

SUPERCONDUCTIVITY IN PSEUDOFERROELECTRICS

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Recently, superconductivity has been discovered in¹ SrTiO₃ and in mixed titanates² which can be denoted as pseudoferroelectrics, since their static dielectric constant ϵ is large and temperature dependent, and since a low-energy optical mode has been observed which shifts with temperature as $[\epsilon(T)]^{1/2}$ in accordance with Cochran's³ theory of ferroelectricity. The occurrence of superconductivity in these compounds has been explained with the help of Cohen's theory⁴ of superconductivity in semiconductors. This theory stresses the importance of intervalley electron transitions involving large momentum transfers and giving rise to a phonon-induced electron-electron interaction which is weakly screened, compared with the direct Coulomb interaction. Cohen's theory has led to the discovery and accounted for the explanation of superconductivity in germanium tellurides with carrier concentrations as small as $8.5 \times 10^{20} \text{ cm}^{-3}$.⁵

It is the purpose of this note to point out that intervalley transitions must not necessarily be invoked to explain the occurrence of superconductivity in SrTiO₃ and similar polar substances. Instead, we shall find that the contemporary theory of electron-phonon interactions in isotropic superconductors,⁶ based on the dynamic dielectric constant of the electron-phonon system for a polar substance, can account for the observed values of the transition temperature. The physical point is based on the observation that (1) the phonon spectrum of polar substances consists of one acoustical branch and of one or more optical branches, and that (2) the dielectric constant exhibits dispersion at the frequencies of the optical branches. Therefore, at frequencies smaller than those of the lowest optical branch, the acoustical phonons provide an attractive electron-electron interaction, whereas the direct Coulomb repulsion is small because of the large static dielectric constant, $\epsilon \sim 1000$. In other words, in the important low-frequency range of acoustic phonons the Coulomb repulsion is small, since the displacement polarization can follow a conduction electron. This qualifies a comment by Keldysh.⁷

For the quantitative discussion let us presume a simple electron-phonon model for a polar substance, namely, that the conduction electrons interact only with longitudinal phonons of an acoustical branch with maximum frequency ω_a and of an optical branch with maximum frequency $\omega_0 > \omega_a$. This model can be applied to SrTiO₃ where the real part of the longitudinal dielectric constant changes from its "static" value $\sim 10^3$ to a value of the order of 8 (which is close to the optical dielectric constant $\epsilon_\infty = 5.2$), after going through the first dispersion at the frequencies of the lowest optical branch. For larger frequencies only a small fraction of the displacement polarization follows the electron; this fraction is accounted for in the low-frequency dispersion. Then, for our model of a polar substance, the Dyson equation for the effective electron-electron interaction is shown in Fig. 1.⁸ Here $D(\omega, q)$ stands for an optical phonon or an acoustical phonon Green's function,

$$D_o(\omega, q) = |g_o(q)|^2 \left(\frac{1}{\omega - \Omega_o(q) - i0^+} - \frac{1}{\omega + \Omega_o(q) - i0^+} \right), \quad (1)$$

$$D_a(\omega, q) = |g_a(q)|^2 \left(\frac{1}{\omega - \Omega_a(q) - i0^+} - \frac{1}{\omega + \Omega_a(q) - i0^+} \right), \quad (2)$$

$$g_o(q) = -i \left(\frac{4\pi\alpha}{V} \right)^{1/2} \frac{\Omega_o(q)}{q} \left(\frac{1}{2m^* \Omega_o(q)} \right)^{1/4}, \quad (3)$$

$$g_a(q) = - \left(\frac{N_c}{2m \frac{c}{a} \Omega_a(q)} \right)^{1/2} \times \sum_i \langle \vec{k}' | \nabla U | \vec{k} \rangle \cdot \vec{\epsilon}_i(i) \exp(i\vec{q} \cdot \vec{r}_i), \quad (4)$$

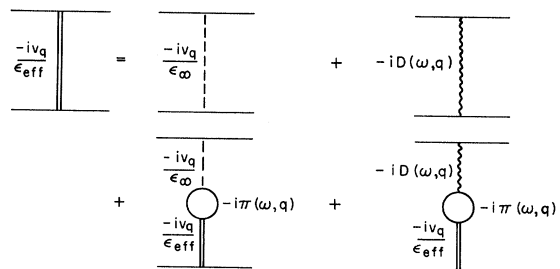


FIG. 1. Schematic diagram of Dyson's equation for the effective electron-electron interaction in a polar substance.

where $\vec{k}' - \vec{k} = \vec{q}$. Here $\Omega_0(q)$ and $\Omega_a(q)$ are the bare phonon frequencies in the absence of electron-phonon interactions, $\alpha =$ Fröhlich's coupling constant, $m^* =$ rigid lattice mass of an electron, $N_c =$ number of unit cells per cm^3 , $M_c =$ ionic mass per unit cell, $U = U(\vec{r} - \vec{\rho}_i)$ is the potential of ion i at equilibrium site $\vec{\rho}_i$, and $\vec{\epsilon}_q(i)$ is the polarization vector of a longitudinal phonon (defined in Ref. 6). In the equation

for the effective electron-electron interaction (Fig. 1) occurs the free-electron polarizability $\pi(\omega, q)$ which, in the random phase approximation (RPA), can be written in terms of Lindhard's dielectric constant of a free-electron gas, $\epsilon_{\text{RPA}}(\omega, q) = v_q \pi_{\text{RPA}}(\omega, q)$, where $v_q = 4\pi e^2 / q^2$ occurs in the equation for the effective electron-electron interaction (Fig. 1). The solution for the effective interaction is given by

$$\frac{v_q}{\epsilon_{\text{eff}}(\omega, q)} = \frac{v_q}{\epsilon_{\infty} + v_q \pi(\omega, q)} + v_q \left(\frac{1}{\epsilon_{\infty} + v_q \pi(\omega, q)} - \frac{1}{\epsilon + v_q \pi(\omega, q)} \right) \frac{\omega_0^2(q)}{\omega^2 - \omega_0^2(q)} + \frac{2\Omega_a(q) |g_a(q)|^2}{(1 + v_q \pi(\omega, q) / \epsilon_{\infty})^2} \frac{1}{\omega^2 - \omega_a^2(q)}, \quad (5)$$

where $\pi = \pi_{\text{RPA}}$, and where $\omega_0(q)$ and $\omega_a(q)$ are the renormalized phonon frequencies. The first term of Eq. (5) represents the direct Coulomb interaction between electrons screened by the rigid ionic lattice and by conduction electrons. The second term corresponds to the optical-phonon-induced electron-electron interaction; it is caused by the screened displacement polarization. The last term accounts for the interaction induced by acoustical phonons. Using Eq. (5) we can write down the interaction kernel in Eliashberg's gap equation,

$$\Delta(\omega) = \frac{1}{Z(\omega)} \int_{\Delta_{00}}^{\omega_c} d\omega' \text{Re} \left\{ \frac{\Delta'}{(\omega'^2 - \Delta'^2)^{1/2}} \right\} [K^{\text{ph}}(\omega, \omega') - U], \quad (6)$$

where $\Delta_{00} = \Delta(\omega = \Delta_{00})$ is the zero-temperature gap parameter and where $Z(\omega)$ is the renormalization parameter. The phonon part of the kernel is $K_0 + K_a$, where

$$K_0(\omega, \omega') = \frac{N(0)}{2k_{\text{F}}^2} \int_0^{2k_{\text{F}}} q dq \bar{g}_0(q) \left| \frac{1}{\omega' + \omega + \omega_0(q) - i0^+} + \frac{1}{\omega' - \omega + \omega_0(q) - i0^+} \right|, \quad (7)$$

and where K_a is given by a corresponding expression. The coupling parameters are

$$\bar{g}_0(q) = -i \left(\frac{4\pi\alpha(q)}{V} \right)^{1/2} \frac{\omega_0(q)}{q} \left(\frac{1}{2m^*\omega_0(q)} \right)^{1/4}, \quad (8)$$

$$\bar{g}_a(q) = - \left(\frac{\Omega_a(q)}{\omega_a(q)} \right)^{1/2} \frac{g_a(q)}{1 + v_q \pi[\omega_a(q), q] / \epsilon_{\infty}}. \quad (9)$$

Here $\alpha(q)$ is Fröhlich's coupling constant modified by screening effects.⁹ Equation (6) has been derived by Eliashberg under the assumption that the Fermi energy is larger than the maximum phonon frequency. This condition requires that in SrTiO_3 the electron concentration $n > 10^{20} \text{ cm}^{-3}$ ($m^*/m = 5$). Then one can take $\omega = 0$ in $\pi(\omega, q)$. With $v_q \pi(0, q) = k_{\text{TF}}^2 / q^2$, where k_{TF}^{-1} is the Thomas-Fermi screening distance, and ignoring the dispersion of optical phonons, $\omega_0(q) = \omega_0$, we find

$$K_0(\omega, \omega') = \lambda_0 \frac{\omega_0}{2} \left(\frac{1}{\omega + \omega' + \omega_0 - i0^+} + \frac{1}{\omega - \omega' + \omega_0 - i0^+} \right), \quad (10)$$

where

$$\lambda_0 = a^2 \ln \left(1 + \frac{1}{a^2} \right) - \frac{\epsilon_{\infty}}{\epsilon} a^2 \ln \left(1 + \frac{\epsilon}{\epsilon_{\infty} a^2} \right), \quad (11)$$

with $a^2 = k_{\text{TF}}^2 / 4\epsilon_{\infty} k_{\text{F}}^2$. Since short-wavelength phonons play a dominant role, $K_a(\omega, \omega')$ can also be rewritten in the form of Eq. (10), assuming an Einstein distribution centered at $\omega_a(2k_{\text{F}})$.¹⁰ The cou-

pling constant is given by

$$\lambda_a = \frac{N(0)}{k_{\text{TF}}^2} \int_0^{2k_{\text{F}}} q dq \frac{|\bar{g}_a(q)|^2}{\omega_a(q)}. \quad (12)$$

An *ab initio* calculation of λ_a has not been performed. As for the q dependence of $\bar{g}_a(q)$, it is determined by the matrix element in Eq. (4). The ionic potentials are of the Coulomb form; then

$$\lim_{q \rightarrow 0} \left| \sum_i \langle \vec{k}' | \nabla U(\vec{r} - \vec{\rho}_i) | \vec{k} \rangle \cdot \vec{\epsilon}_q(i) \exp(i\vec{q} \cdot \vec{\rho}_i) \right|^2 = \frac{\text{const.}}{q^2}.$$

With the fair assumption that this q dependence is approximately valid for all values of q , one finds

$$\lambda_a = \frac{C}{2} \frac{a^2}{1+a^2}, \quad (13)$$

where $C \sim 1$. With $C=1$, Eq. (10) goes into the expression derived by Anderson and Morel¹⁰ for metals, except that k_{TF} is replaced by $k_{\text{TF}}/(\epsilon_\infty)^{1/2}$. The interaction kernel of Eq. (6) contains the pseudo-Coulomb potential,

$$U = \frac{\mu}{1 + \mu \ln(\xi/\omega_c)}; \quad \mu = \frac{a^2}{2} \ln\left(1 + \frac{1}{a^2}\right). \quad (14)$$

We are interested in electron concentrations n at least one order of magnitude smaller than in metals. However, Éliashberg's calculation presumes that the Fermi energy $\xi \gtrsim \omega_c (= 8\omega_0)$. The corresponding concentration range is $10^{20} \lesssim n \lesssim 5 \times 10^{21} \text{ cm}^{-3}$. For this range the denominator in Eq. (14) is approximately equal to one. Only if $\xi \gg \omega_0$ is the Coulomb potential μ reduced by an amount significant for superconductivity in polar substances, as pointed out by Gurevich, Larkin, and Firsov.¹¹ This

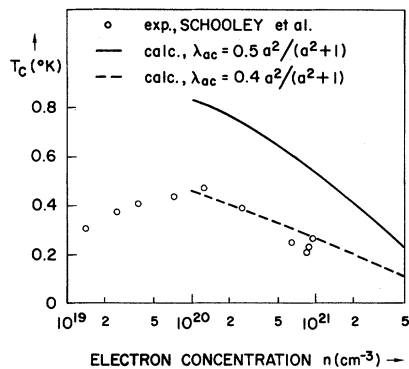


FIG. 2. Comparison between experimental and theoretical values of the transition temperature T_c for SrTiO_3 . The experimental values are taken from Schooley, Hosler, Ambler, Becker, Cohen, and Koonce.¹

reduction is clearly not responsible for the occurrence of superconductivity in SrTiO_3 , since transitions to the superconducting state have been observed for $n < 10^{19} \text{ cm}^{-3}$ ($\xi < \omega_0$). With $U = \mu$, Eq. (6) has been solved for SrTiO_3 with n as a variable parameter and with $m^*/m = 5$, $\epsilon = 10^3$, $\epsilon_\infty = 5.2$, and $\omega_0 = 7 \times 10^{12} \text{ sec}^{-1}$; $\omega_a = \omega_a(2k_{\text{F}})$ is read from an experimental dispersion curve.¹² In solving the gap equation we make the weak-coupling approximation, $\Delta(\omega) = \Delta_{00}$ under the square root; renormalization is taken into account. The result for T_c , found from the BCS relation for weak-coupling superconductors, $3.5k_{\text{B}}T_c = 2\Delta_{00}$, is shown in Fig. 2. For $\lambda_a = 0.4a^2/(1+a^2)$ there is good agreement between theory and experiment. A semiempirical determination of λ_a using Morel's¹³ relation between electrical resistivity ρ and λ_a and the experimental results of Frederikse, Thurber, and Hosler¹⁴ is not feasible, since $\rho_{\text{exptl.}} \propto T^{-3}$ at low temperatures, whereas for acoustical phonon scattering $\rho_{\text{theor.}} \propto T^{-1}$; however, at 78°K, $\rho_{\text{exptl.}}$ and $\rho_{\text{theor.}}$ are of comparable magnitude. Finally, let us mention that the validity of our calculation, but not that of the physical argument, is restricted to $10^{20} \lesssim n \lesssim 5 \times 10^{21} \text{ cm}^{-3}$. For smaller concentrations the Éliashberg theory does not apply in its present form, since $\xi \lesssim \omega_0$. For larger concentrations, the interactions between electrons have a shorter range, and the dielectric constants ϵ_∞ and ϵ must be replaced by q -dependent functions.

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SINGLE-PARTICLE AND EQUILIBRIUM COLLECTIVE EFFECTS OF HYDROXYL IMPURITIES IN KCl

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Quantum-mechanical polarizability data for OH^- in KCl are combined with calculated equilibrium dipole-ordering data for a dilute system of dipoles in an NaCl-type lattice, and a comparison is made with low-temperature dielectric measurements on KCl:OH at 10^2 cps.

The low-temperature behavior of certain substitutional impurities in alkali halides has attracted considerable recent attention. Theoretical studies of the low-temperature dielectric properties of OH^- -doped KCl have been concerned either with the quantum-mechanical polarizability of a single dipole neglecting collective effects,¹ or with the collective dipole ordering using the classical polarizability relation.²⁻⁴ There are now sufficient experimental and calculated data available on the KCl:OH system to include both the single-particle and equilibrium collective effects in the same treatment, and the purpose of this Letter is to carry out such a treatment.

Starting with the Fröhlich theory⁵ for a dielectric that does not display a spontaneous polarization, the following expression is obtained⁴:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_m - 1}{\epsilon_m + 2} + \frac{4\pi}{3} N \alpha(T) \left[1 + \left\langle \sum_{j>1} \vec{\sigma}_1 \cdot \vec{\sigma}_j \right\rangle \right], \quad (1)$$

where ϵ and ϵ_m are the dielectric constants of the doped and pure crystal, N is the impurity dipole concentration, $\alpha(T)$ is the polarizability of a single impurity in the crystal, and the average $\langle \rangle$ is the dipole ordering term, the $\vec{\sigma}_j$ being unit dipoles (dipole No. 1 is selected as the reference dipole). We will next con-

sider the single-particle term, $\alpha(T)$, and the collective term, $\langle \rangle$, individually, and then return to Eq. (1) for comparison with experimental data.

The energy-level scheme of a dipole in an octahedral crystal field (see Fig. 1) consists of a ground-state singlet with energy -2Δ (A_{1g}), a triplet with 0 energy (T_{1u}), and a doublet with energy Δ (E_g); and the recently measured⁶ zero-field splitting is

$$\Delta/k = 0.30 \pm 0.03^\circ\text{K}.$$

The polarizability of a dipole with this level scheme is given by^{7,8}

$$\alpha(T) = \frac{\mu_1^2 (1 - e^{-2\beta\Delta}) + 2\mu_2^2 (e^{-2\beta\Delta} - e^{-3\beta\Delta})}{\Delta (1 + 3e^{-2\beta\Delta} + 2e^{-3\beta\Delta})}, \quad (2)$$

$$\beta = 1/kT,$$

where μ_1 and μ_2 are the dipole transition matrix elements between the levels A_{1g} - T_{1u} and T_{1u} - E_g , respectively. For later comparison with experimental data it will be convenient to express Eq. (2) in a form that displays the high-temperature (classical) limit, $\mu^2/3kT$, where $\mu^2 = \mu_1^2 + \mu_2^2$. To do this, the linear term of the Taylor expansion of each exponential in the numerator of Eq. (2) is added and sub-