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Dynamical screening and superconducting state in intercalated layered metallochloronitrides

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An essential property of layered systems is the dynamical nature of the screened Coulomb interaction. Low-energy collective modes appear as a consequence of the layering and provide for a superconducting-pairing channel in addition to the electron-phonon-induced attractive interaction. We show that taking into account this feature allows to explain the high critical temperatures ($T_c \sim 26$ K) observed in recently discovered intercalated metallochloronitrides. The exchange of acoustic plasmons between carriers leads to a significant enhancement of the superconducting critical temperature that is in agreement with the experimental observations.

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Screening of the Coulomb interaction takes very different forms in layered conductors and three dimensional (3D) isotropic metals. We show that the dynamic screening in layered systems can lead to a Coulomb-induced enhancement of the superconducting pairing and might be an essential addition to the usual electron-phonon contribution. This important feature results from the existence of low-energy electronic collective modes characteristic for layered materials.

The aim of the present paper is to explain the nature of the superconducting state in layered intercalated metallochloronitrides.[1] It has been shown that intercalation of metallic ions and organic molecules into the parent compound (Zr,Hf)NCl leads to a superconductor with rather high critical temperature ($T_c \sim 26$ K).[1] Based on experimental studies[1–7] and band-structure calculations[8,9] it was concluded that (i) electron-phonon mediated pairing is insufficient to explain the high T_c's observed and that (ii) there is no evidence for the presence of strong correlations; the system can be described within Fermi-liquid theory. In addition, these compounds do not have magnetic ions which excludes a magnetic mechanism as well. No explanation has been suggested so far as to what pairing mechanism can allow to reach the observed critical temperatures. The theory proposed below shows that such high T_c's can be obtained by including the additional pairing contribution arising from the interaction of carriers with acoustic plasmons; this is the manifestation of the dynamic screening effect of the Coulomb interaction.

The description of layered conductors can be made by neglecting the small interlayer hopping in a first approximation. On the other hand, it is essential to take into account the screened interlayer Coulomb interaction which has an important dynamic part. Indeed, it is known that for usual 3D materials this interaction can be considered in the static limit since electronic collective modes are very high in energy (the optical plasmon energies are of the order 5–30 eV in metals; see, e.g., Ref. 10). Therefore, the Coulomb repulsion enters the theory of superconductivity as a single constant pseudopotential μ^*. The situation is very different in layered conductors: incomplete screening of the Coulomb interaction results from the layering.[11] The response to a charge fluctuation is time dependent and the frequency dependence of the screened Coulomb interaction becomes important. This leads to the presence of *low*-energy electronic collective modes: the acoustic plasmons. It is this particular feature of layered materials that brings about an additional contribution to the pairing interaction between electrons.

The order parameter $\Delta(\mathbf{k},\omega_n)$ of the superconducting state is described by

$$\Delta(\mathbf{k},\omega_n)Z(\mathbf{k},\omega_n) = T\sum_{m=-\infty}^{\infty}\int \frac{d^3\mathbf{k}'}{(2\pi)^3}\Gamma(\mathbf{k},\mathbf{k}';\omega_n-\omega_m)F^{\dagger}(\mathbf{k},\omega_m), \tag{1}$$

where $F^{\dagger}=\langle c^{\dagger}_{k,\uparrow}c^{\dagger}_{-k,\downarrow}\rangle$ is the Gor'kov pairing function and $Z(k,\omega_n)$ is the renormalization function, defined by

$$Z(\mathbf{k},\omega_n)-1=\frac{T}{\omega_n}\sum_{m=-\infty}^{\infty}\int\frac{d^3\mathbf{k}'}{(2\pi)^3}\times\Gamma(\mathbf{k},\mathbf{k}';\omega_n-\omega_m)G(\mathbf{k},\omega_m). \tag{2}$$

$G=\langle c^{\dagger}_{k,\sigma}c_{k,\sigma}\rangle$ is the usual Green function, and Γ the total interaction kernel; $\omega_n=(2n+1)\pi T$. We use the thermodynamic Green's-function formalism (see, e.g., Ref. 12). The T_c for layered superconductors is obtained by solving the set of Eqs. (1) and (2) self-consistently.

The interaction kernel is composed of two parts, $\Gamma=\Gamma_{ph}+\Gamma_c$, where

$$\Gamma_{ph}(\mathbf{q};|n-m|)=|g_\nu(\mathbf{q})|^2 D(\mathbf{q},|n-m|), \tag{3}$$

$$\Gamma_c(\mathbf{q};|n-m|)=\frac{V_c(\mathbf{q})}{\epsilon(\mathbf{q},|n-m|)}. \tag{4}$$

The first term, Γ_{ph}, is the usual pairing contribution resulting from the electron-phonon interaction. $D(q,n-m)=\Omega_\nu^2(q)[\omega_n-\omega_m)^2+\Omega_\nu^2(q)]^{-1}$ is the phonon temperature Green's function, and $\Omega_\nu(q)$ the phonon frequency; summation over phonon branches ν is assumed. The second contribution to the interaction kernel, Γ_c, is the Coulomb part written in its most general form as the ratio of the bare Coulomb interaction $V_c(\mathbf{q})$ and the dielectric function $\epsilon(\mathbf{q},\omega_n-\omega_m)$. Both functions have to be calculated for a layered structure.

The Coulomb interaction for conducting layers separated by spacers of dielectric constant ϵ_M can be written in the form[11,13]

$$V_c(\mathbf{q})=\frac{2\pi e^2}{\epsilon_M q_\parallel}R(q_\parallel,q_z)=\frac{\lambda_c}{N(E_F)}\tilde{V}_c(\mathbf{q}_\parallel;q_z), \tag{5}$$

where $q_\parallel(q_z)$ is the in-plane (out-of-plane) component of the wave vector. In the last expression, $N(E_F)$ is the 2D electronic density of states (DOS) at the Fermi energy E_F, and $\tilde{V}_c(\mathbf{q}_\parallel;q_z)=R(\mathbf{q}_\parallel,q_z)/(2k_F\mathbf{q}_\parallel)$ with

$$R(\mathbf{q}_\parallel,q_z)=\frac{\sinh(q_\parallel L)}{\cosh(q_\parallel L)-\cos(q_z L)}. \tag{6}$$

L is the interlayer spacing and $\lambda_c=e^2/\hbar v_F 2\epsilon_M$ is the dimensionless Coulomb interaction constant (v_F is the Fermi velocity). The dielectric function $\epsilon(\mathbf{q},\omega_n-\omega_m)$ has been calculated for a layered system[13–15] in the random-phase approximation (RPA). It has been shown there that the plasmon spectrum contains anisotropic bands $\omega_{pl}=\omega_{pl}(\mathbf{q}_\parallel,q_z)$ that can be labeled by q_z and which are the low-frequency acoustic modes.

Equations (1) and (2) can be cast into the following matrix form near T_c (see our paper, Ref. 15):

$$\sum_m \sum_{k_z'} K_{n,m}(|q_z|)\Phi_m(k_z')=\eta\Phi_n(k_z), \tag{7}$$

where $q_z\equiv k_z-k_z'$ are the wave-vector components normal to the conducting layers and $\Phi_m(k_z')=\Delta_m(k_z')/\sqrt{2m+1}$ is the reduced order parameter. In the case of a layered superconductor, the matrix K takes the form

$$K_{n,m}(|q_z|)=\frac{1}{N_z}\frac{1}{\sqrt{2n+1}\sqrt{2m+1}}\Big\{\lambda[D(n-m)+D(n+m+1)]+\lambda_c[\Gamma_c^I(|n-m|;|q_z|)+\Gamma_c^I(|n+m+1|;|q_z|)]-\mu^*\theta(\Omega_c-|\omega_m|)-\delta_{n,m}\sum_{p=0}^{2n}[\lambda D(n-p)+\lambda_c\Gamma_c^I(|n-p|;|q_z|)]\Big\}. \tag{8}$$

$n-m$ is shorthand for the difference of Matsubara frequencies $\omega_n-\omega_m=2\pi\tilde{T}(n-m)$ [with $\tilde{T}=k_BT/\Omega$; we consider an Einstein phonon $\Omega_\nu(\mathbf{q})\equiv\Omega$]. Ω_c is the cutoff used to define the pseudopotential μ^*, and N_z is the number of q_z points considered in the Brillouin zone. All but the static Coulomb repulsion μ^* are temperature-dependent quantities. The critical temperature of the superconducting phase transition T_c is reached when the highest eigenvalue is $\eta=1$.

$\Gamma_c^I(n,|q_z|)$ is the frequency-dependent contribution of the screened Coulomb interaction arising from acoustic plasmons. It has been shown by Morawitz *et al.*[14] that the DOS of the low-energy collective modes is peaked at $q_z=\pi$ and $q_z=0$. Furthermore, it was demonstrated that the $q_z=0$ term is repulsive and can therefore be included into the pseudopotential μ^*.[15] The main plasmon contribution to the pairing is thus obtained for $q_z=\pi/L$ and has the form

$$\Gamma_c^I(n-m)=\frac{\lambda_c}{2\pi}\int_0^{\tilde{q}_c}\frac{d\tilde{q}}{\sqrt{1-\tilde{q}^2}}\frac{\tilde{V}_c(\tilde{q})}{\epsilon(\tilde{q},n-m)}, \tag{9}$$

where $\tilde{q}\equiv q_\parallel/2k_F$, and $\tilde{q}_c=\min\{1,|\omega_n-\omega_m|/4E_F\}$ divides the (ω,q) space into the regions $\omega>qv_F$ and $\omega<qv_F$. The first region corresponds to the dynamic response and contains plasmon excitations, including the acoustic plasmon branches. In the second region the response can be treated in the static approximation and represents the usual repulsive part of the screened Coulomb interaction. We calculate the value of the critical temperature from Eqs. (7)–(9).

In order to demonstrate the importance of dynamic screening for superconductivity we calculate T_c for the following set of realistic parameters: $L=15$ Å, $\lambda=0.5$, $\Omega=70$ meV, $\epsilon_M=3$, $v_F=5\times10^7$ cm/s, $\mu^*=0.1$, and $m^*=m_e$. As will be seen below, these values are close to those found in metallochloronitrides. With these parameters, the Coulomb interaction constant defined earlier is $\lambda_c=0.6$. One can, therefore, use RPA in first approximation and neglect vertex corrections.

With use of aforementioned values for the three quantities λ, Ω, and μ^* one can, in a first step, calculate the value $T_{c,ph}$ which is the critical temperature in the absence of dynamic screening ($\Gamma_c^I=0$). One obtains $T_{c;ph}=12$ K. If we now take into account the effect of dynamic screening and calculate T_c using all parameters given above, we obtain $T_c=25$ K. This demonstrates that the value of T_c in layered superconductors can be drastically affected (enhanced) by the dynamic part of the screened Coulomb interaction.

We now apply our approach to a specific case among intercalated metallochloronitrides, namely, the compound $Li_{0.48}(THF)_y$HfNCl which has a $T_c=25.5$ K.[1] We selected this compound as a study case because there has been relatively detailed experimental and theoretical work done on this layered material. From Refs. 5 and 6 the interlayer distance L and characteristic phonon frequency Ω are equal to $L=18.7$ Å and $\Omega=60$ meV, respectively. The effective mass and Fermi energy have been estimated from band-structure calculations.[8] Accordingly, $m^*/m_e \simeq 0.6$ where m_e is the free-electron mass and $E_F \simeq 1$ eV. Finally, according to Ref. 6 we take $\mu^*=0.1$. Selecting the values $\epsilon_M=1.8$ and $\lambda=0.3$ and calculating T_c with Eqs. (3)–(9), we obtain $T_c=24.5$ K, which is close to the experimental value.[1] In absence of the plasmon part ($\Gamma_c^I=0$) we obtain $T_{c,ph}=0.5$ K which indeed confirms that the conventional electron-phonon mechanism cannot explain the high critical temperature observed in this material.

We point out that the calculation just performed for $Li_{0.48}(THF)_y HfNCl$ makes use of reasonable, but still adjustable parameters λ and ϵ_M. A more detailed analysis requires the experimental determination of these quantities prior to our calculation. It would thus be of interest to perform tunneling measurements which would allow to determine the function $\alpha^2(\Omega)F(\Omega)$ [$F(\Omega)$ is the phonon density of states whereas $\alpha^2(\Omega)$ describes the coupling], and correspondingly λ (along with μ^*; see, e.g., Refs. 16 and 17). Another method to determine λ requires to measure the electronic heat capacity. Indeed, as is known, the Sommerfeld constant contains the renormalization factor $1+\lambda$ while the magnetic susceptibility is unrenormalized (see, e.g., Ref. 17). Comparing these two quantities one can extract the value of the coupling constant λ. Such measurements, along with optical data, would allow to carry out more detailed calculations of T_c for specific metallochloronitrides.

TABLE I. Determination of T_c ($T_{c,ph}$) in presence (absence) of the contribution due to dynamic screening of the Coulomb interaction. The parameters are those taken for $Li_{0.48}(THF)_y HfNCl$; $\mu^*=0.1$, $\Omega=60$ meV, $m^*/m=0.6$, $E_F=1$ eV, and $L=18.7$ Å.

λ	ϵ_M	$T_{c,ph}$ (K)	T_c (K)
0.5	2.2	11	24.9
0.4	1.95	4.3	25.3
0.3	1.8	0.5	24.6

In absence of such experimental data, we present in Table I a few typical examples of calculated T_c for various realistic values of the parameters λ and ϵ_M in $Li_{0.48}(THF)_y$ HfNCl. Note that in all cases the optical plasmon energy at $\mathbf{q}=0$ is of the order $\omega_{pl,opt}(\mathbf{q}=0)\simeq 1-1.3$ eV, in agreement with band-structure calculation estimates. A more detailed analysis of other metallochlorinitrides will be described elsewhere.

In conclusion, the dynamical screening of the Coulomb interaction is an essential feature of layered structures that provides for an additional contribution to the pairing and leads to a drastic enhancement of T_c. The theory presented here enables us to give an explanation for the high critical temperatures observed in intercalated layered metallochloronitrides.

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