debye}}$, and for degenerate semiconductors where acoustic phonons provide the

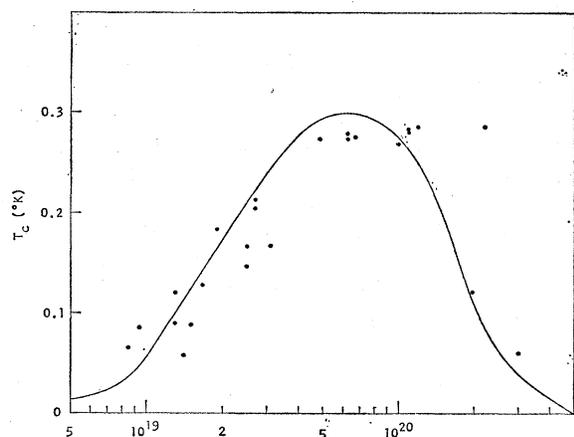


FIG. 5. Transition temperature as a function of the electron concentration.

⁴² S. C. Hunter and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A220**, 542 (1953).

TABLE I. Values for the frequency factor $\tilde{\omega}$ found from Eq. (5) with $V(k, k')$ given by the attractive interaction, Eq. (20).

n (cm ⁻³)	5×10^{18}	10^{19}	2×10^{19}	5×10^{19}	10^{20}	2×10^{20}	5×10^{20}
$\tilde{\omega}/2\omega_s(2k_F)$	1.26	1.48	1.83	1.85	1.57	1.18	1.10

attractive interaction, $\tilde{\omega} \approx 2\omega(2k_F)$.⁴² From an integration of Eq. (5), we find $\tilde{\omega} \sim 2\omega_s(2k_F)$; numerical values are given in Table I. The Coulomb interaction has been neglected in calculating $\tilde{\omega}$, since it is much smaller than the attractive interaction.

The comparison of T_c with experimental data is shown in Fig. 5. The initial increase of T_c is due to $N(0)$ and, to a small extent, to $\tilde{\omega}$. The final decrease of T_c is due to $\omega_s(2k_F)$ in the denominator of the matrix element, the screening of the matrix element by conduction electrons, and the increase of the Coulomb interaction caused by a decrease of lattice screening.

V. SUMMARY

For degenerate semiconductors, a T_c formula is derived by using Bogoliubov's asymptotic method. This formula is applied to calculate the electron-concentration dependence of T_c for strontium titanate. The result is shown in Fig. 5. The maximum in the T_c versus n curve is due to a maximum in the attractive electron-phonon interaction which is caused by the intravalley exchange of soft phonons of symmetry character A_{1g} . At low concentrations, the attractive interaction increases as the density of states at the FS. At high concentrations, the interaction decreases because of the increase of the phonon frequency $\omega_s(2k_F)$ and because of the enhanced screening of the electron-phonon interaction. Furthermore, at high concentrations the enhancement of the Coulomb repulsion due to the declining lattice screening of this repulsion contributes to a rapid decrease of the total electron-electron interaction.

Note added in proof. In a recent paper on superconducting semiconductors, C. S. Koonce and M. L. Cohen (KC) [Phys. Rev. **177**, 707 (1969)] claim that the Coulomb interaction given by Eq. (8) and derived earlier [J. Appel, Phys. Rev. Letters **17**, 1045 (1966)] is incorrect. However, it can be shown that Eq. (A16) of KC is identical with our Eq. (8). To this end, it is convenient to write the square ratio between the renormalized and unrenormalized LO phonon frequencies in the form

$$\omega_l^2/\Omega_l^2 = (\epsilon_\infty/\epsilon_0)[\epsilon_0(\omega, q)/\epsilon_\infty(\omega, q)].$$

Inserting this expression into Eq. (A17) of KC, we find with some algebra our Eq. (8).

ACKNOWLEDGMENTS

It is a pleasure to thank Professor W. Kohn for constructive discussions. I would like to thank Pro-

essor E. Burstein for some stimulating conversations and Professor Birman and Dr. Worlock for some helpful comments. A correspondence with Dr. Unoki and Dr. T. Sakudo and a report of work prior to publication from Professor Shirane and Professor Yamada are gratefully acknowledged.

APPENDIX A: BCS COUPLING PARAMETER FOR ACOUSTIC PHONONS

In an insulator the bare matrix element for intravalley scattering of electrons by acoustic phonons is given by

$$g^{(0)}(q) = i[1/2MN\omega^{(0)}(q)]^{1/2}qD, \quad (\text{A1})$$

where D is the deformation-potential constant and $\omega^{(0)}(q)$ is the acoustic-phonon frequency. In a degenerate semiconductor, the matrix element becomes⁴²

$$g(q) = i\left(\frac{1}{2MN\omega(q)}\right)^{1/2} q \left(\frac{n}{2N(0)} + \frac{q^2}{k_{\text{TF}}^2} D\right) / \left(1 + \frac{q^2}{k_{\text{TF}}^2}\right), \quad (\text{A2})$$

where k_{TF}^{-1} is the screening radius and $\omega(q) = uq$ is the renormalized phonon frequency. The BCS coupling parameter is given by the FS average of the quantity

$$\frac{2|g(q)|^2 N(0)}{\omega(q)} = -\frac{1}{2} \frac{n}{N} \frac{2}{3} \frac{E_F}{Mu^2} \left(\frac{k_{\text{TF}}^2}{k_{\text{TF}}^2 + q^2}\right)^2 \left(1 + \frac{3}{2} \frac{q^2}{k_{\text{TF}}^2} \frac{D}{E_F}\right)^2. \quad (\text{A3})$$

Here it is taken into account that $n/2N(0) = \frac{2}{3}E_F$, if one assumes that $m^* = m_b$. The average is given by

$$N(0)V = \frac{N(0)}{2k_F^2} \int_0^{2k_F} q dq \frac{2|g(q)|^2}{\omega(q)} \\ \simeq -\frac{n}{N} \frac{2}{3} \frac{E_F}{Mu^2} \left(1 + \frac{3}{4a^2} \frac{D}{E_F}\right)^2 \frac{a^2}{2(1+a^2)}, \quad (\text{A4})$$

where $a^2 = k_{\text{TF}}^2/4k_F^2$. With a deformation-potential constant of 15 eV and the parameters for SrTiO_{3-x} ($u = 7 \times 10^5$ cm/sec, $E_F = 7.2 \times 10^{-16} n^{2/3}$ eV), the BCS coupling parameter $N(0)V \simeq 10^{-2}$ for $n = 10^{20}$ cm⁻³ ($a^2 = 4$).

APPENDIX B: MATRIX ELEMENT FOR THE ELECTRON-SOFT-PHONON INTERACTION

In SrTiO_3 , the phase transition cubic \rightarrow tetragonal ($O_h^1 \rightarrow D_{4h}^{18}$) leads to an increase of the size of the unit cell. Therefore, more phonon branches occur in the tetragonal Brillouin zone. In Raman scattering and neutron diffraction, several new zone-center phonons are observed (see Fig. 6). Furthermore, it is found that the phase transition does not affect the frequencies of those zone-center phonons present before the transition.

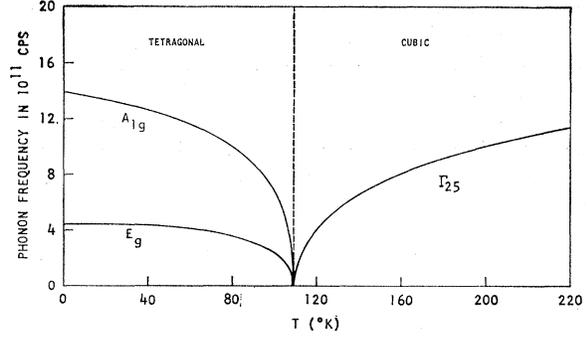


FIG. 6. Temperature dependence of the soft modes in SrTiO_{3-x} according to Raman scattering measurements by Fleury, Scott, and Worlock (Ref. 25) and neutron diffraction measurements by Shirane and Yamada (Ref. 26).

In particular, two new *soft* phonons of *even* symmetry have been found experimentally. The symmetries are A_{1g} or Γ_1 and E_g or Γ_5 in the notation for representations of molecular vibrations or of crystal phonons, respectively. The crucial question is: Do these soft optical phonons interact with the conduction electrons? The answer is given by the selection rules for intravalley scattering which depend on the symmetry character of both the phonons and electrons involved in these processes.

The unscreened matrix element for the interaction between a conduction electron in state \mathbf{k} and a phonon with wave vector \mathbf{q} and branch index j is given by

$$g^{(0)}(\mathbf{q}j) = \int_{\text{crystal}} \psi_{\mathbf{k}'}^* \mathcal{H}_{\text{pert}}(\mathbf{q}j) \psi_{\mathbf{k}} d\mathbf{r}. \quad (\text{B1})$$

The perturbation of the periodic potential caused by the phonon $\mathbf{q}j$ is given by

$$\mathcal{H}_{\text{pert}}(\mathbf{q}j) = \sum_{l\kappa} \mathbf{u}_{qj}(l\kappa) \cdot \nabla_{\mathbf{u}_{qj}} V[\mathbf{r} - \mathbf{R}(l\kappa)], \quad (\text{B2})$$

where $\mathbf{u}_{qj}(l\kappa)$ is the displacement vector of the κ th atom in the l th unit cell; $\mathbf{R}(l\kappa)$ is the position of the displaced atom. The displacement vector \mathbf{u}_{qj} can be written in terms of the eigenvector $\mathbf{e}(\kappa|\mathbf{q}j)$:

$$\mathbf{u}_{qj}(l\kappa) = (MN)^{-1/2} \mathbf{e}(\kappa|\mathbf{q}j) e^{i[\mathbf{q} \cdot \mathbf{R}^0(l) - \omega_j(\mathbf{q})t]}, \quad (\text{B3})$$

where M is the ionic mass in a unit cell and N is the number of cells per unit volume; $\mathbf{R}^0(l)$ is the origin of the l th unit cell. The time-dependent factor is unimportant and is set equal to unity.

To find the selection rules for the matrix element $g^{(0)}(\mathbf{q}j)$, one must know the transformation properties of the phonon eigenvectors $\mathbf{e}(\kappa|\mathbf{q}j)$ under a symmetry operation that sends the undistorted crystal into itself, leaving the coordinate system fixed. To formulate these transformation properties, the degeneracy of the phonon frequencies must be taken into account. Therefore,

Maradudin and Vosko,⁴³ in their work on phonon symmetries, replace the branch index j by a double index $\sigma\lambda$, where σ labels the distinct frequency values for a given \mathbf{q} , and λ ($=1, 2, \dots, f_\sigma$) labels the independent eigenvectors associated with the eigenvalue $\omega_\sigma^2(\mathbf{q})$. The index σ is here incorporated into \mathbf{q} . In terms of the eigenvector $\mathbf{e}(\kappa|\mathbf{q}\lambda)$, the matrix element has the form

$$g^{(0)}(\mathbf{q}\lambda) = \sum_{\kappa} \int_{\text{crystal}} \psi_{\mathbf{k}'}^* \mathcal{H}_{\text{pert}}(\kappa|\mathbf{q}\lambda) \psi_{\mathbf{k}} d\mathbf{r}, \quad (\text{B4})$$

where

$$\mathcal{H}_{\text{pert}}(\kappa|\mathbf{q}\lambda) = \frac{1}{(MN)^{1/2}} \mathbf{e}(\kappa|\mathbf{q}\lambda) \cdot \sum_l \nabla_{\mathbf{u}_{\mathbf{q}\lambda}} V[\mathbf{r} - \mathbf{R}(l\kappa)] e^{i\mathbf{q} \cdot \mathbf{R}^0(l)}. \quad (\text{B5})$$

Under a symmetry operation that leaves \mathbf{q} invariant, the perturbations $\mathcal{H}_{\text{pert}}(\kappa|\mathbf{q}\lambda)$ with $\lambda=1, \dots, f_\sigma$ are transformed into linear combinations of one another. The transformation is described by an f_σ -dimensional matrix. This matrix is the same as that describing the transformation of the eigenvectors $\mathbf{e}(\kappa|\mathbf{q}\lambda)$. The sum in Eq. (B5) is invariant under a symmetry transformation because

$$\nabla_{\mathbf{u}_{\mathbf{q}\lambda}} V[\mathbf{r} - \mathbf{R}(l\kappa)] = -\nabla_{\mathbf{r}} V[\mathbf{r} - \mathbf{R}^0(l\kappa)]. \quad (\text{B6})$$

In summary: $\mathcal{H}'(\kappa|\mathbf{q}\lambda)$ and $\mathbf{e}(\kappa|\mathbf{q}\lambda)$ have the same transformation properties; they transform according to the same representation of the group of \mathbf{q} .

The matrix element $g(\mathbf{q}\lambda) \neq 0$, provided that the inner Kronecker product of the representations of $\psi_{\mathbf{k}'}$ and $\psi_{\mathbf{k}}$ contains the representation according to which the $\mathbf{e}(\kappa|\mathbf{q}\lambda)$ transforms.⁴⁴ In the special case $q=0$, the matrix

element is finite if the symmetric Kronecker product between the representations of $\psi_{\mathbf{k}}$ contains the $q=0$ phonon symmetry. The symmetry of the $q=0$ displacement field is higher than that for any finite q . Consequently, if the matrix element is finite for $q=0$, it will also be finite near $q=0$.

In the case of strontium titanate, the symmetries of the new soft phonons at $q=0$ are even and are given by the representations $A_{1g}(\Gamma_1)$ and $E_g(\Gamma_5)$ of the tetrahedral point group. For the first case, the matrix element is finite because the symmetric Kronecker product between two representations of a finite group contains the identity A_{1g} . For the second case, the matrix element vanishes for $\mathbf{k}=\mathbf{k}'=0$, since the symmetric Kronecker products between the possible representations for $\psi_{\mathbf{k}=0}$ do not contain the two-dimensional representation E_g .

According to Eq. (B4), the matrix element for the A_{1g} phonon has the form

$$g^{(0)}(0) = i[1/2MN\omega_s(0)]K\mathcal{E}, \quad (\text{B7})$$

where \mathcal{E} is the deformation-potential constant and $K = (\pi/a, \pi/a, \pi/a)$. The constant \mathcal{E} is proportional to the order parameter φ for the phase transition cubic \rightarrow tetragonal and vanishes at the transition temperature T_a . The values of \mathcal{E} depends on the displacement field of the A_{1g} phonon and on the electronic structure. The displacement field consists of a rotation of oxygen ions around the tetragonal axis accompanied by a small dilatation of all ions in the direction of the axis. The wave functions of the conduction electrons have a large amplitude at the Ti^{+++} ions and a small amplitude at the O^{--} ions. The motion of the conduction electrons is affected by the A_{1g} phonon for two reasons. First, even a small dilatation along the tetragonal axis has a large effect, because a longitudinal polarization interacts strongly with the conduction electrons. Second, the motion of the O^{--} ions is important, since their long-range Coulomb potentials have a large effect on the energy of an electron at a neighbor Ti^{+++} site.

⁴³ A. A. Maradudin and S. H. Vosko, Rev. Mod. Phys. **40**, 1 (1968).

⁴⁴ J. L. Birman, M. Lax, and R. Loudon, Phys. Rev. **145**, 620 (1966).