Reply to Comment on "Superconductivity at low density near a ferroelectric quantum critical point: doped SrTiO₃"

Peter Wölfle¹ and Alexander V. Balatsky²

¹Institute for Condensed Matter Theory and Institute for Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
²Nordita, Stockholm, SE 10691, Sweden

(Dated: November 1, 2019)

In our paper (Wölfe and Balatsky, Phys. Rev. B 98, 104505 (2018)) we presented a microscopic theory of superconductivity for doped SrTiO₃ by proposing two pairing mechanisms acting simultaneously with relative strength depending on the closeness to the ferroelectric quantum critical point. The first mechanism rests on the dynamically screened Coulomb interaction, and the second assumed a coupling to the soft transverse optical phonon. In their comment Ruhman and Lee point out an error in our estimate of the deformation potential coupling to the soft mode. We agree that this type of coupling cannot explain the gigantic isotope effect observed experimentally, so that a different coupling mechanism needs to be found. As for the first pairing mechanism, Ruhman and Lee maintain the view expressed in their paper (Ruhman and Lee, Phys. Rev. B 94, 224515 (2016)) that the energy range over which the usual longitudinal optical phonon mediated interaction operates is limited by the Fermi energy. We object to this view and in this reply present evidence that the cutoff energy is much larger. In a weak coupling system such as SrTiO₃ the cutoff is given by the energy beyond which quasiparticles cease to be well defined.

I. INTRODUCTION

In their Comment Ruhman and Lee criticize our derivation of the cutoff frequency in the gap equation, ωₐ, by arguing that at energies beyond the Fermi energy εₑ an uncontrollable set of additional contributions in perturbation theory would have to be taken into account. We object to this statement as unfounded, as explained in detail below. As for the second part of our paper devoted to the explanation of the isotope effect, we agree with Ruhman and Lee to have made an error in evaluating the deformation potential coupling of carriers to the soft TO phonon mode. This coupling is indeed negligible and the results for the transition temperatures Tₖ obtained by using that interaction are incorrect. In the following we present results of a reevaluation of Tₖ by using an interaction of the screened Coulomb interaction. We give the specifics below.

In their paper on superconductivity in lightly doped SrTiO₃ Ruhman and Lee, (1) apply the usual method of separating pair interaction into a longitudinal optical (LO) phonon mediated attractive part and a repulsive Coulomb interaction part, which they treat by subtracting a μ⁺ parameter of conventional magnitude to the pair coupling. This conventional procedure requires the Fermi energy εₑ ≫ ω_LO, the optical phonon frequency and thus is no longer valid once the Fermi energy falls below the longitudinal phonon energy, as is the case for densities n < 3*10²⁰ cm⁻³. They further assume, (2) a frequency cutoff in the gap equation of order Fermi energy εₑ, without justification. The resulting transition temperatures calculated by them are orders of magnitude too low at low density. They conjecture that the doping reduces the dielectric constant by a factor of ≈ 20 even at the low doping end. There is no experimental indication for such a drastic change of the dielectric properties induced by light doping.

We believe to have resolved both difficulties, (1) and (2), in our work in which (1) we use the fully screened Coulomb interaction, thus avoiding (a) the splitting off of the phonon mediated interaction and (b) treating the remaining static Coulomb interaction only approximately. We (2) show that the ionic screening is so strong as to keep the dimensionless screened Coulomb interaction in the weak coupling regime not only for energies less than the Fermi energy, but up to the LO phonon energy scale. A detailed evaluation of the dimensionless coupling function is presented below, demonstrating that the coupling is indeed much less than unity for typical momenta and frequencies up to the phonon scale. The frequency cutoff ω₂ in the gap equation is provided by the energy beyond which the electron self energy exceeds the energy itself. We present below a calculation of the transition temperature again using a hard cutoff approximation, for calculational convenience. The resulting transition temperature as a function of doping is in good agreement with experiment.

As for the isotope effect we do not yet have a convincing derivation of the coupling of charge carriers to the soft TO phonon of the required strength, ready to be reported here. We note, however, that additional support for the existence of the strong isotope effect is coming from the observed gigantic increase of Tₖ by applying pressure and tensile strain, moving the system closer to the QCP.

II. SUPERCONDUCTIVITY MEDIATED BY THE SCREENED COULOMB INTERACTION

The superconducting state of an interacting Fermi system is characterized by a gap parameter Δ(k,iωₙ) obtain-
able from the gap equation:

$$\Delta(k,\omega_n) = -T \sum_{\omega_{m},p} \frac{V_{\text{pair}}(k,p;\omega_n,\omega_{m})\Delta(p,\omega_{m})}{(\omega_{m} + i\Sigma(p,\omega_{m}))^2 + \epsilon_{p}^2 + \Delta^2(p,\omega_{m})}$$

(1)

assuming spin singlet pairing (for a review see). The pair interaction is given as the sum of the screened Coulomb interaction and a exchange contribution

$$V_{\text{pair}}(k,p) = V_C(k-p) + V_X(k,p)$$

(2)

where $k = (k,\omega_n)$, etc., are momentum and Matsubara frequency variables.

In doped SrTiO$_3$ the Coulomb interaction is screened by ionic and electronic charges

$$V_C(q) = \frac{4\pi\epsilon^2}{q^2 \epsilon_{\text{ion}}(q) + 4\pi\epsilon^2 \chi_{\text{el}}(q)}$$

(3)

where $\epsilon_{\text{ion}}(q)$ is the dielectric function of the undoped system and $\chi_{\text{el}}(q)$ accounts for the screening effected by the itinerant electronic charges. The ionic screening is dominated by the soft transverse optical phonon mode ($\omega_{\text{TO}}$) and its longitudinal partner ($\omega_{\text{LO}}$); for a discussion of electron densities the electron spectrum deviates from the simple parabolic form, leading to a slower growth of the density of states than assumed above, which also supports the choice of $\lambda(q,\omega)$ as a preferable measure of the interaction strength. In Fig. 1 we first show the coupling function at the Fermi energy $\lambda(k_F,\epsilon_F)$ versus electron density $n$ (in units of cm$^{-3}$). At low electron densities the electron spectrum deviates from the simple parabolic form, leading to a slower growth of the density of states than assumed above, which also supports the choice of $\lambda(q,\omega)$ as a preferable measure of the interaction strength. In Fig. 1 we first show the coupling function at the Fermi energy $\lambda(k_F,\epsilon_F)$ versus electron density $n$ (in units of cm$^{-3}$). At low density $\lambda(k_f,\epsilon_f)$ is seen to be very much less than unity, getting larger at higher density, but remaining less than unity in the whole density regime. One should note that the cutoff frequency $\omega_c(n)$ approaches the Fermi energy for densities $n \gtrsim 10^{10}$ cm$^{-3}$ anyway, and then the issue of the cutoff exceeding the Fermi energy is absent. The smallness of $\lambda(k_F,\epsilon_F)$ at low density suggests that $\lambda$ will remain small at much higher frequencies and momenta. The coupling function increases with frequency, but as shown in Fig. 2 it never exceeds unity, for frequencies $\omega < 6\omega_D = 2300$K.

As shown below, the exchange terms $V_X(k,p)$ of the interaction are systematically small and may be neglected, except for a contribution involving exchange of the soft phonon. The latter will be important near the ferroelectric transition, but we will omit this contribution here.

Let us first discuss the behavior of the interaction function $V_C(q,\omega)$ for large momenta and frequencies. In the limit of large $q$ we have $V_C \propto q^{-2}$, which together with the fall off of the Green’s function provides convergence of the momentum integration. In the limit of large frequency one finds $V_C = 4\pi\epsilon^2/(q^2\epsilon_{\infty})$, such that the frequency summation is not convergent unless the high frequency behavior of the self energy $\Sigma(p,\omega_{m})$ is taken into account. We estimated in our paper that the imaginary part of $\Sigma(p,\omega+i0)$ analytically continued to the real frequency axis grows with $\omega$, exceeding $\omega$ beyond a frequency $\omega_c$. For $\omega > \omega_c$, $\Sigma(p,\omega_{m}) = \omega_{m}$ and the Green’s function falls of faster than $\omega_{m}^{-2}$ thus ensuring convergence of the $\omega_{m}$ summation in the gap equation. We therefore used $\omega_c$ as a density dependent frequency cutoff $\omega_c(n)$. We found $\omega_c$ to vary with density in the range of 600K to 2500K, which is much higher than the Fermi energy at low doping (see Fig. 1). A full-scale evaluation of the selfenergy is beyond the scope of the present work.

In order to justify the neglect of higher order correction terms to the gap equation at such elevated frequencies we now show that the system indeed remains in the weak coupling regime for frequencies up to $\omega_c(n)$. We define a dimensionless coupling function $\lambda(q,\omega) = N(\epsilon_F)V_C(q,\omega)$ as a measure of the strength of the interaction ($N(\epsilon_F) = m_1k_F/\pi^2$ is the density of states at the Fermi energy). We adopt this definition of the coupling as the relevant one, rather than the alternative definition $\lambda_1(q,\omega) = N(\epsilon_g)V_C(q,\omega)$, where $N(\epsilon_g) = m_1q/\pi^2$, because $\lambda_1(q,\omega)$ is usually multiplied by a factor $k_F/\epsilon_B$ and $\lambda_1(q,\omega)(k_F/\epsilon_B) = \lambda(q,\omega)$. The factor $k_F/\epsilon_B$ arises in higher order expressions such as vertex corrections, crossed interaction terms, and more, from the angular integral of the vector $q$ in the arguments of single particle Green’s functions, e.g. $G(k+q,i(\omega_n+i\nu))$. At higher electron densities the electron spectrum deviates from the simple parabolic form, leading to a slower growth of the density of states than assumed above, which also supports the choice of $\lambda(q, \omega)$ as a preferable measure of the interaction strength. In Fig. 1 we first show the coupling function at the Fermi energy $\lambda(k_F, \epsilon_F)$ versus electron density $n$ (in units of cm$^{-3}$). At low density $\lambda(k_f, \epsilon_f)$ is seen to be very much less than unity, getting larger at higher density, but remaining less than unity in the whole density regime. One should note that the cutoff frequency $\omega_c(n)$ approaches the Fermi energy for densities $n \gtrsim 10^{10}$ cm$^{-3}$ anyway, and then the issue of the cutoff exceeding the Fermi energy is absent. The smallness of $\lambda(k_F, \epsilon_F)$ at low density suggests that $\lambda$ will remain small at much higher frequencies and momenta. The coupling function increases with frequency, but as shown in Fig. 2 it never exceeds unity, for frequencies $\omega < 6\omega_D = 2300$K. In Fig. 2 the coupling is shown for the typical momentum at frequency $\omega$, defined as $q_{\text{typ}} = k_F + \sqrt{2m_1\omega}$. Also shown is the dependence on density. For completeness we also show the coupling function $\lambda_1(q_{\text{typ}}, \omega)$ in the inset of Fig. 2 which is still less than unity in the relevant frequency range $\omega < \omega_c$. We may conclude from Figs. 1, 2 that in the frequency range up to $6\omega_D$ higher order contributions such as vertex corrections and exchange interaction terms, which are of second or higher order in the coupling $\lambda$ may be safely neglected. This conclusion holds provided there is no additional instability in the system such as a charge or spin density wave instability, in the neighborhood of which even a small interaction
FIG. 1. Coupling function $\lambda(k_F, \epsilon_F)$ versus the logarithm of density.

FIG. 2. Coupling function $\lambda(q_{typ}, \omega)$ versus frequency at various densities $n$. The inset shows coupling function $\lambda_1(q_{typ}, \omega)$ versus frequency in the relevant region $\omega < \omega_c$.

FIG. 3. Cutoff frequency $\omega_c$ (red line) and Fermi energy (blue line) in units of $\omega_D$ versus the logarithm of density.

may be critically enhanced. There is no experimental indication of any other instability in addition to the ferroelectric instability. The latter is expected to give rise to an enhanced pairing interaction mediated by the soft transverse optical phonon close to the ferroelectric quantum critical point.

In our paper we presented the results obtained for the combined pair interaction $V_C + V_X$ with $V_X$ given by the TO-phonon mediated exchange interaction, which was unfortunately not correctly derived. Now we assume that $V_X$ is negligible if the system is not yet close to the ferroelectric transition, i.e. in the absence of isotope doping or applied pressure, but will be important close to the transition. We reevaluate the transition temperature $T_c$ from Eq. 1 above in the limit $\Delta \to 0$. For calculational convenience we again use a hard frequency cutoff $\omega_c(n)$.

In our paper we distinguished three different density regimes, for which we found different density power laws, which we combined into an interpolation formula

$$\omega_c(n) = \frac{\omega_D}{(c_1(\frac{k_F(q_{typ})}{\epsilon_F})^{-1/2} + c_2(\frac{k_F(q_{typ})^2}{\epsilon_F})^{-1} + c_3(\frac{k_F(q_{typ})}{\epsilon_F})^{-1}}$$

with parameters $c_1$, $c_2$, $c_3$ and where the Fermi wave number $k_F(n) = (3\pi^2n)^{1/3}$ and $q_{typ}^2/2m = \omega_D$ have been used. The prefactors of these power laws were estimated by order of magnitude in Appendix A of 2. In the numerical solution of the linearized gap equation we assumed reasonable values for the prefactors such that the resulting transition temperatures $T_c$ were in agreement with the data. In Fig. 3 the cutoff frequency is plotted as a function of $n$, using the parameters $c_j$ specified above. For comparison the Fermi energy is shown as well. At low density $\omega_c$ is seen to be orders of magnitude larger than the Fermi energy. At high density the cutoff frequency approaches the Fermi energy from above.

In Matsubara space $V_C(q, i\omega_n)$ is a positive definite function, which implies that the eigenfunctions $\Delta(k, i\omega_n)$ of the linearized gap equation must necessarily have zero’s in frequency space 12,13. We find an even frequency eigenfunction $\Delta(k, i\omega_n)$ featuring two zero’s at $\pm \omega_n$.

In Fig. 4 the result for $T_c$ versus $\log_{10}n$ is shown for the choice of parameters $(c_1, c_2, c_3) = (0.49, 1.55, 0.118)$ as compared to the values $(1.1, 0.6, 0.036)$ used in our earlier evaluation 2 for the combined pair interaction in which the attractive TO phonon mediated interaction was taken sufficiently strong so that the eigenfunction did not have
zeros. It should be noted that the two components of the pair interaction in that calculation partially compensate each other, leading to a distinctly different frequency dependence, which explains the change in the $\epsilon_j$, $j = 1, 2, 3$. A more quantitative evaluation of the parameters $\epsilon_j$, for the two cases of pair interaction, $V_C$, and $V_C + V_X$ would lead to somewhat different values. Also shown in Fig. 4 are experimental data, which are reasonably well accounted for by our theory.

III. THE WEAKLY ATTRACTION FERMI GAS

In order to clarify the question of the energy cutoff in the gap equation further it is useful to consider a system of weakly interacting fermions allowing for controlled approximations. We consider a Fermi gas with quasiparticle energy $\epsilon_k = (k^2 - k_F^2)/2m$ and weak attractive interaction of the form

$$V_{\text{pair}}(k, k') = \begin{cases} -V_0, & |\xi_k|, |\xi_{k'}| < p_c^2/2m \\ 0, & \text{else} \end{cases}$$

We now assume that $p_c \gg k_F$ and that the dimensionless coupling $\lambda(\epsilon) = V_0N(\epsilon) \ll 1$, for $\epsilon < \epsilon_c = p_c^2/2m$, where $N(\epsilon) = mk/\pi^2$ and $\epsilon = k^2/2m$. In this case higher order terms in perturbation theory contributing to both, the irreducible particle-particle vertex (the full pair interaction) and the self energy are negligible. The linearized gap equation takes the form

$$\Delta = -\sum_p V_{\text{pair}}(k, p) \frac{\tanh \frac{\xi_p}{2\xi_p}}{2\xi_p} \Delta$$

The transition temperature follows as

$$T_c \approx \epsilon_F \exp\left[-\frac{1}{N_0|\Gamma_0|}\right]$$

where $\Gamma_0$ may be interpreted as scattering amplitude. For the above model one finds

$$\frac{1}{N_0|\Gamma_0|} = \frac{1}{N_0V_0} - \frac{p_c}{k_F}(1 + O(\lambda(\epsilon_c)))$$

where $N_0 = mk_F/2\pi^2$ is the density of states (of one spin component) at the Fermi level. In the usual limit of attraction only within a narrow energy shell about the Fermi level, the weak coupling result is recovered, $T_c \approx \epsilon_c \exp\left[-\frac{1}{N_0V_0}\right]$. In the opposite case, $p_c \gg k_F$, which is the situation realized in weakly doped SrTiO$_3$, the transition temperature may be enhanced by orders of magnitude due to the strong renormalization of the scattering amplitude $\Gamma_0$ by virtual processes involving states in the high energy region $\epsilon_F < \xi_p < \epsilon_c$.

IV. CONCLUSION

The observed superconductivity of lightly doped STO challenges the “conventional wisdom” accumulated over 60 years of theoretical effort to understand many different manifestations of this phenomenon. Fortunately, the situation here is much simpler than that posed by the enigmatic strong coupling superconductors, in particular the cuprates, in that the charge carriers in STO are in the weak coupling limit. The extremely strong ionic screening reduces the strength of the (dimensionless) dynamic Coulomb interaction to about 0.01 to 0.2, depending on density and energy, up to the LO phonon energy. As a consequence, the contribution of high energy ($\epsilon > \epsilon_F$) virtual processes to pairing is not cut off by higher order contributions such as vertex corrections, but is found to enhance the critical temperature at the lowest densities by orders of magnitude. This physics has been known by the pioneers of superconductivity, e.g. Gorkov and Melik-Barkhudarov, who stated that for a Fermi gas with weak attraction the bare interaction has to be replaced by the scattering amplitude, which may be much larger than the bare interaction owing to scattering into high energy intermediate states. The question is then what determines the frequency cutoff in the gap equation. Here we propose that the growth of the electron self energy $\Sigma(\omega)$ with energy provides a cutoff at $\omega_c = \Sigma(\omega_c)$. The strong fall off of the Green’s function with energy beyond that point ensures convergence of the frequency summation in the gap equation. The ultimate energy limit $\omega_c$ beyond which the weak coupling treatment would no longer be valid is given by the energy at which the dimensionless coupling $\lambda(\omega_c) \approx 1$. As shown above (see Figs. 1, 2), $\omega_c \ll \omega_x$, implying that $\omega_x$ is not relevant. The effect
of the cutoff $\omega_c$ has been discussed in the context of the plasmon exchange mechanism for conventional metals\textsuperscript{15}. A different lesson to be learned from the pioneers, here Bogoliubov and Anderson, is that in the case of the pair interaction given by the screened Coulomb interaction, which is a positive definite function (in Matsubara frequency space) the gap function must change sign as a function of frequency (leading for even-frequency pairing to a kind of "d-wave" pairing in frequency space). The observed "dome" in $T_c$ versus log $n$ can be fully accounted for by the limiting effect of strong electronic screening on the high density side and the cutoff energy $\omega_c \propto k_F^{1/2}$ derived from electron-phonon scattering at low density. As for the observed strong isotope effect, which may be expected to arise from a pair interaction contribution mediated by the soft TO phonon mode, we have to withdraw our earlier proposal of a deformation potential electron-phonon coupling. We do, however, take the present observations of the isotope effect at face value, noting that in the meantime new data on the effect of strain on $T_c$ also suggest a strong coupling of carriers to the soft mode\textsuperscript{8}. Work on deriving a sufficiently strong alternative e-ph coupling is in progress.

V. ACKNOWLEDGEMENTS

PW acknowledges support by a Distinguished Senior Fellowship of Karlsruhe Institute of Technology. AVB is supported by ERC Synergy HERO (810451) and KAW 2018-0104.

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