Theory of superconductivity due to Ngai’s mechanism in lightly doped SrTiO₃

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We develop a theory of superconducting pairing in low-density Strontium titanate due to quadratic coupling of electron density to soft transverse optical phonons [1]. It leads to static attractive potential between electrons which decay length l₀ ≈ 70nm that scales inversely with soft optical gap ω₁. For low electron densities n ≤ 10¹⁸cm⁻³ attraction between electrons is local and transition temperature Tc was found using Ref. [2]. The Tc(n) dependence in agreement with experimental data [3] for low doping was calculated. Next, we show that suppression of Tc by hydrostatic pressure [1] and strong increase of Tc due to isotop substitution ¹⁶O → ¹⁸O observed in [4] are explained within our theory.

Introduction. Strontium titanate (STO) is a wide-gap band insulator known for more than a century for its unusual properties related to its proximity to a ferroelectric transition, see Refs [6–8] for recent reviews. It can be transformed to a very dilute metal by tiny doping, either by oxygen deficiency or by substitution of small portion of Ti atoms with Nb. The key feature of this metal which makes it very different from majority of various metals and doped semiconductors is that Coulomb interaction is due to isotop substitution [5]: 35% substitution ¹⁶O → ¹⁸O increases Tc by factor ~ 1.5 and also increases upper critical field nearly twice. An important step forward was made in Ref. [12] which put support to the early idea [1] about relevance of coupling between electron density and two soft transverse optical (TO) phonons, those existence was known since Ref. [15]. Namely, Ref. [14] provide arguments based upon analysis of optical absorption spectra in favor of large magnitude of this electron coupling to two TO phonons, of the form ψ†ψu², where ψ is the electron annihilation operator and u is the TO phonon displacement amplitude. Very low gap known for these phonons at low temperatures, kω₁ ≈ 1.5meV, is directly related to large ε₀ value, ω₁ ∝ 1/√ε₀.

In the present Letter we further develop the ideas proposed in Refs. [11,14] and use quadratic coupling between electrons and TO phonons as phenomenological input for our theory. We concentrate on the lowest-density limit n < nₖ = 1.5 · 10¹⁸cm⁻³ where single-band Fermi-liquid in realized [3], and demonstrate that electron-electron interaction mediated via two TO phonons leads to consistent description of superconducting Tc(n) evolution with n, Ref. [3], and of its giant isotop effect [5]. Paired by two-phonon exchange differs a lot from usual single-phonon exchange but leads to a simple picture: electrons attract each other via static potential which decays with a distance as −V(r) ∝ r⁻³e⁻²r/l₀, where l₀ = s/ω₁ ≈ 3.3 nm is the characteristic length related to soft polarization TO mode; for the velocity of the TO mode we use s = 7.5 · 10⁶cm/s, see [16]. At low electron densities we consider, kF₁l₀/2 < 0.6 and electron-electron scattering can be considered short-range. Frequency dispersion of e-e scattering occurs then at the energy scale ϵ ≥ ω₁, and it is relatively weak in the low-density region, since E₁(n) does not exceed ω₁ considerably.

Superconductivity in a bulk Fermi-gas with local attraction was studied theoretically long ago by Gor’kov and Melik-Barhudarov [2], see also more recent paper [19]. They found expression for Tc similar to the one known for usual BCS theory, with the major exception that Debye energy is replaced by Fermi energy in
the prefactor, \( T_c \approx 0.27 E_F e^{-1/\lambda_0} \). Dimensionless coupling constant \( \lambda_0 = v_0 V_0 \), where \( V_0 \) is the renormalized electron-electron scattering potential in the \( l = 0 \) scattering state (s-wave), and \( v_0 \) is the density of states at Fermi-level per single spin projection. Below we demonstrate that attractive short-range potential does indeed appear due to two TO phonon exchange, and calculate \( T_c \) as function electron density \( n \). Then we extend our results to the case of partial isotopic substitution \( {}^{16}\text{O} \to {}^{18}\text{O} \), which reduces \( \omega_T \) and thus increases \( V_0 \) and \( T_c \).

Electron-electron interaction mediated by a pair of TO phonons. We start with the action for coupled electron-phonon system close to ferroelectric transition:

\[
S = S_e^{(0)} + S_{ph}^{(0)} + S_{\text{int}}
\]

\[
S_{ph}^{(0)} = \frac{m}{2} \int d^3x\, dt\left[ \frac{\dot{\bar{u}}_a^2}{2} - s^2(\nabla_\beta u_\alpha)^2 - \omega_T^2 u_\alpha^2 \right]
\]

\[
S_{\text{int}} = -g\rho_m \int d^3x\, d^3\psi(\bar{\psi})^u_a
\]

and \( S_e^{(0)} \) is just the action of free electron gas with effective mass \( m_e = 1.8m_0 \), according to the data from Ref. 21 for low electron densities in STO, \( m_0 \) being free electron mass. Here \( u_\alpha \) is displacement coordinate for TO soft optical phonon, \( \psi(x) \) is the electron field operator and \( \rho_m = 5.11g/cm^3 \) is the mass density of STO. The action \( S_{ph}^{(0)} \) describes long-wave-length TO phonons with momenta \( q \ll K_{BZ} \), where \( K_{BZ} \) is the boundary of the Brillouin zone. Whenever high-\( q \) cut-off will be needed in the further calculations, we introduce it by using the simplest TO phonon lattice spectrum of the form appropriate for cubic lattice, with the BZ including \( p_{x,y,z} \in (\pm \frac{\alpha}{a}, \pm \frac{\alpha}{a}) \):

\[
\omega^2(p) = \omega_T^2 + \frac{4\lambda^2}{a^2} \left( \sin^2 \frac{p_x a}{2} + \sin^2 \frac{p_y a}{2} + \sin^2 \frac{p_z a}{2} \right)
\]

where \( a \approx 0.4nm \) is the lattice spacing. The coupling constant \( g \) in Eq. (1) has natural dimension Length\(^3\)/Time\(^2\); we represent it in the form

\[
g = \lambda a^3 \omega_L^2
\]

where \( h\omega_L \approx 0.1eV \) is the largest longitudinal optical gap of STO, and \( \lambda \approx 1 \) is the dimensionless coupling constant of the problem. In a recent paper 21 the same type of electron coupling to TO phonons was employed to study theoretically high-temperature transport properties of lightly doped STO; comparison of this theory predictions with the data 22 provide the value of the coupling constant \( \lambda \approx 0.9 \).

Static interacting potential between two electrons can be obtained from the action (1) by integrating out the phonons; the corresponding diagram is shown in Fig. 1.
Note that dependence on $q$ is relatively weak, as well as dependence of $V(\epsilon,q)$ on $\epsilon$ (to be discussed below); the reason is that major (logarithmic) contribution to the integral in Eq.(3) comes from TO phonons with momenta $p$ in a broad range $k_F \leq p \leq \pi/a$. For the same reason the effects of renormalization of phonon spectrum due to interaction with electrons are weak at low concentrations $n_e \leq 1.5 \cdot 10^{18} \text{cm}^{-3}$; we will discuss these effects later on. For completeness, we provide the e-e potential in coordinate space at $r \geq a$ ($K_1$ is the MacDonald function):

$$V(r) = \frac{W}{2\pi l_0 r^2} K_1 \left(\frac{2r}{l_0}\right)$$ (9)

**Superconducting transition temperature.** Attractive e-e interaction defined by Eqs.(8) decays exponentially at $r > l_0/2$ so it can be considered as nearly local in the range of electron densities $n < n_{c1} = 1.5 \cdot 10^{18} \text{cm}^{-3}$. Then we can employ the theory [2] for superconductivity in a Fermi-gas with local instantaneous attraction. The result [2] for $T_c$ is

$$T_c = \zeta E_F \exp \left(-\frac{1}{\nu_0 V_0}\right) \quad \zeta = \frac{\epsilon C}{\pi} \left(\frac{2}{\epsilon}\right)^{7/3} \approx 0.27$$ (10)

where $\nu_0 = m_e k_F/2\pi^2 \hbar^2$ is the DoS per one spin projection and $V_0$ is the $l = 0$ harmonics of the pairing potential [8] evaluated at the Fermi-surface. Assuming FS to be spherical (which is good approximation for STO at low densities), we find (here $\theta$ is the azimuthal angle at the FS, so $q = 2k_F \sin \frac{\theta}{2}$):

$$V_0 = \frac{1}{2} \int_0^\pi |V(0,q)| \sin \theta d\theta = W \left(\ln \frac{n}{\eta} - \frac{1}{6} k_F^2 l_0^2\right)$$ (11)

The plot of $T_c(n)$ dependence which follows from Eqs.(10)-(11), together with definition of $W$ in Eq.(7), is shown in Fig. 2 together with the data from Ref. [3].

![Fig. 2: Critical temperature as function of conduction electron density for several values of electron-phonon interaction constant $\lambda$. Orange points represent experimental data from Ref. [3]](image)

The choice of electron-phonon coupling constant $\lambda = 1.1$ provides the best correspondence with the data. Some discrepency is still present, and it will be discussed below.

**Suppression of $T_c$ by hydrostatic pressure.** Relevance of STO proximity to ferroelectric critical point to the origin of superconductivity was extensively discussed in Ref. [4]. In particular, they present data on the effect of hydrostatic pressure upon $T_c$ and upon dielectric constant $\epsilon$, see Fig.2 in Ref.[4] which demonstrate that decrease of $\epsilon$ leads to sharp fall of $T_c$. According to the standard Lyddane-Sachs-Teller relation, $\epsilon(P)/\epsilon = (\omega_T/\omega_F(P))^2$ where subscript $P$ stands for pressure-modified values. Using the data from Fig.2b of Ref.[4], we calculated, following our theory, $T_c(P)$ for our largest electron density $n_e = 1.2 \cdot 10^{18} \text{cm}^{-3}$. The result is present in Fig. 3.

![Fig. 3: Plot for critical temperature-pressure dependence for two values of electron density indicated in the plot, obtained with $\lambda = 1.1$ and $\omega_F(P)$ dependence extracted from the data of Ref. [4]].(image)

Accurate comparison of our prediction for $T_c$ suppression with the corresponding data from Ref. [4] is not possible since they studied the sample with much higher electron density $n = 3.4 \cdot 10^{19} \text{cm}^{-3}$, the overall trend is similar. Our theory predicts a bit smaller suppression effect: factor 2.5 between $P = 0$ and $P = 4$ KBar, while experiment [4] provides suppression factor close to 4, at the electron density which is 30 times higher. One cannot exclude that hydrostatic pressure may decrease a little the coupling constant $\lambda$, which would lead to additional suppression of $T_c$, not accounted in our results in Fig.3.

**Isotopic enhancement of $T_c$.** In classical weak-coupling superconductors with phonon mechanism of e-e attraction, isotopic substitution of some part of atoms by their heavier isotops leads usually to weak suppression of $T_c$ with increase of the typical atom mass $M$. The reason is that $T_c = 1.13\omega_D^{-1}/\lambda\eta$ is proportional to the Debye frequenec $\omega_D \propto 1/\sqrt{M}$, while effective coupling constant $\lambda\eta$ is independent on $\omega_D$; the latter statement is not entirely evident, but it follows from Eliashberg theory of phonon-coupled superconductors [10]. Recent experimental data present in Ref. [5] demonstrate sharp departure from the usual behaviour: substitution of 35% of Oxygen atoms $^{16}O$ by their heavy isotop $^{18}O$ resulted in a factor $\approx 1.5$ raise of $T_c$ for the whole range of studied electron densities, $4 \cdot 10^{19} \text{cm}^{-3} < n < 10^{20} \text{cm}^{-3}$.
Another set of data demonstrating the same effect (for higher electron densities) can be found in Ref. [23].

To explain this giant positive isopop effect, we note that under such an isopop substitution, insulating STO becomes a ferroelectric [13]. It means that in the isopop-modified material the TO gap $\omega_T \to 0$. To take it into account within our theory of superconductivity in STO, we need just to calculate the amplitude $V_0$ at $\omega_T = 0$. Now logarithmic integral in Eq. (6) diverges at the lower limit, while for $V(q)$ we find, instead of Eq. (8), the following result:

$$V(q) = -W \ln \frac{\eta n}{qa}$$

Calculating the $l = 0$ scattering amplitude like in Eq. (11), we find

$$V_0 = -W \left( \ln \frac{\eta e^{3/2}}{2k_F a} \right)$$

We calculated, using Eqs. (13) and (11), the ratio of transition temperatures for isopop-substituted and native STO at the two values of carrier concentrations, $n_{\text{low}} = 5.4 \times 10^{17} \text{cm}^{-3}$ and $n_{\text{high}} = 1.2 \times 10^{18} \text{cm}^{-3}$ and found

$$\left( \frac{T_c}{T_c} \right)_{n_{\text{low}}} = 2.5 \quad \left( \frac{T_c}{T_c} \right)_{n_{\text{high}}} = 1.8$$

The data [5] provide increase of $T_c$ by factor 1.5 at even higher concentrations, starting from $n = 4 \times 10^{18} \text{cm}^{-3}$, which seems to be quite consistent with our results in Eq. (14). For a weaker isopop substitution $\omega_T$ can be only partially suppressed, so the enhancement of $T_c$ will be smaller. We calculated transition temperature $T_c$ as function of partially suppressed TO gap $\omega_T$. It was done by means of numerical integration starting from $\omega = 0$ version of Eq. (4); the result is present in Fig. 4 and can serve as a prediction for future experiments with isopop-substituted STO.

FIG. 4: Critical temperature as function of the TO phonon gap $\omega_T$ for two values of the electron density.

Note that relative enhancement of the upper critical field $H_{c2}$ observed in Ref. [5] due to isopop substitution is higher than the corresponding increase of $T_c$ - roughly it is a factor 2 instead of 1.5. We expect it to be related with additional disorder which accompanies partial isopop substitution. Indeed, normal-state resistance of isopop-substituted samples is enhanced, see Ref. [23].

Conclusions. We developed a theory able to predict superconducting transition temperature in lightly doped STO as function of conduction electron density $n \leq n_{c1} = 1.5 \times 10^{18} \text{cm}^{-3}$; the theory has single fitting parameter $\lambda$ which determines electron coupling to a pair of TO phonons. Comparison with the data for $T_c(n)$ from Ref. [3] selects the optimal value this parameter $\lambda = 1.1$, which is close to the value 0.9 found by totally different method in Ref. [21]. We note that the estimate for effective strength of e-e attraction $\lambda_{2ph} \approx 0.28$ found in Ref. [11] for much higher values of $n_c$ does not include large logarithmic factor we discovered, see Eq. (6). It is due to integration over large phase volume of two virtual TO phonons. Our theory is in good qualitative agreement with experiments on $T_c$ effects due to isopop substitution [5, 23] and hydrostatic pressure [4].

The limitation of low densities used in our theory was used, in the first place, in order to concentrate on the simplest situation of a single band filled by conduction electrons, while at higher $n$ second band starts to be filled [3] and more involved calculations are necessary. There are few effects which we neglected so far while they are present, in principle, in the single-band problem as well. First of them is the renormalization of effective phonon gap $\omega_T$ due to the presence of the coupling to electrons. Apparently it is given by replacement $\omega_T^2 \to \omega_T^2 + 2gn$ which could lead to considerable effect even in our range of $n$. However, comparison with the data [24] for $n > 10^{19} \text{cm}^{-3}$ shows much smaller increase of the gap, compatible with $\Delta \omega_T^2 \approx 0.3 gn$, which does not lead to any noticeable effect at $n \leq n_{c1}$. The difference between the data from Ref. [24] and naive expectations is probably due to the fact that TO phonons interact both with conduction electrons and with ion defects (O deficiency or Nb substitution), and these defects partially suppresses the increase of the gap caused by electrons.

The second relevant effect is due to frequency-dependence of the effective e-e interaction, Eq. (4). Indeed, static approximation is definitely fine when $E_F < \hbar \omega_T$. In fact, $E_F$ starts to exceed $\hbar \omega_T$ already at $n > 7 \times 10^{17} \text{cm}^{-3}$. However, analysis of Eq. (4) shows that $V(e,0) - V(0,0) \approx W \sqrt{\frac{e^2}{\omega_T^2}}$ while $-V(0,0) = W \ln \frac{2}{n^n}$ $\approx 3.8W$. Thus we expect that retardation effects are relatively minor up to $n_{c1}$, while at higher $n$ the theory should be augmented to take them into account; the same is needed for the accurate analysis of $T_c$ enhancement due to isopop substitution leading to $\omega_T$ suppression.

A separate comment refers to the preprint [25] where tendency to superconductivity was observed down to extremely low electron densities $3.5 \times 10^{16} \text{cm}^{-3}$, with mid-
point $T_c \approx 50 - 70mK$ weakly dependent on $n$ below $10^{18} cm^{-3}$. Simultaneously, the absence of diamagnetic shielding expected for any bulk superconducting state was reported [25]. We expect that the origin of both these observations is related with large-scale variations of Oxygen vacancy densities over the sample; then resistivity-defined $T_c$ is controlled by the regions of larger electron densities, while diamagnetic currents are very weak due to percolative nature of coupling on large scale.

The absence of Coulomb interaction in doped STO makes it rare representative of a superconductor where universal effect of $T_c$ suppression by disorder [26] is not operating. Moreover, it may demonstrate the opposite effect of $T_c$ enhancement by strong disorder, predicted earlier in bulk [27] and 2D [28] materials with suppressed Coulomb interaction. It might be possible to reach the necessary range of strong disorder, $k_Fl \sim 1$, by heavy-dose electron irradiation of STO crystal, along the lines of Ref. [29]. However, such an irradiation may lead to increase of the gap $\omega_T$ and thus decrease of effective attraction, so $\omega_T$ dependence on irradiation should be controlled.

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