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### Author

Kresin, V.Z.

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### Non-Phonon Mechanisms of Superconductivity in High $T_c$ Superconducting Oxides and Other Materials and Their Manifestation

V.Z. Kresin

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NON-PHONON MECHANISMS OF SUPERCONDUCTIVITY IN HIGH  $T_c$  SUPERCONDUCTING  
OXIDES AND OTHER MATERIALS AND THEIR MANIFESTATION

Vladimir Z. Kresin

Materials and Chemical Sciences Division  
Lawrence Berkeley Laboratory  
University of California, Berkeley  
Berkeley, California 94720

ABSTRACT

Low dimensionality and the unusual parameter values in the high  $T_c$  materials lead to a key contribution of the plasmon mechanism of superconductivity. In addition, these systems provide a unique opportunity to observe a multigap structure. The problem of the lattice instability is discussed. A manifestation of non-phonon mechanisms (NPM) in  $Nb_3Ge$  and the contribution of the intramolecular vibrations are analyzed. Proximity systems containing high  $T_c$  superconductors are promising from the point of view of possible applications.

I. INTRODUCTION

Recently discovered high  $T_c$  materials<sup>1,2</sup> are characterized by "exotic" properties. This paper is concerned with the description of properties and with the analysis of the mechanisms of high  $T_c$  superconductivity. In addition we are going to analyze the appearance of the non-phonon mechanism in some conventional systems. The structure of the paper is as follows. Section II contains analysis of the properties of high  $T_c$  materials. The problems of the lattice instability, the appearance of a multigap structure and the influence of the proximity effect will be discussed. We are going to discuss in detail the plasmon mechanism and its coexistence with strong electron-phonon interaction. Section III contains an analysis of some conventional systems.

II. HIGH  $T_c$  MATERIALS

A recent exciting development, the discovery of new high  $T_c$  superconducting oxides<sup>1,2</sup> brought up the problem of mechanisms of superconductivity in these materials. An analysis of their structure and parameters leads to the conclusion that their superconducting state is greatly affected by NPM, namely, by exchange of 2D (two-dimension) plasmons.

# 1. Low Dimensionality and "Exotic" Properties of High $T_c$ Superconductors

Main parameters. Lattice instability. The new high  $T_c$  materials are low dimensional systems. For example,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x=2$ ) is two dimensional (the interlayer distance  $d \approx 6.5 \text{ \AA}$ ), while  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$  contains one dimensional chains. S. Wolf and the present author<sup>3</sup> have carried out our evaluation of the parameters of high  $T_c$  materials based on specific heat data.<sup>4</sup> We think that these data are the most reliable source; they can be used with high accuracy for analysis even polycrystalline samples.

Low dimensionality is taken into account in a consistent way and plays a key role in the analysis.<sup>3</sup> According to,<sup>3</sup>  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is characterized by a large value of the effective mass:  $m^* \approx 5 m_e$ . A most striking feature is the small value of the Fermi energy:  $\epsilon_F \approx 0.12 \text{ eV}$ .

The situation with such a small value of  $\epsilon_F$  along with large, comparable value of the energy gap  $\Delta$  is unique. In connection with it I would like to stress that the superconducting transition affects the state of the lattice and this influence is determined by the parameter  $\sim (\Delta/\epsilon_F)^2$  (see refs. 5 and 6). This parameter is usually small. However, the situation is entirely different in high  $T_c$  superconducting oxides. A large value of  $(\Delta/\epsilon_F)$  leads to a drastic change of the phonon spectrum. The following increase in  $T_c$  (and  $\Delta$ ) leads to the lattice instability. We think that the upper limit of  $T_c$  is determined by this factor.

Coherence length. Multigap structure. According to the analysis<sup>3</sup> the coherence length  $\xi_0$  appears to be very small ( $\sim 20 \text{ \AA}$ ). Such small value of  $\xi_0$  leads to the unique opportunity to observe a multigap structure.<sup>7</sup> The appearance of a such structure is connected with the presence of the overlapping energy bands.

The two-gap model has been introduced by Suhl, Matthias and Walker.<sup>8</sup> Afterwards it has been studied by Geilikman, Zaitsev, and the present author<sup>6,9</sup> and by the present author in ref. 10. The difficulty of observing multigap effects, as well as effects caused by gap anisotropy are due to the Anderson theorem.<sup>11</sup> Namely, the inequality  $\ell \ll \xi_0$  ( $\xi_0$  is the coherence length,  $\ell$  is the mean free path) results in the gap averaging into a single one. Interband transitions are the main mechanism of this averaging.

The new high  $T_c$  materials provide a unique opportunity to observe, under certain conditions, effects due to the presence of several gaps. For relatively clean samples, the criterion  $\xi_0 \ll \ell$  can be met.

Note that the Anderson criterion allows one to determine whether one is dealing with a multigap case. Indeed, additional doping of these materials will result in a decrease of  $\ell$  and, subsequently, in becoming less than  $\xi_0$ , when a transition to the one-gap picture will

take place. Such a transition can be observed experimentally, because the tunneling spectrum and the temperature dependences, e.g., of the kinetic coefficients are different in the one gap and multigap cases.

High  $T_c$  superconductivity and the proximity effect. The proximity effect allows one to induce the superconducting state in materials which are not superconductors by themselves. If, for example, this material is a semiconductor, then, as a result, one can take advantage of both superconductivity and semiconducting properties. An important example of such an application of the proximity effect is the tunneling system Nb-InAs-Nb, studied experimentally.<sup>12</sup> An externally applied electric field changes noticeably the amplitude of the flowing Josephson current, which is promising from the point of view of making a three-terminal device. A theoretical analysis<sup>13a</sup> shows that the sharpness of the field effect depends strongly on the temperature and increases with increasing  $T$ . That is why the use of high  $T_c$  superconductors, namely, the systems  $S_h$ -InAs- $S_h$ , or  $S_h$ -S-InAs-S- $S_h$ , where  $S_h$  is a high  $T_c$  superconductor, and S is a conventional material (e.g., Nb or NbN) is promising for the field effect.

Another interesting proximity system is  $S_\alpha$ - $S_\beta$  consisting of two superconductors (assume that  $T_c^\alpha > T_c^\beta$ ). Such a system is characterized by a single  $T_c$  with  $T_c^\alpha > T_c > T_c^\beta$  (a general expression has been obtained by the present author in ref. 13b. As a result of the proximity effect, one effectively increases the  $T_c$  of the  $S_\beta$  superconductor.

Consider the case with  $S_\beta$  is an A-15 compound with high values of such critical parameters as the critical current and the critical field. If  $S_\alpha$  is a high  $T_c$  superconductor, one can use the proximity effect in order to increase  $T_c$  of the A-15 film and to take advantage of its high values of the critical parameters.

## 2. Mechanisms of High $T_c$ Superconductivity. Plasmon Mechanism.

The low dimensionality along with the presence of several overlapping energy bands and a small value of  $\epsilon_F$  makes the appearance of the plasmon mechanism of superconductivity very favorable. This mechanism has been proposed by the present author (see refs. 14 and 15) and then developed by H. Morawitz and the author.<sup>16</sup> Later the plasmon mechanism in high  $T_c$  oxides has been studied in.<sup>17</sup> The new materials are characterized by a relatively small carrier concentration  $n$ ,<sup>18</sup> and it is important that the intensity of the electron-plasmon interaction increases with decreasing  $n$ .

As is known in the three dimension (3D) case the plasmon branch has a gap  $\omega_0$  at momentum  $q=0$ , and the plasma frequency is very high. In the 2D case the situation is entirely different. Namely, the plasmon dispersion relation does not contain an energy gap and in the region of small  $q$  has the form (see, e.g., ref. 19)  $\omega \sim q^{1/2}$ . As a matter of fact, there are several plasmon branches. The existence of the  $\omega \sim q^{1/2}$  branch is connected with the low dimensionality of the system and is present even for a single 2D group of carriers. The presence of several overlapping energy bands lead to the appearance of

an additional acoustic plasmon branch. In the 3D case this acoustic branch was introduced in;<sup>20</sup> its contribution to the superconducting state was studied in.<sup>21-24</sup>

The presence of the plasmon branches results in electron-electron attraction which appears to be large for systems with small carrier concentration.

The effect at the plasmon branch  $\omega \sim q^{1/2}$  on the superconducting properties of an inversion layer was studied in.<sup>25</sup> Our approach is based on the method of the thermodynamic Green's function. The plasmon mechanism is affected by a number of factors. The high  $T_c$  oxides do not contain just one 2D sheet. They have a layered structure and, strictly speaking, one should take into consideration the interlayer interaction. One can show (see below) that the main contribution comes from the short wavelength region and the interlayer interaction does not play an important role. Moreover, it is necessary to take into account the presence of several energy bands.

The order parameter  $\Delta(\omega_n, \vec{\kappa})$  describing the pairing in a 2D layer is described by the following equation, which is a generalized Eliashberg's equation:

$$\Delta(\omega_n, \vec{\kappa}) = \frac{\Gamma}{(2\pi)^2 Z} \sum_{n'} \int d\vec{\kappa} \Gamma(\omega_n - \omega_{n'}, \vec{\kappa} - \vec{\kappa}') F^+(\omega_{n'}, \vec{\kappa}') \quad (1)$$

Here  $\omega_n = (2n+1)\pi T$ ,  $\vec{\kappa}$  is the 2D momentum,  $F^+$  is the anomalous Green's function, and  $\Gamma$  is the total vertex. The vertex  $\Gamma$  can be written as a sum of the plasmon and phonon terms:  $\Gamma = \Gamma_{pl} + \Gamma_{ph}$ .

Consider the vertex  $\Gamma_{pl}(\omega, \vec{\kappa})$ . Its poles correspond to collective excitations, i.e., plasmons.

Let us study the properties of a single 2D sheet. Consider the general case of overlapping energy bands. The structure of the vertex in the 3D case was studied by Geilikman<sup>22a</sup> and by Geilikman and the author.<sup>26</sup> The case of 2D bands has been studied by Tavger and author.<sup>27</sup> According to<sup>22a, 27</sup>, the vertex  $\Gamma_{11} \equiv \Gamma_{11;11}$  is equal to:

$$\Gamma_{11} = (V_{11} + \Pi_{22} R) S^{-1} \quad (2)$$

where

$$S = 1 + V_{11} \Pi_1 + V_{22} \Pi_2 + \Pi_1 \Pi_2 R \quad (3)$$

$$R = V_{12}^2 - V_{11} V_{22}.$$

Here  $V_{11}$ ,  $V_{12}$ ,  $V_{22}$  are Coulomb matrix elements and  $\Pi_1$ ,  $\Pi_2$  are polarization operators. The case of a single 2D energy band is described by Eqs. (2) and (3) with  $\Pi_{22} = 0$ . Equations (2) and (3) are written in the random phase approximation. The quantities  $\Pi_1$  and  $\Pi_2$  are given by

$$\Pi_i(\vec{q}, \omega) = -\frac{m_i}{2\pi^2} \int_0^{2\pi} d\phi \frac{\cos\phi}{\alpha_i - \cos\phi + i\delta \cos\phi} \quad i = \{1, 2\} \quad (4)$$

Here  $\alpha_i = (\omega/V_{Fi}q)$ ,  $V_{Fi}$  is the Fermi velocity for  $i$ -th band; the polar axis is chosen along the 2D vector  $\vec{q}$ . Consider the region in the  $(\omega, q)$  plane which corresponds to  $\alpha_1 \gg 1$ ,  $\alpha_2 \gg 1$ . Then  $\Pi_i = -(\epsilon_{iF}/\pi)q^2/\omega^2$ . The equation  $S=0$  determines the plasmon branch  $\omega_{p\ell; b}$  which has the dispersion relation  $\omega \sim q^{1/2}$  in the region of small  $q$ . Contrary to the usual (see below) acoustic plasmon branch, the branch  $\omega_{p\ell; b}$  exists even in the case of a single energy band. The dispersion relation  $\omega \sim q^{1/2}$  and the absence of an energy gap at  $q=0$  is a consequence of the low dimensionality. The analysis of a more general case  $\alpha_i > 1$  will be given separately. If  $\alpha_1 \ll 1$ ,  $\alpha_2 \ll 1$ , we obtain

$$\Pi_1 \approx m_1/\pi; \quad \Pi_2 = -(\epsilon_{2F}/\pi) q^2/\omega^2 \quad (5)$$

As a result, we obtain the acoustic plasmon branch  $\omega_{p\ell, a} \sim q$ . For 3D system this branch, which is due to the presence of the overlapping bands was obtained in,<sup>19</sup> see also.<sup>20-24</sup> The vertex  $\Gamma(\omega_n, \vec{\kappa})$  obtained by substituting  $\omega \rightarrow -i\omega_n$ , can be written in the form:

$$\Gamma(\omega_n, \vec{\kappa}) = \Gamma_0 + D_{\text{eff}}(\omega_n, \vec{\kappa}) \quad (6)$$

where  $\Gamma_0 = v_1^{\text{src}}$  describes the Coulomb repulsion and

$$D_{\text{eff}} = \Gamma_0 \frac{\omega_{p\ell, a}^2(q)}{\omega_{p\ell, a}^2(q) + \omega_n^2} \quad (7)$$

has the form of the usual phonon Green's function with the dispersion relation  $\omega_{q\ell, a}(q)$  and describes the electron-electron attraction via plasmon exchange.

Consider the effect of the interlayer interaction. One has to introduce quantity  $\Gamma_i(\vec{\kappa}, z; \omega)$ ; this function is the Fourier component of the vertex  $\Gamma(\vec{r}, \omega)$  with respect to  $\vec{r}$  (the axis  $z$  is chosen to be perpendicular to the layer). Let layer "a" be located at  $z=0$  and let us evaluate the quantity  $\Gamma_i(\vec{\kappa}, 0; \omega)$ . The equation for this quantity contains the same terms as Eq. (2), but, in addition, we should take into account its Coulomb interaction with other sheets. For example, the presence of sheet  $b$  at  $z=d$  leads to the appearance of the terms  $v_1^{ab}(q_1, d) \Pi^b(q_1; d; \omega) \Gamma^{ba}$ , etc. These additional terms contain  $(v_1^{ab})^2$  in the lowest order ( $v_1^{ab}$  describes the Coulomb interaction between carriers, in layers "a" and "b"). It is easy to see that the additional contribution of  $\Gamma_1$  due to the presence of a layer at  $z=d$  is proportional to  $e^{-2q_1 d}$ . Hence, in the region of small  $q_1$  it is

necessary to take into account the interlayer interaction and we are dealing with a 3D problem. But this interaction can be neglected in the short wavelength region ( $2q_d \gg 1$ ). For the high temperature oxide  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ,  $d = 6.5\text{\AA}$ .<sup>1</sup> The Fermi momentum  $p_F \approx 3.7 \times 10^{-20}$  gm x cm sec<sup>-1</sup> (see ref. 3), and therefore, if  $q_1 \gtrsim 0.5 p_F$ , we can consider the 2D sheet only.

The above analysis was carried out in the RPA (see e.g., refs. 28 and 29). One can show<sup>16</sup> that the main conclusions concerning the different plasmon branches the effective electron-electron attraction via plasmon exchange are valid for high  $T_c$  systems and play an important role in the understanding of the basic mechanisms of high  $T_c$  superconductivity.

Strong electron-phonon coupling. Consider the phonon part of the total vertex  $\Gamma$  (see Eq. (1)). Speaking of the electron-phonon interaction (EPI), one should stress that the BCS theory, based on an analysis of EPI, does not restrict the values of  $T_c$  to the low temperature region. The Eliashberg equation (see below, Eq. (8)) is valid if  $\tilde{\Omega} \ll \epsilon_F$ , where  $\tilde{\Omega}$  is the characteristic phonon frequency ( $\tilde{\Omega} \sim \Omega_D$ ) and has a solution with a high  $T_c \gtrsim \tilde{\Omega}$  (strong EPI). We are going to describe the mechanism of the appearance of strong electron-phonon coupling  $\lambda$  and the problem of describing a state with arbitrary  $\lambda$ .

The low dimensionality implies the necessity to analyze the properties of a 2D gas of carriers. Such a system is characterized by a Fermi curve  $\epsilon(\vec{k}) = \epsilon_F$  instead of a Fermi surface ( $\vec{k}$  is the two-dimensional momentum). If the 2D system of carriers contains a subgroup with a high DOS near the Fermi level (its presence in the superconducting high  $T_c$  oxides is due to the mixed valence state of Cu), then the Fermi curve has sections which are almost linear nesting states. Such a situation has been studied by the author.<sup>30</sup> In<sup>30</sup> the properties of a size-quantizing Bi film were studied. Although Bi films and the layered superconducting oxides are entirely different systems, there is a strong analogy in some aspects of their behavior (anisotropy of the Fermi curve, small carrier concentration, etc.). The method developed<sup>30</sup> can be applied to study the low dimensional superconductors.

One can show by analogy with<sup>30</sup> that the presence of linear sections (nesting state) of the Fermi curve leads to lattice instability. This instability comes from the interaction of phonons with electronic states attached to these linear sections and manifests itself in the appearance of an imaginary pole in the phonon Green's function. The transition (at some  $T = T_p$ ) to the charge density wave state becomes favorable. A decrease in temperature in the region  $T > T_p$  is accompanied by a decrease in the phonon frequency (phonon softening). If  $T_c > T_p$  (such situation is perfectly realistic for the high  $T_c$  materials), then a low phonon mode with finite momentum appears, and the smallness of the phonon frequency makes EPI strong ( $\lambda \sim \tilde{\Omega}^{-2}$ ).

The  $T_c$  for an arbitrary value of the electron-phonon coupling can be determined<sup>31</sup> from the usual Eliashberg equation which can be written in the form (at  $T = T_c$ ):

$$\Delta(n)Z = \sum_{n'} [K_{n-n'}^{-2\mu*}] \Delta(n') \left| 2n'+1 \right|^{-1} \Big|_{T_c} \quad (8)$$

where

$$K_{n-n'} = 2 \int d\Omega g(\Omega) \Omega \left[ \Omega^2 + (n-n')^2 (2\pi T)^2 \right]^{-1} \quad (9)$$

and  $Z$  is the renormalization function

$$Z = 1 + (2n+1)^{-1} \sum_{n'} K_{n-n'} (2n'+1) / |2n'+1|_{T_c}^{-1}; \quad (10)$$

$$g(\Omega) = \alpha^2(\Omega) F(\Omega).$$

Equations (8) and (10) can be solved by the matrix method developed by Owen and Scalapino.<sup>32</sup> The solution for any  $\lambda$  is obtained by the author;<sup>31</sup> with high accuracy, it can be written in the form (if  $\mu^*=0$ )

$$T_c = 0.25 \tilde{\Omega} [e^{\frac{2}{\lambda}} - 1]^{-1}. \quad (11)$$

$$\tilde{\Omega} = \langle \tilde{\Omega}^2 \rangle^{1/2}, \langle \Omega^2 \rangle = (2/\lambda) \int d\Omega g(\Omega) \Omega$$

If  $\lambda \lesssim 1$ , we obtain  $T_c = 0.25 \tilde{\Omega} \exp(-1/\lambda)$ ,  $\lambda = \int \Omega dr g(\Omega) \Omega^{-1}$ , see ref. 33; one can show that (see ref. 31) that the expression

$T_c = 1.14 \tilde{\Omega} \exp\{(1+0.5\rho)\rho^{-1}\} = 0.25 \tilde{\Omega} \exp(-1/\lambda)$  does not differ noticeable from the well-known expression obtained in ref. 34; here  $\rho = \lambda(1+\lambda)^{-1}$ . In the opposite limit we obtain from Eq. (11)  $T_c = 0.18\lambda^{1/2} \tilde{\Omega}$ , in accord with refs. 34-36.

If  $\mu^* \neq 0$ , we obtain

$$T_c = 0.25 \tilde{\Omega} [\exp(2/\lambda_{\text{eff}}) - 1]^{-1} \quad (12)$$

where  $\lambda_{\text{eff}} = (\lambda - \mu^*)(1 + 2\mu^* + \lambda\mu^*t(\lambda))^{-1}$ , the function  $t(\lambda)$  is defined.<sup>31</sup>

Strong EPI has been found in organic superconductor (see ref. 37). A major manifestation of the strong coupling is the difference  $\beta - \beta_{\text{BCS}}$ , where  $\beta = \varepsilon_0/T_c$ , and  $\varepsilon_0$  is the energy gap at  $T=0$ . In the weak coupling approximation,  $\beta \equiv \beta_{\text{BCS}} = 1.76$ . The organic superconductor  $\beta - (\text{ET})_2 \text{AuI}_2$  is characterized by the value  $\beta \approx 4\beta_{\text{BCS}}$ , obtained from tunneling spectroscopy.<sup>37</sup> Tunneling data show large value  $\beta \gg \beta_{\text{BCS}}$  for the new high  $T_c$  superconductors.

Recent experimental data (D. Morris and A. Zettl, private communication) show the presence of the isotope effect in La-Sr-Cu-O. This means that the electron-phonon interaction contributes to superconductivity. However, the coupling constant  $\lambda_{\text{ph}}$  is not large enough to provide high  $T_c$ . Indeed, according to neutron data,  $\tilde{\Omega} \approx 120\text{K}$ , and hence in superconducting oxides  $\pi T_c \sim \tilde{\Omega}$ . In this case, the electron-phonon interaction could provide high  $T_c$  if  $\lambda_{\text{ph}}$  were large enough (according to Eq. (12) this would require  $\lambda_{\text{ph}} \approx 5$ ).

But if this were so, the ratio  $2\epsilon_0/T_c$  would have to be large.<sup>7</sup> At present, a lot of data indicate that  $2\epsilon_0/T_c \approx 5$  which corresponds to intermediate coupling ( $\lambda_{ph} \approx 2$ ).

Hence, the electron-phonon interaction plays an important role, but in order to provide high  $T_c$ , it is necessary to have an additional mechanism. We think that 2D plasmons (this type of excitations exists in the materials of interest) provide this additional attraction.

We came to the conclusion that our concept of a coexistence of phonon and non-phonon mechanisms proposed in<sup>14-15</sup> is receiving experimental support. In the next section we are going to discuss the problem of the coexistence of the phonon and non-phonon mechanisms.

Coexistence of the Plasmon and Electron-Phonon Mechanisms. The Possibility of Experimental Observation of the Plasmon Mechanism.

Based on the generalized Eliashberg equation (1) one can evaluate  $T_c$  and the order parameter. It is important that the part of  $\Gamma_{p\ell}$  which provides the electron-electron attraction via exchange of 2D plasmons can be written in the form of the usual D-function. As a result, Eq. (1) can be written as a usual Eliashberg equation:

$$\Delta(\omega_{n'}) Z = \pi T \sum_{\omega_n} \int d\Omega [g(\Omega) D(\omega_n - \omega_{n'}, \Omega) - 2\mu^*] \frac{\Delta(\omega_n)}{|\omega_n|} \quad (13)$$

Here  $D(\omega_n, \Omega) = \Omega^2 / (\Omega^2 - \omega_n^2)$  is a D-function, and  $g(\Omega) = g_{ph}(\Omega) + g_{p\ell}(\Omega)$  where  $g_i(\Omega) = \alpha_i(\Omega) F_i(\Omega)$ ,  $i = \{ph; p\ell\}$ .  $F_i$  is the phonon (plasmon) density of states,  $\alpha_i$  describe the electron-phonon and the electron-plasmon interactions, respectively. In addition, one can introduce the coupling constant  $\lambda = 2 \int d\Omega g(\Omega) / \Omega$  which can be written as a sum  $\lambda = \lambda_{e,ph} + \lambda_{e;p\ell}$ ,  $\lambda_i = 2 \int d\Omega g_i(\Omega) / \Omega$ .

The critical temperature in the presence of both the electron-phonon and the plasmon mechanisms can be evaluated from Eq. (13) (see ref. 15). We assume weak electron-plasmon coupling (a more general case will be described elsewhere). Then we obtain

$$T_c = T_c^{ph} (\Omega_{p\ell} / T_c^{ph})^h \quad (14)$$

Here  $T_c^{ph}$  is the critical temperature in the absence of the plasmon mechanism,  $\Omega_{p\ell} \approx 0.5 \epsilon_F$ ,  $h = \lambda_{p\ell} (\lambda_{ph} + \lambda_{p\ell})$ . Note that the large value of the ratio  $\Omega_{p\ell} / T_c^{ph}$  makes the contribution of 2D plasmons crucial even for small  $\lambda_{p\ell}$ . For example, if  $\lambda_{ph} = 1.5$ ,  $\Omega_{p\ell} / T_c^{ph} = 15$ , we obtain  $T_c \approx 2T_c^{ph}$ .

The very important question arises of how to detect the presence of the non-phonon plasmon mechanism. Such a separation can be carried out experimentally because the plasmons are excitations of carrier system whereas the phonons involve ionic motion. It would be important to carry out a tunneling and neutron scattering experiment. Tunneling spectroscopy based on inversion of the Eliashberg equation will display all modes, including plasmons. As for neutron scattering, it will show

the function  $F_{\text{ph}}(\Omega)$  only, because neutron scattering is not affected by the carriers subsystem. Usually  $F_{\text{ph}}(\Omega)$  and  $g_{\text{ph}}(\Omega)$  have a similar structure (position and number of peaks, the value of  $\Omega_{\text{max}}$ ). If the plasmons play an important role (this is the case for the high  $T_c$  superconductors), then comparison of the neutron and tunneling data would allow one to detect the presence of the additional (plasmon) mode. It would be particularly important to compare the frequency ranges.

It is essential to stress two points. First of all, the smallness of the Fermi energy (e.g., for  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  the value  $\epsilon_F \approx 0.12$  eV, see ref. 3), leads to the plasmon edge within the region suitable for tunneling spectroscopy.

In addition, the electron-plasmon coupling constant  $\lambda_{p\ell}$  depends on the carrier concentration ( $\lambda_{p\ell} \sim v_F^{-1} \sim n^{-1/2}$ , see, e.g., ref. 15 and increases with decreasing  $n$ . This is important because the new high  $T_c$  materials are characterized by small values of  $n$ . This fact makes the plasmon contribution crucial for explaining high  $T_c$  in these materials.

### III. NON-PHONON MECHANISMS OF SUPERCONDUCTIVITY IN CONVENTIONAL SUPERCONDUCTING SYSTEMS

Despite the considerable theoretical progress and support for the existence of a non-phonon mechanism (NPM) of superconductivity, (see e.g., refs. 38-40, 21-27) the situation with NPM remains peculiar. Strictly speaking, it is impossible to point out a single superconductor and state that the superconductivity in this material is caused by NPM. We do not have any definite experimental evidence of a non-phonon mechanism. Unusual properties of high  $T_c$  superconductors make the appearance of the non-phonon mechanism very favorable (see above). NPM does not necessarily lead to high  $T_c$ . On the other hand, it is known that the BCS theory based on an analysis of the electron-phonon interaction (EPI) is not restricted to small  $T_c$  values. It is difficult to imagine a situation in which EPI would not play any role. Rather, it is more realistic that the phonon and non-phonon mechanisms coexist, although their relative contributions may be different. One can synthesize materials with the desired structure favorable for appearance of NPM. But there are also many existing superconductors which might benefit greatly from NPM. Substances containing non-uniform structures with spatial separation between different groups of electrons, or those with complex band structures, can be expected to have a significant contribution from NPM. We should be able to prove experimentally the presence of a non-phonon mechanism. In other words, it should be possible to separate the contributions of NPM and EPI.

It has been noted (see above, Sec. II) that the analysis of the tunneling and neutron data will allow one to determine the presence of the plasmon mechanism in the high  $T_c$  oxides. In this section we consider the usual low  $T_c$  superconducting system.

Non-phonon contribution from a high frequency peak. Consider the case when the non-phonon mode is located higher than the tunneling

region. In the paper<sup>41</sup> the present author proposed a method allowing one to carry out a separation of this mode. The method is based on tunneling spectroscopy and on measurements of electronic heat capacity, or on the temperature dependence of the effective mass.

The powerful technique of tunneling spectroscopy allows one to determine the function  $g(\Omega) = \alpha^2(\Omega) F(\Omega)$  ( $F(\Omega)$  is the phonon density of states,  $\alpha^2(\Omega)$  describes EPI). This function can be obtained by an inversion procedure (see, e.g., refs. 42-43) based on the Eliashberg equation

$$\Delta(\omega) = Z^{-1}(\omega) \int d\omega' \left\{ \int d\Omega g(\Omega) [D(\omega'+\omega) + D(\omega'-\omega) - \mu^*] \operatorname{Re} \{ \Delta(\omega') [\omega'^2 - \Delta^2(\omega')]^{-1/2} \} \right. \quad (15)$$

where  $\Delta(\omega)$  is the order parameter,  $D$  is the phonon Green's function,  $\mu^*$  is the Coulomb pseudopotential, and  $Z$  is the renormalization function. It is important that the Eliashberg equation (15) is written under the assumption that the superconducting state is caused by EPI only; this interaction corresponds to the energy range suitable for tunneling spectroscopy.

The same function  $g(\Omega)$  affects the behavior of the electronic heat capacity  $C_e(T)$ . EPI leads to a deviation of  $C_e(T)$  from the linear law. The analysis of the tunneling data and the behavior  $C_e(T)$  allows one to determine the presence of the NPM (see ref. 41).

Recently a detailed analysis of the properties of  $\text{Nb}_3\text{Ge}$  aimed at the search for NPM has been carried out by Kihlstrom, Hovda, Wolf, and the present author.<sup>44</sup> The obtained results manifest a major contribution of NPM to the superconducting state  $\text{Nb}_3\text{Ge}$ .

$\text{Nb}_3\text{Ge}$  has the highest  $T_c$  among A-15 compounds ( $T_c^{\text{Nb}_3\text{Ge}} = 22.3\text{K}$ ). Band structure calculations<sup>45</sup> show that  $\text{Nb}_3\text{Ge}$  is an unusual material among A-15 superconductors, and the usual EPI is not sufficient to provide its high  $T_c$ . The density of states at the Fermi level is relatively small (see e.g., ref. 46). On the other hand, the band structure of  $\text{Nb}_3\text{Ge}$  is favorable for an NPM.<sup>24,45</sup> The presence of overlapping bands might result in pairing in one band via virtual transitions to another band.<sup>22a</sup> In addition, the acoustic plasmon branch (see above) can also provide electron-electron attraction.

The selection of  $\text{Nb}_3\text{Ge}$  was motivated by these reasons. An analysis based on the method<sup>41</sup> (see ref. 44) has resulted in a picture entirely different from those obtained for  $\text{Pb}$  and  $\text{V}_3\text{Si}$ . According to<sup>44</sup> one can state that the non-phonon mechanism plays the key role in  $\text{Nb}_3\text{Ge}$ .

Pairing via molecular excitations. In the previous section, we studied the case when the energy of virtual transitions  $\Delta\varepsilon_{\text{virt.}}$  exceeds greatly the tunneling region. Let us discuss now a different case when

$\Delta\epsilon_{\text{virt.}}$  lies within this region. For concreteness consider the system studied by the author.<sup>47</sup> If the superconductor contains complex molecules (e.g., if the molecules are placed on the surface of a thin film), then additional electron-electron attraction arises via vibrational excitation of the molecules. This might result in an increase in  $T_c$  (see ref. 47). This change of  $T_c$  can be treated on the basis of the interesting theory of local modes developed in.<sup>48</sup> From this point of view, aromatic molecules are best because their vibrational spacing is relatively small ( $\sim 10^2\text{K}$ ) and the contribution to coupling is notable. This mechanism of superconductivity based on intramolecular virtual excitations can be detected by the tunneling technique and will manifest itself as an additional peak. The position of the peak can be obtained from the second derivative of the tunneling characteristic.

It is important that the molecular frequencies are known independently from molecular spectroscopy. If the position of the peak coincides with the molecular frequency, this will manifest a new mechanism of superconductivity, namely the effect of intramolecular degrees of freedom on pairing.

#### SUMMARY

In this paper we consider several superconducting systems which are greatly affected by non-phonon mechanisms. The main results can be summarized as follows:

1. The low dimensionality and the small value of the carrier concentration in new high  $T_c$  oxides lead to unusual values of the main parameters such as  $\epsilon_F$ ,  $m^*$ ,  $\xi_0$ . As a result, one can observe a multigap structure.
2. The state of the lattice is greatly affected by the superconducting transition.
3. Exchange of 2D plasmons plays a key role in high  $T_c$  superconductivity. Its manifestation can be determined experimentally.

The superconducting state in high  $T_c$  materials is due to the coexistence of the phonon and non-phonon mechanisms.

4. Superconducting state  $\text{Nb}_3\text{Ge}$  is due to non-phonon interaction. Intramolecular excitations can provide additional attraction which can be detected by molecular spectroscopy and by tunneling.
5. Effective increase of  $T_c$  of A-15 superconductors can be achieved with the use of the proximity effect.

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## REFERENCES

1. J. Bednorz and K. Müller, Z. Phys. B66, 189 (1986).
2. S. Uchida, et al., Jpn. J. Appl. Phys. Lett. 26, L1 (1987); C. Chu, et al., Phys. Rev. Lett. 58, 405 (1987); R. Cava, et al., Phys. Rev. Lett. 58, 408 (1987); M. Wu, et al., Phys. Rev. Lett. 98, 908 (1987).
3. V. Z. Kresin and S. Wolf, Solid State Comm. (in press).
4. N. Phillips, et al., (preprint); R. Battlogg, et al., Phys. Rev. B35, 5340 (1987); S. Tanaka, et al., Proc. of MRS meeting (Anaheim, 1987), in press.
5. J. Bardeen and M. Stephen, Phys. Rev. 136, 1485 (1964).
6. B. Geilikman and V. Z. Kresin, in Kinetic and Non-Stationary Phenomena in Superconductors, Wiley, New York (1974), p. 87.
7. V. Z. Kresin, Solid State Comm. (in press); Proc. of MRS meeting (Anaheim, 1987), in press.
8. H. Suhl, B. Mattias, and L. Walker, Phys. Rev. Lett. 3, 552 (1959).
9. B. Geilikman, R. Zaitsev, and V. Kresin, Proc. of LT-X, vol. IIA, Moscow (1967), p. 173; Sov. Phys. - Solid State 9, 642 (1967).
10. V. Z. Kresin, J. Low Temp. Phys. 11, 519 (1973).
11. P. Anderson, J. Phys. Chem. Sol. 11, 26 (1959).
12. H. Takayanagi and T. Kawakami, Phys. Rev. Lett. 54, 2449 (1985).
13. a) V. Z. Kresin, Phys. Rev. B34, 7587 (1986); b) V. Z. Kresin, Proc. LT-17, ed. by U. Eckern, A. Schmid, W. Weber, and H. Wuhl, North-Holland, Amsterdam (1984), p. 1029.
14. See Physics Today 40, 22 (1987); presented at Special Sessions at APS (March, 1987, New York) and MRS (April 1987, Anaheim).
15. V. Z. Kresin, Phys. Rev. B35, xxx, (1987).
16. V. Z. Kresin and H. Morawitz (preprint).
17. J. Ruvalds, Phys. Rev. B35, xxx, (1987).
18. A. Panson, et al., Appl. Phys. Lett. 50, 1104 (1987).
19. T. Ando, A. Fowler, and F. Stern, Rev. Mod. Phys. 54, 437 (1982).
20. D. Pines, Can. J. Phys. 34, 1379 (1956).
21. H. Fröhlich, J. Phys. C1, 544 (1968).
22. a) B. Geilikman, Sov. Phys.-Usp. 8, 2032 (1966); 16, 17 (1973);  
b) E. Pashitskii, Sov. Phys.-JEPT 28, 1267 (1969).
23. J. Ihm, M. L. Cohen, and S. Tuan, Phys. Rev. B23, 3258 (1981).

24. J. Ruvalds, Adv. in Phys. 30, 677 (1981).
25. Y. Takada, J. Phys. Soc. Japan 45, 786 (1978); 49, 1713 (1980).
26. B. Geilikman and V. Z. Kresin, Sov. Phys.-Semiconductors 2, 639 (1968).
27. V. Z. Kresin and B. Tavger, Sov. Phys.-JETP 23, 1124 (1966); Phys. Lett. 20, 595 (1966).
28. D. Pines, Elementary Excitations in Solids (Benjamin, 1963).
29. P. Vashishta and K. Singwi, Phys. Rev. B6, 875 (1972).
30. V. Z. Kresin, J. Low Temp. Phys. 57, 549 (1984).
31. V. Z. Kresin, Phys. Lett. (in press).
32. C. Owen and D. Scalapino, Physica 55, 691 (1971).
33. B. Geilikman, V. Z. Kresin, and N. Masharov, J. Low Temp. Phys. 18, 241 (1975).
34. R. Dynes, Solid State Comm. 167, 331 (1968).
35. P. Allen and R. Dynes, Phys. Rev. B12, 905 (1975); C. Leavens, Solid State Comm. 17, 1499 (1975); S. Louie and M. L. Cohen, Solid State Comm. 22, 1 (1977).
36. V. Z. Kresin, H. Gutfreund, and W. A. Little, Solid State Comm. 51, 339 (1984).
37. M. Hawley, et al., Phys. Rev. Lett. 57, 629 (1986).
38. W. A. Little, Phys. Rev. 134A, 1416 (1964); H. Gutfreund and W. A. Little, in Highly Conducting One Dimensional Systems, ed. by J. Derreese, R. Errard, and V. van Doren (Plenum, New York, 1979), p. 305.
39. High Temperature Superconductivity, ed. by V. Ginzburg and D. Kirzhnits (Plenum, New York, 1982).
40. D. Allander, J. Bray, and J. Bardeen, Phys. Rev. B37, 1020 (1973).
41. V. Z. Kresin, Phys. Rev. B30, 450 (1984).
42. W. McMillan and J. Rowell, in Superconductivity, ed. by R. Parks (Dekker, New York, 1969), vol. 1, p. 561.
43. E. Wolf, Principles of Electron Tunneling Spectroscopy, Oxford University Press, New York, 1985.
44. K. Kihlstrom, P. Hovda, V. Z. Kresin, and S. Wolf (preprint).
45. B. Klein, L. Boyer, D. Papaconstantopoulos, and L. Matteis, Phys. Rev. B18, 641 (1978).
46. G. Stewart, in Superconductivity in d- and f- Band Metals, ed. by W. Buckel and W. Weber, Kernforschungszentrum, Karlsruhe (1982), p. 81.

47. V. Z. Kresin, Phys. Lett. 49A, 117 (1974).
48. H. Schuttler, M. Jarrell, and D. Scalapino, Phys. Rev. 58, 1147 (1987).

*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*