Analysis of the dynamics of noncentral ions in superconductors

A. A. Kosov

V. I. Ul'yanov-Lenin Kazan University, Kazan

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The temperature-Green's-function method and the diagram technique are used to analyze the dynamics of noncentral ions, i.e., ions moving in a two-well potential, in superconductors. The screening by conduction electrons hardens the vibrations of the noncentral ions, while the superconducting correlations soften these vibrations, by weakening the screening effect. Two mechanisms are considered in a description of the effect of superconducting correlations on the ion dynamics. One is the BCS model. The other is the local hole-pair superconductivity model. A simple expression is derived for the temperature dependence of the mean square displacement of the noncentral ions in both the normal and superconducting phases.

INTRODUCTION

In an effort to explain the linear temperature dependence of the specific heat in metallic glasses, Anderson *et al.*[1] and Phillips[2] have discussed a model in which a certain number of atoms or groups of atoms may be in two identical equilibrium positions, close together, and may tunnel between these positions. It was later discovered that a model of this sort could also explain several other experimental results from research on kinetic phenomena in amorphous metals and superconductors.[3,4] Interest has recently returned to the case of ions moving in a two-well potential, i.e., "noncentral ions," in conductors because of evidence which has been found in research on $YBa_2Cu_3O_{7-\delta}$ compounds by EXAFS methods. This evidence suggests that displacements of oxygen in (0 4) sites may play an important role in superconductivity[5] and that the oxygen vibrations are very anharmonic.[6] On the theoretical side there is a need for a comprehensive study of the dynamics of noncentral ions in superconductors. This need is demonstrated by the numerous experimental studies of atomic motions in metal oxides by ion channeling,[7] by the Mössbauer-effect method,[8] etc. These studies imply softening of the vibrations of the atoms of the copper-oxygen subsystem in the superconducting phase and a relationship between the superconducting transition temperature T_c and the ion dynamics. Another reason why a comprehensive theoretical study is needed is that several investigators (e.g., Plakida[9]) have suggested that two-well potentials for oxygen may play a role in shaping the high-temperture mechanism for the superconductivity of ceramics.

In the present paper we examine the dynamics of noncentral ions in superconductors. We are particularly interested in the temperature region bracketing T_c. We focus on this region because we wish to establish the relationship between certain experimental results and the theory derived below. The experimental results in question show that the vibration amplitudes of oxygen and copper ions in chain sites[1)] increase in the superconducting phase in several of the yttrium high-T_c superconductors. According to the arguments in Refs. 8 and 11, this conclusion follows from measurements of the Mössbauer-effect probability, from neutron diffraction, etc. The theory derived below treats the effect of superconducting correlations on the dynamics of noncentral ions in these and similar compounds. Since the question of superconducting correlations in the high T_c superconductors is quite involved, and still far from complete resolution, we will be discussing two mechanisms, which represent extreme cases in terms of the extent to which the charge carriers are collectivized. The first mechanism involves *s*-band pairing of the BCS type (this mechanism is discussed in Sec. 2). The second involves the formation of local pairs of holes in filled *p* shells of O^{2-} ions of (0 4)–(Cu 1)–(0 4) chains in $YBa_2Cu_3O_{7-\delta}$, with hybridization with *s* electrons in addition to the exciton mechanism, studied by Pedan and Kulik[12] (Sec. 3).

1. FORMULATION OF THE PROBLEM

The minimum which has been observed in the electrical resistance of many amorphous metals, with a logarithmic temperature dependence,[13] has attracted interest to the role played by noncentral ions in electron scattering, because of the similarity to the behavior of the magnetic impurities responsible for the Kondo effect. Kondo stated[14] that an angular variation caused in the screening of noncentral ions by conduction electrons by the orbital motion of the latter might, by playing the role of the spins of conduction electrons, lead to a Kondo-like anomaly in the electrical conductivity of amorphous metals. Such anomalies have been studied on the basis of the following operator for the interaction of conduction electrons with noncentral ions:[4]

$$\hat{\mathcal{H}}_{int}=\sum_{\mathbf{k}\mathbf{k}'\sigma}(M_{\mathbf{k}'\mathbf{k}}\tau_3+N_{\mathbf{k}'\mathbf{k}}\tau_1)c^+_{\mathbf{k}'\sigma}c_{\mathbf{k}\sigma},$$

$$M_{\mathbf{k}'\mathbf{k}}=V_0(\mathbf{k}'-\mathbf{k})\int d^3R\Phi_1(R)\Phi_2(R)\exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}],$$

$$N_{\mathbf{k}'\mathbf{k}}=\frac{1}{2}V_0(\mathbf{k}'-\mathbf{k})\int d^3R[\Phi_1^2(R)-\Phi_2^2(R)]\exp[i(\mathbf{k}-\mathbf{k}')\mathbf{R}]. \quad (1)$$

Here $c^+_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}$ are the field operators of *s* electrons with a wave vector $\mathbf{k}$ and a spin σ; $V_0(\mathbf{k})$ is the Fourier transform of the Coulomb interaction $V(\mathbf{r}-\mathbf{R})$ between the noncentral ions and the *s* electrons; $\mathbf{r}$ and $\mathbf{R}$ are the coordinates of the electron and the noncentral ion, respectively; $\Phi_1(R)$ and $\Phi_2(R)$ are the wave functions of the atom in the different wells of the two-well potential (Fig. 1); and τ_i are the Pauli

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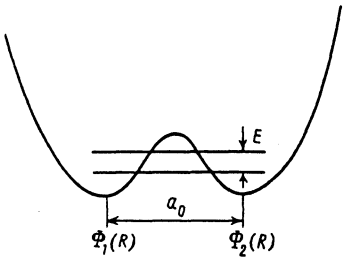

FIG. 1. The two-well atomic potential. Here E is the tunneling-induced splitting of the energy, and a_0 is the distance between the wells.

matrices in the space of the symmetrized wave functions

$$\psi_s=\frac{1}{\sqrt{2}}(\Phi_1+\Phi_2), \quad \psi_a=\frac{1}{\sqrt{2}}(\Phi_1-\Phi_2).$$

The unperturbed Hamiltonian of the noncentral ions in terms of these wave functions is

$$\hat{\mathcal{H}}_{ion}=-\sum_j \varepsilon_j \tau_{3j}, \quad \varepsilon_j=\frac{1}{2}E_j, \tag{2}$$

where E_j is the energy of ion j associated with the tunneling between wells.

Exploiting the analogy with localized spins, we analyze the dynamics of the noncentral ions by the diagram technique which has been developed by Barnes and Zitkova-Wilcox[15] for metals with magnetic impurities and which was generalized to the case of superconductors in Ref. 16. For this purpose we introduce pseudofermion field operators[17] $a_{j\alpha}^+$ and $a_{j\alpha}$:

$$\tau_j=\sum_{\alpha\beta} a_{j\alpha}^+ \tau_{\alpha\beta} a_{j\beta}.$$

To get rid of the nonphysical states accompanying the transition to spin fermions, we add a projection operator to the total Hamiltonian:

$$\hat{\mathcal{H}}_{pr}=\lambda \sum_{j\alpha} a_{j\alpha}^+ a_{j\alpha}. \tag{3}$$

The Hamiltonian of the system of interacting noncentral ions and s electrons with BCS superconducting correlations is thus written

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}_0+\hat{\mathcal{H}}_{pr}+\hat{\mathcal{H}}_{int},$$

$$\hat{\mathcal{H}}_0=\hat{\mathcal{H}}_s+\hat{\mathcal{H}}_{ion},$$

$$\hat{\mathcal{H}}_s=\sum_{k\sigma}\varepsilon_{k\sigma}c_{k\sigma}^+c_{k\sigma}+\sum_k(\Delta c_{k+}^+c_{-k-}^++\text{H.a.}).$$

Here $\varepsilon_{k\sigma}$, is the energy of the band s electrons, and Δ is the superconducting order parameter. The operators $\hat{\mathcal{H}}_{int}$, $\hat{\mathcal{H}}_{ion}$ and $\hat{\mathcal{H}}_{pr}$ are given by (1)–(3).

We introduce the following temperature Green's functions:

$$G_{k'k\sigma}(\tau,\tau')=-\langle T_\tau c_{k'\sigma}(\tau)c_{k\sigma}^+(\tau')\rangle,$$

$$F_{k'k\sigma}^+(\tau,\tau')=-\langle T_\tau c_{k',-\sigma}^+(\tau)c_{k\sigma}^+(\tau')\rangle,$$

$$D_{j\alpha}(\tau,\tau')=-\langle T_\tau a_{j\alpha}(\tau)a_{j\alpha}^+(\tau')\rangle.$$

The unperturbed Green's functions corresponding to the operator $\hat{\mathcal{H}}_0+\hat{\mathcal{H}}_{pr}$ in frequency space are

$$G_{k'k\sigma}^0(\omega_n)=-\frac{i\omega_n+\varepsilon_{k\sigma}}{\varepsilon_{k\sigma}^2+\omega_n^2+\Delta^2}\delta_{kk'},$$

$$F_{k'k\sigma}^{0+}(\omega_n)=\sigma\frac{\Delta\delta_{kk'}}{\varepsilon_{k\sigma}^2+\omega_n^2+\Delta^2},$$

$$D_{j\alpha}^0(\omega_n)=-(\lambda-\varepsilon_{j\alpha}-i\omega_n)^{-1}, \quad \varepsilon_{j1}=\varepsilon_j; \quad \varepsilon_{j2}=-\varepsilon_j,$$

where $\omega_n=\pi T(2n+1)$ are the Matsubara frequencies corresponding to Fermi statistics. We find the perturbed functions from the Dyson equations. The Dyson equation for pseudofermion functions is shown in graphical form in Fig. 2. The dashed line and the double dashed line represent unperturbed and perturbed ion functions. A solid line with arrows going in the same direction corresponds to the Green's function G, while a solid line with arrows going in opposite directions corresponds to an anomalous function F^+. The analytic expression for the complete Green's function D and for the eigenenergy parts of second order in $\hat{\mathcal{H}}_{int}$ which are shown in Fig. 2 is as follows:

$$D_{j\alpha}(\omega_n)=-(\lambda-\varepsilon_{j\alpha}-\Sigma_{j\alpha}(\omega_n)-i\omega_n)^{-1}, \tag{4}$$

$$\Sigma_{j\alpha}^{(2)}(\omega_n)=-\frac{1}{2}T^2\sum_{kk'k_1k_1'}\sum_{\omega_1\omega_2\sigma}[C_{k'k_1\sigma}(\omega_2)G_{k_1'k\sigma}(\omega_2+\omega_1-\omega_n)$$

$$-F_{k'k_1'\sigma}(\omega_2)F_{k_1k\sigma}^+(\omega_2+\omega_1-\omega_n)][M_{kk'}M_{k_1k_1'}D_{j\alpha}(\omega_1)$$

$$+N_{kk'}N_{k_1k_1'}D_{j\beta}(\omega_1)], \quad \beta\neq\alpha. \tag{5}$$

The complete electron functions G and F^+ were found by the diagram technique in Ref. 4 to second order in $\hat{\mathcal{H}}_{int}$. It was shown that the presence of noncentral ions in a sample does not shift the transition temperature T_c, because the Coulomb interaction $\hat{\mathcal{H}}_{int}$ is invariant under time reversal. Fur-

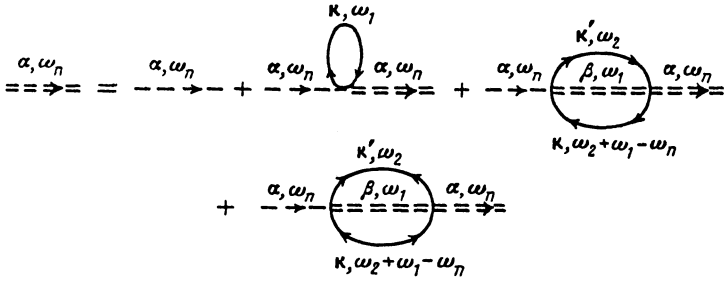

FIG. 2. Diagram equation for the Green's function of a noncentral ion.

thermore, these noncentral ions do not cause any significant changes in the energy spectrum of the conduction electrons. It was shown in Ref. 4 that the parameter representing the rupture of Cooper pairs in compounds with noncentral ions can be derived in a higher-order perturbation theory—in third and higher orders. Accordingly, we restrict the discussion here to the zeroth functions G^0 and F^{0+}.

2. DYNAMICS OF NONCENTRAL IONS; PAIRING IN THE *s* BAND

The position operator $\hat{x}_j$ of the jth noncentral ion, is given in the pseudofermion representation by

$$\hat{x}_j=\frac{1}{2}a_0(a_{j1}^{+}a_{j2}+a_{j2}^{+}a_{j1}),$$

$$a_0=x_{11}-x_{22}, \qquad x_{\alpha\alpha}=\int d^3R\,\Phi_\alpha^{*}(R)\hat{x}\Phi_\alpha(R).$$

Since we are ultimately interested in the mean square displacement $\langle x_j^2\rangle$, to find it we determine the following two-particle function of the operator $\hat{x}_j$:

$$\langle \hat{x}_j(\tau)\hat{x}_j(\tau')\rangle=\frac{a_0^2}{4}\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{z}[\Lambda_{12}^{j}(\tau,\tau')+\Lambda_{21}^{j}(\tau,\tau')],$$

$$\Lambda_{\alpha\beta}^{j}(\tau,\tau')=\langle T_\tau a_{j\alpha}^{+}(\tau)a_{j\beta}(\tau')[a_{j\alpha}^{+}(\tau')a_{j\beta}(\tau')$$

$$+a_{j\beta}^{+}(\tau')a_{j\alpha}(\tau')]\rangle, \qquad Z=e^{\beta\varepsilon_1}+e^{\beta\varepsilon_2}, \quad \beta=1/T. \tag{6}$$

The Bethe–Salpeter diagram equation for the two-particle functions $\Lambda_{\alpha\beta}^{j}(\omega_n,\omega_n+\omega_0)$ has the structure shown in Fig. 3. To write the diagram equation of Fig. 3 in compact analytic form, we use the identity

$$D_\alpha(\omega_n+\omega_0)D_\beta(\omega_n)=(\varepsilon_\beta-\varepsilon_\alpha-i\omega_0)^{-1}\{D_\beta(\omega_n)-D_\alpha(\omega_n+\omega_0)$$
$$+[\Sigma_\beta(\omega_n)-\Sigma_\alpha(\omega_n+\omega_0)]D_\alpha(\omega_n+\omega_0)D_\beta(\omega_n)\}. \tag{7}$$

Using identity (7) for the functions $\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$, we find

$$\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)=\frac{1}{\varepsilon_\beta-\varepsilon_\alpha-i\omega_0}\{D_\beta(\omega_n)-D_\alpha(\omega_n+\omega_0)$$
$$+[\Sigma_\beta(\omega_n)-\Sigma_\alpha(\omega_n+\omega_0)]\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$$
$$+\frac{1}{2}T^2\sum_{\omega_1\omega_2\sigma}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}_1\mathbf{k}_1'}[G_{\mathbf{k}'\mathbf{k}_1\sigma}(\omega_2)G_{\mathbf{k}_1'\mathbf{k}\sigma}(\omega_2+\omega_n-\omega_1)$$

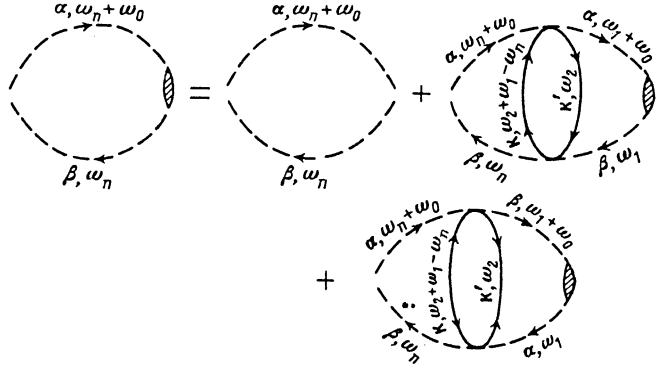

FIG. 3. Diagram equation for the two-particle Green's function $\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$.

$$-F_{\mathbf{k}'\mathbf{k}_1'\sigma}(\omega_2)F_{\mathbf{k}_1\mathbf{k}\sigma}^{+}(\omega_2+\omega_n-\omega_1)][M_{\mathbf{k}\mathbf{k}'}M_{\mathbf{k}_1\mathbf{k}_1'}(D_\alpha(\omega_n+\omega_0)$$
$$-D_\beta(\omega_n))\Lambda_{\alpha\beta}(\omega_1,\omega_1+\omega_0)-N_{\mathbf{k}\mathbf{k}'}N_{\mathbf{k}_1\mathbf{k}_1'}(D_\alpha(\omega_n+\omega_0)$$
$$-D_\beta(\omega_n))\Lambda_{\beta\alpha}(\omega_1,\omega_1+\omega_0)]\}. \tag{8}$$

After we split up the vertex parts of $\Lambda_{\alpha\beta}(\omega_1,\omega_1+\omega_0)$ and the coefficients between them, which are coupled by the frequencies ω_1 (see the Appendix), we can reduce Eq. (8) to the following system of equations:

$$\begin{cases}(E-iA-i\omega_0)\Pi_{21}(\omega_0)-iA\Pi_{12}(\omega_0)=\left(1-i\dfrac{2A}{E}\right)\mathrm{th}\dfrac{E}{2T},\\ iA\Pi_{21}(\omega_0)+(E+iA+i\omega_0)\Pi_{12}(\omega_0)=\left(1+i\dfrac{2A}{E}\right)\mathrm{th}\dfrac{E}{2T},\end{cases} \tag{9}$$

where

$$\Pi_{\alpha\beta}(\omega_0)=\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z}T\sum_{\omega_n}\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0),$$

$$A=2\pi\rho^2QT\left[\exp\left(\frac{\Delta}{T}\right)+1\right]^{-1}, \qquad Q=\int\frac{d\Omega_{\mathbf{k}}\,d\Omega_{\mathbf{k}'}}{4(\pi)^2}|N_{\mathbf{k}\mathbf{k}'}|^2.$$

In the long-wave approximation, i.e., with $N_{\mathbf{k}\mathbf{k}'}\approx iV_0a_0(k_x-k_x')$, we have the following expression[4] for Q:

$$Q=\frac{1}{6}(V_0a_0k_F)^2,$$

where k_F and ρ are the wave vector and density of states of the s electrons at the Fermi level. The dependence of the Coulomb potential V_0 on the wave vector can be ignored in finding the coefficient Q. In deriving Eqs. (9) we have also discarded the real parts of the eigenenergy parts of the Green's function $D_{j\alpha}(\omega_n)$.

Solving Eqs. (9) with the help of (6) for $\langle x^2\rangle$, we find

$$\langle x^2\rangle=\langle\hat{x}(\tau)\hat{x}(\tau')\rangle|_{\tau'\to\tau-0}=\frac{a_0^2}{4}T\sum_{\omega_0}[\Pi_{12}(\omega_0)+\Pi_{21}(\omega_0)]$$

$$=2a_0^2\,\mathrm{th}\frac{E}{2T}T\sum_{\omega_0}\frac{E+2A\omega_0/E}{E^2+2A\omega_0+\omega_0^2}. \tag{10}$$

Evaluating the sum over the Bose frequency $\omega_0=2n\pi T$ in (10), we find the following expression for $\langle x^2\rangle$:

$$\frac{\langle x^2\rangle}{a_0^2}=\frac{\dfrac{E-2A^2/E}{(E^2-A^2)^{1/2}}\,\mathrm{sh}\dfrac{(E^2-A^2)^{1/2}}{T}+\dfrac{2A}{E}\sin\dfrac{A}{T}}{\mathrm{ch}\dfrac{(E^2-A^2)^{1/2}}{T}-\cos\dfrac{A}{T}}\,\mathrm{th}\frac{E}{2T}. \tag{11}$$

With $A=0$, i.e., if there is no coupling of noncentral ions with conduction electrons, we find from (11) the obvious result $\langle x^2\rangle/a_0^2$, as expected.

Figure 4 shows the temperature dependence of $\langle x^2\rangle$ calculated for various values of the parameters $\pi\rho^2Q$ and E/T_c in the normal and superconducting phases. It follows from this figure that the screening by conduction electrons reduces the mean square displacements of noncentral ions, while the superconducting correlations weaken this screening effect (they reduce the function A) and thereby make $\langle x^2\rangle$ larger than in the normal phase. This effect is more obvious for $E/T_c>I$, i.e., in the case of intense ion tunneling.

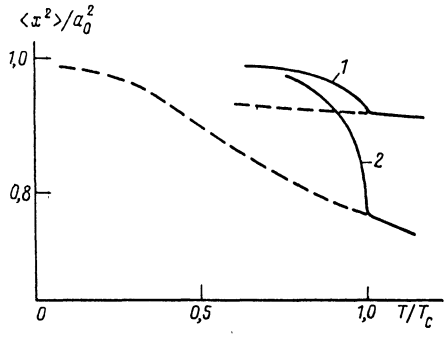

FIG. 4. Temperature dependence of the mean square displacement of a noncentral ion according to the BCS model with the parameter values $\pi\rho^2 Q = 0.5$ and (*1*) $E/T_c = 1.0$ or (*2*) $E/T_c = 2.0$. The broken lines for $T < T_c$ show the course of the curves when superconducting correlations are ignored.

If we assume that an analog of the Kondo effect operates in the atomic motion above the transition temperature T_c (Ref. 14), then we should incorporate in our calculations diagrams of third and higher orders in the interaction $\hat{\mathscr{H}}_{\text{int}}$, as was done, for example, in Ref. 4 for the case of one-particle electron functions. Such calculations can be carried out in the manner of the calculations for two-particle Green's functions in a study of the relaxation characteristics of localized spins in metals.[18] After the results of Ref. 18 are extended to the case at hand, they imply that the Kondo anomalies lead to a pronounced decrease in $\langle x^2\rangle$ by increasing the function A substantially. In certain cases, this decrease apparently proceeds until the potential is no longer a two-well potential at all. The incorporation of superconducting correlations will be even more noticeable in the softening of the ion vibrations in this case. This fact was pointed out in Ref. 19 in the course of an analysis of the anharmonicity of oxygen vibrations in the high T_c superconductors.

3. DYNAMICS OF NONCENTRAL IONS IN CONNECTION WITH LOCAL-PAIR SUPERCONDUCTIVITY IN METAL OXIDES

The BCS mechanism discussed in the preceding section of this paper apparently does not operate in the metal oxides. Numerous studies show that electron and hole states of the p shells of oxygen ions play an important role in the superconductivity of the high T_c superconductors. Of particular interest for a study of the dynamics of oxygen ions in copper-oxygen chains in the $YBa_2Cu_3O_{7-\delta}$ compounds is the exciton mechanism for the superconductivity of local pairs of holes which form in filled shells of O^{2-} ions of (0 4)–(Cu 1)–(0 4) chains, as developed in Ref. 12. We believe, however, that this mechanism needs considerable development before it is applied to the dynamics of noncentral ions. The reason is that a one-hand model was discussed in Ref. 12, while the experimental evidence points to a more complex energy spectrum for the carrier band in the superconducting cuprates. Band-theory calculations have also shown that a narrow peak forms near the Fermi level in the density of states of $YBa_2Cu_3O_{7-\delta}$. This peak is formed primarily by the p_z orbitals of chain oxygen ions.[20] Izyumov and Katsnel'son[21] used those calculations and a model assuming hybridization of localized and band electrons through displacements of atoms from their equilibrium positions. They showed that a two-well potential could form for the ions which are the carriers of a localized electronic state. There are also other studies which indicate an interrelationship between the dynamics of oxygen ions in chains and the electronic structure of the high T_c superconductors (e.g., Ref. 22). Combining the facts listed above, we construct the following Hamiltonian for analyzing the ion and electron components of a metal oxide:

$$\hat{\mathscr{H}}=\hat{\mathscr{H}}_{ion}+\hat{\mathscr{H}}_{Lp}+\hat{\mathscr{H}}_{l}+\hat{\mathscr{H}}_{pr}+\hat{\mathscr{H}}_{i-h},$$

$$\hat{\mathscr{H}}_{Lp}=-W_1\sum_{mn\sigma\neq\sigma'} b^+_{m1\sigma}b^+_{m2\sigma'}b_{n2\sigma'}b_{n1\sigma} \qquad (12)$$

$$+\frac{1}{2}W_2\sum_{mnl\sigma} b^+_{ml\sigma}b_{ml\sigma}b^+_{nl\sigma}b_{nl\sigma}+\mu\sum_{ml\sigma} b^+_{ml\sigma}b_{ml\sigma},$$

$$\hat{\mathscr{H}}_{ion}=-\sum_{ml\alpha}\varepsilon_{ml\alpha}a^+_{ml\alpha}a_{ml\alpha}, \qquad \varepsilon_{ml1}=\varepsilon_{ml}, \qquad \varepsilon_{ml2}=-\varepsilon_{ml},$$

$$\hat{\mathscr{H}}_{pr}=\lambda\sum_{ml\alpha}a^+_{ml\alpha}a_{ml\alpha}, \qquad \hat{\mathscr{H}}_{l}=\sum_{\mathbf{k}\sigma}\varepsilon_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}{}^+c_{\mathbf{k}\sigma},$$

$$\hat{\mathscr{H}}_{i-h}=q\sum_{\mathbf{k}ml\sigma}x_{ml}[b^+_{ml\sigma}c_{\mathbf{k}\sigma}\exp(i\mathbf{k}\mathbf{R}_{ml})+\text{H.a.}],$$

$$x_{ml}=\frac{a_0}{2}(a^+_{ml1}a_{ml2}+a^+_{ml2}a_{ml1}).$$

Here $\hat{\mathscr{H}}_{Lp}$ determines the motion of local pairs of holes in copper-oxygen chains,[12] and the operator $\hat{\mathscr{H}}_{i-h}$ represents the interaction of oxygen ions in chains with s electrons and p_z holes. The indices m and n run over the neighboring copper-oxygen chains. The index l, which takes on the values of 1 and 2, specifies the noncentral oxygen ion in one chain; $b^+_{ml\sigma}$ and $b_{ml\sigma}$ are the field operators of the p_z holes at the l th oxygen ion of the mth chain; 2μ is the energy of a local pair measured from the Fermi level; q is the electron-phonon coupling parameter; $\mathbf{R}_{ml}$ is the radius vector of the (ml)th oxygen atom; W_1 and W_2 are the matrix elements of the superconducting and Coulomb interchain interactions; and $a^+_{ml\alpha}$ and $a_{ml\alpha}$ are pseudofermion field operators.

We define the Green's functions

$$K_{ml\sigma}(\tau,\tau')=-\langle T_\tau b_{ml\sigma}(\tau)b^+_{ml\sigma}(\tau')\rangle,$$

$$L^+_{ml\sigma}(\tau,\tau')=-\langle T_\tau b^+_{ml,-\sigma}(\tau)b^+_{ml\sigma}(\tau')\rangle,$$

$$G_{\mathbf{k}'\mathbf{k}\sigma}(\tau,\tau')=-\langle T_\tau c_{\mathbf{k}'\sigma}(\tau)c_{\mathbf{k}\sigma}{}^+(\tau')\rangle,$$

$$D_{ml\alpha}(\tau,\tau')=-\langle T_\tau a_{ml\alpha}(\tau)a^+_{ml\alpha}(\tau')\rangle.$$

If we assume that all the copper-oxygen are under idential conditions, the unperturbed K and L^+ Green's functions take the following form in the frequency representation:

$$K_{ml\sigma}(\omega_n)=K(\omega_n)=-\frac{i\omega_n+\mu^*}{(\mu^*)^2+\Delta^2+\omega_n{}^2},$$

$$L^+_{ml\sigma}(\omega_n)=L^+_\sigma(\omega_n)=-\sigma\frac{\Delta}{(\mu^*)^2+\Delta^2+\omega_n{}^2},$$

$$\mu^*=\mu+W_2\sum_{ml\sigma}n_{ml\sigma}=\mu+W_2zn,$$

$$\Delta=W_1\sum_{ml\sigma}\alpha_{ml\sigma}=W_1z\alpha.$$

$$\alpha_{ml\sigma}=L^{+}_{ml\sigma}(0), \quad n_{ml\sigma}=K_{ml\sigma}(0).$$

Here z is the number of nearest-neighbor chains, n is the average number of p_z holes at an oxygen ion, and α is the superconducting parameter, which is nonzero for $T<T_c$. The quantities α and n are found from the self-consistent equations

$$2n-1=-\frac{\mu^*}{[(\mu^*)^2+\Delta^2]^{1/2}}\,\mathrm{th}\,\frac{[(\mu^*)^2+\Delta^2]^{1/2}}{T},$$
$$\alpha=\frac{\Delta}{[(\mu^*)^2+\Delta^2]^{1/2}}\,\mathrm{th}\,\frac{[(\mu^*)^2+\Delta^2]^{1/2}}{T}. \tag{13}$$

It follows from (13) that a superconducting transition [or a solution of Eqs. (13)] is possible at $\alpha\neq 0$ only under the condition

$$-(W_1+W_2)z<\mu<W_1 z. \tag{14}$$

Under condition (14), T_c and the order parameter Δ at $T=0$ are given by

$$T_c=\frac{W_1|W_2 z+2\mu|}{(2W_1+W_2)\ln\dfrac{(2W_1+W_2)z+|W_2z+2\mu|}{(2W_1+W_2)z-|W_2z+2\mu|}},$$
$$\Delta(T=0)=\Delta_0=W_1 z\left[1-\left(\frac{W_2 z+2\mu}{2W_1 z+W_2 z}\right)^2\right]^{1/2}. \tag{15}$$

In contrast with the BCS theory, which predicts $2\Delta_0/T_c=3.52$, we find various values for $2\Delta_0/T_c$, from 0 to 4, from (15) by varying μ and W_2/W_1. For example, we find

$$\frac{2\Delta_0}{T_c}=\begin{cases} 4{,}00 & \text{with } \mu=-0{,}5W_2 z \\ 3{,}92 & \text{with } \mu=0,\ W_2/W_1=1 \\ 2{,}10 & \text{with } \mu=0{,}94\ W_1 z,\ W_2/W_1=2 \\ 1{,}30 & \text{with } \mu=0{,}975\ W_1 z,\ W_2/W_1=6. \end{cases}$$

Figure 5 shows a diagram for the eigenenergy part of the pseudofermion function $D_{ml\alpha}(\omega_n)=D_\alpha(\omega_n)$ of second order in the interaction $\hat{\mathscr{H}}_{i-h}$. The wavy line with two arrows going in the same direction represents the Green's function of the local pairs, $K_{ml\sigma}(\omega_n)$. The solid line and the dashed line represent the functions G and D, as in the preceding section of this paper.

After a summation over the interanl frequencies, the expression for the eigenenergy part, shown in Fig. 5, becomes

$$\Sigma^{ml}_{1(2)}(\omega_n)=\Sigma_{1(2)}(\omega_n)=2q^2\sum_{\mathbf{k}}[f(\lambda-\varepsilon_{2(1)})-f(\varepsilon_{\mathbf{k}})]$$

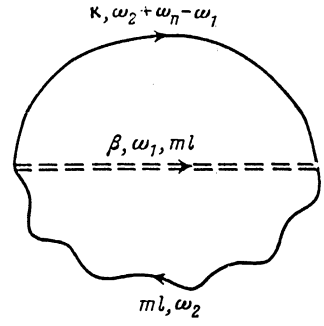

FIG. 5. Diagram of second order in $\hat{\mathscr{H}}_{i-h}$ for the self-energy part of the Green's function of a noncentral ion.

$$\times\left\{\left(1+\frac{\mu^*-[(\mu^*)^2+\Delta^2]^{1/2}}{2[(\mu^*)^2+\Delta^2]^{1/2}}\right)\right.$$
$$\times\frac{f(\varepsilon_{\mathbf{k}}-\lambda+\varepsilon_{2(1)}+i\omega_n)-f([(\mu^*)^2+\Delta^2]^{1/2})}{\lambda-\varepsilon_{2(1)}-\varepsilon_{\mathbf{k}}+[(\mu^*)^2+\Delta^2]^{1/2}-i\omega_n}$$
$$+\frac{\mu^*-[(\mu^*)^2+\Delta^2]^{1/2}}{2[(\mu^*)^2+\Delta^2]^{1/2}}$$
$$\left.\times\frac{f(-[(\mu^*)^2+\Delta^2]^{1/2})-f(\varepsilon_{\mathbf{k}}-\lambda+\varepsilon_{2(1)}+i\omega_n)}{\lambda-\varepsilon_{2(1)}-\varepsilon_{\mathbf{k}}-[(\mu^*)^2+\Delta^2]^{1/2}-i\omega_n}\right\}. \tag{16}$$

The pseudofermion function $D_{ml\alpha}(\omega_n)$, on the other hand, is written

$$D_{ml\alpha}(\omega_n)=-(\lambda-\varepsilon_{ml\alpha}-\Sigma_\alpha{}^{ml}(\omega_n)-i\omega_n)^{-1}.$$

An analytic equation for the two-frequency function $\Lambda^{ml}_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$, shown graphically in Fig. 6, can be written in the form

$$\Lambda_{\alpha\beta}{}^{ml}(\omega_n,\omega_n+\omega_0)=\frac{1}{\varepsilon_{ml\beta}-\varepsilon_{ml\alpha}-i\omega_0}\{D_{ml\beta}(\omega_n)-D_{ml\alpha}(\omega_n+\omega_0)$$
$$+[\Sigma_\beta{}^{ml}(\omega_n)-\Sigma_\alpha{}^{ml}(\omega_n+\omega_0)]\Lambda_{\alpha\beta}{}^{ml}(\omega_n,\omega_n+\omega_0)$$
$$+[\Sigma_\alpha{}^{ml}(\omega_n)-\Sigma_\beta{}^{ml}(\omega_n+\omega_0)]\Lambda_{\beta\alpha}{}^{ml}(\omega_n,\omega_n+\omega_0)\}. \tag{17}$$

Substituting (16) into Eqs. (17), and splitting the equations up in terms of the frequency ω_n, as in the preceding section of this paper, we find the following system of coupled equations:

$$(E-iB-i\omega_0)\Pi_{21}{}^{ml}(\omega_0)-iB\Pi_{12}{}^{ml}(\omega_0)=\left(1-\frac{2iB}{E}\right)\mathrm{th}\,\frac{E}{2T},$$
$$iB\Pi_{21}{}^{ml}(\omega_0)+(E+iB+i\omega_0)\Pi_{12}{}^{ml}(\omega_0)=\left(1+\frac{2iB}{E}\right)\mathrm{th}\,\frac{E}{2T},$$

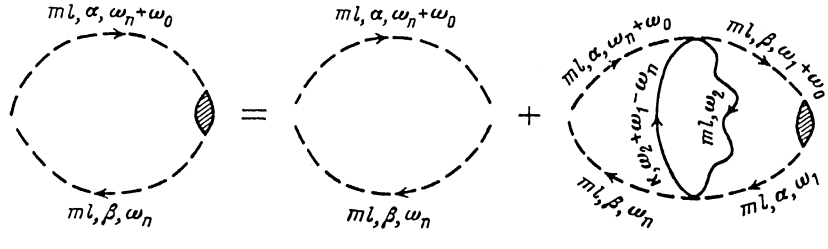

FIG. 6. Diagram equation for the vertex part of the two-particle Green's function $\Lambda^{ml}_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$, as determined in the local-pair superconductivity model.

$$\Pi_{\alpha\beta}{}^{ml}(\omega_0) = \lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z_{ml}} T\sum_{\omega_n}\Lambda_{\alpha\beta}{}^{ml}(\omega_n, \omega_n+\omega_0), \qquad (18)$$

$$B = 4\pi\rho q^2 f([(\mu^*)^2+\Delta^2]^{1/2})[1-f([(\mu^*)^2+\Delta^2]^{1/2})],$$

$$Z_{ml} = \sum_{\alpha}\exp\left(\frac{\varepsilon_{ml\alpha}}{T}\right).$$

Equations (18) are of the same form as Eqs. (9). Consequently, expression (11), with A replaced by B, holds for the mean square displacement in this case. If, on the other hand, both of the mechanisms which we are considering here are operating in the ion dynamics, then $\langle x^2\rangle$ should be calculated from (11) with A replaced by $A+B$.

Figure 7 shows the temperature dependence of $\langle x^2\rangle a_0^2$ found from (11) (with A replaced by B) for various values of the parameters $\pi\rho q^2/E$, W_2/W_1, $2\mu/W_1 z$, and E/T_c [the average values of n and α, which appear in the expression for B, were found from self-consistent equations (13)]. It follows from Fig. 7 that the greatest increase in $\langle x^2\rangle$ in the superconducting phase occurs for negative values of μ and those values of the matrix elements W_2/W_1 which correspond to the maximum value of the ratio $2\Delta_0/T_c$. As a result, there is a sharper decrease in the function B in the superconducting phase. Comparison of Figs. 4 and 7 reveals precisely the opposite behavior of $\langle x^2\rangle$ during screening of the noncentral ions by s electrons and local pairs of p_z holes in the normal phase. The reason is that the density of local pairs at an O^{2-} ion in the normal phase according to (13) depends strongly on the temperature (it decreases for $\mu>0$ and increases for $\mu<0$ with decreasing temperature). It passes this complicated behavior on to the function B in (18). A general trend which follows from Figs. 4 and 7 is the effect of screening of the ions and, correspondingly, an increase in $\langle x^2\rangle$ in the superconducting phase as the ratio of the tunneling energy to the transition temperature, E/T_c, increases.

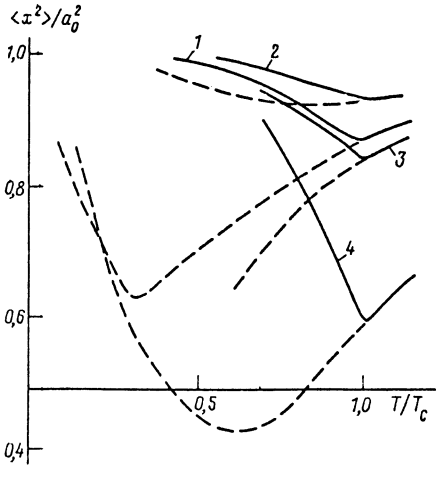

FIG. 7. Temperature dependence of the mean square displacement of a noncentral ion according to the local-pair superconductivity model with $\pi\rho q^2/E = 0.75$. *1*—$E/T_c = 1.0$, $2\mu/w_1 z = -2$, $w_2/w_1 = 4$; *2*—$E/T_c = 1.0, 2\mu/w_1 z = 1, w_2/w_1 = 4$; *3*—$E/T_c = 1.0, 2\mu/w_1 z = -2$, $w_2/w_1 = 12$; *4*—$E/T_c = 2.0$, $2\mu/w_1 z = -2$, $w_2/w_1 = 4$. The dashed lines for $T<T_c$ show the course of the curves when superconducting correlations are ignored.

CONCLUSION

The calculations above, which confirm the trend which follows from the symmetry properties of the Coulomb interaction of conduction electrons and ions—i.e., the tendency of the superconducting correlations to weaken the screening effect and to soften the vibrations of noncentral ions, depending on the nature of these correlations—have made it possible to identify the basic properties which "control" the dynamics of the noncentral ions in both the normal and superconducting phases. These properties are the ratio E/T_c, of the energy associated with the tunneling of an ion, on the one hand, to the superconducting transition temperature, on the other, and the energy of the localized p_z states, reckoned from the Fermi level (μ). These properties can be determined experimentally, along with the temperature dependence of $\langle x^2\rangle$. Expression (11), which is a simple expression, containing only algebraic functions, may prove convenient for analyzing experimental results when these properties are found experimentally. This expression may therefore be convenient for testing the superconductivity mechanism proposed here.

I wish to thank E. V. Makarov for useful consultations regarding the dynamics of ions in metal oxides.

APPENDIX

Barnes and Zitkova-Wilcox[15] have analyzed in detail the solution of integral equations for the vertex parts of two-particle functions of localized spins in the pseudofermion representation. In the present paper, we have adhered precisely to that previous paper in the summation over frequencies. Since we do not have room to reproduce here all the mathematics involved in the summation in system (8), we will simply demonstrate a typical sequence of events. As an example we consider the following term in (8):

$$\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z}T^3\sum_{\omega_n\omega_1\omega_2}\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}_1\mathbf{k}_1'}Y_{\mathbf{k}\mathbf{k}'}Y_{\mathbf{k}_1'\mathbf{k}_1}[G_{\mathbf{k}'\mathbf{k}_1}(\omega_2)G_{\mathbf{k}_1'\mathbf{k}}(\omega_2+\omega_n-\omega_1)$$
$$-F_{\mathbf{k}'\mathbf{k}_1'}(\omega_2)F_{\mathbf{k}_1\mathbf{k}}(\omega_2+\omega_n-\omega_1)]D_i\omega_n)\Lambda_{\alpha\beta}(\omega_1,\omega_1+\omega_0)$$
$$=T\sum_{\omega_n}\sum_{\mathbf{k}\mathbf{k}'}\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z}\sum_{\gamma\delta}\frac{\gamma\delta R_\gamma' R_\delta}{4\mu_{\mathbf{k}}\mu_{\mathbf{k}'}}[f(-\lambda+\varepsilon_i+\mu_{\mathbf{k}}\delta+i\omega_n)$$
$$-f(\gamma\mu_{\mathbf{k}'})]\frac{f(\lambda-\varepsilon_i)-f(\mu_{\mathbf{k}}\delta)}{\lambda-\varepsilon_i+\gamma\mu_{\mathbf{k}'}-\mu_{\mathbf{k}}\delta-i\omega_n}\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)$$
$$=\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z}T\sum_{\omega_n}\sum_{\mathbf{k}\mathbf{k}'}\sum_{\gamma\delta}\frac{\gamma\delta R_\gamma' R_\delta}{4\mu_{\mathbf{k}}\mu_{\mathbf{k}'}}[f(\lambda-\varepsilon_i)-f(\mu_{\mathbf{k}}\delta)]$$
$$\times[f(-\lambda+\varepsilon_i+\mu_{\mathbf{k}}\delta+i\omega_n)$$
$$-f(\gamma\mu_{\mathbf{k}'})]\left[\frac{1}{\lambda-\varepsilon_\alpha-i\omega_n-i\omega_0}-\frac{1}{\lambda-\varepsilon_i+\gamma\mu_{\mathbf{k}'}-\mu_{\mathbf{k}}\delta-i\omega_n}\right]$$
$$\times\frac{D_\beta(\omega_n)\Gamma_{\alpha\beta}}{\varepsilon_\alpha-\varepsilon_i+\gamma\mu_{\mathbf{k}'}-\mu_{\mathbf{k}}\delta+i\omega_0}$$
$$=\sum_{\mathbf{k}\mathbf{k}'}\sum_{\gamma\delta}\frac{\gamma\delta}{4\mu_{\mathbf{k}}\mu_{\mathbf{k}'}}\frac{R_\gamma' R_\delta f(\mu_{\mathbf{k}}\delta)[1-f(\gamma\mu_{\mathbf{k}'})]}{\varepsilon_\alpha-\varepsilon_i+\gamma\mu_{\mathbf{k}'}-\mu_{\mathbf{k}}\delta+i\omega_0}$$
$$\times\left[T\sum_{\omega_n}\lim_{\lambda\to\infty}\frac{e^{\beta\lambda}}{Z}\Lambda_{\alpha\beta}(\omega_n,\omega_n+\omega_0)\right.$$

$$-\frac{\exp[\beta(\varepsilon_i-\gamma\mu_{k'}+\mu_k\delta)]-\exp(\beta\varepsilon_\beta)}{(\varepsilon_\beta-\varepsilon_i+\gamma\mu_{k'}-\mu_k\delta)Z}\Gamma_{\alpha\beta}\Bigg]. \tag{A1}$$

Here δ and γ take on the values ± 1. In (A1) we have used the following notation:

$$\Lambda_{\alpha\beta}(\omega_n, \omega_n+\omega_0)=D_\alpha(\omega_n+\omega_0)D_\beta(\omega_n)\Gamma_{\alpha\beta},$$
$$\mu_k=(\varepsilon_k{}^2+\Delta^2)^{1/2},$$
$$R_\gamma' R_\delta=Y_{kk'}Y_{k'k}(\varepsilon_{k'}+\gamma\mu_{k'})(\varepsilon_k+\mu_k\delta)-Y_{kk'}Y_{-k,-k'}\Delta^2,$$

where $Y_{kk'}$, $=M_{kk'}$, or $N_{kk'}$, and $f(y)$ is the Fermi function. After analytic continuation of the frequency ω_0 to the real axis, $i\omega_0\to\omega+i0$, and after the relation $(y+i0)^{-1}=p/y-i\pi\delta(y)$ is used, we can carry out the summation over the vectors $\mathbf{k}$ and $\mathbf{k}'$ (Ref. 4). After we go through some analogous steps with all the compounds in Eq. (8), the latter could be written in the form of a system of equations (9).

[1)]Another important reason for the selection of these particular sites of copper and oxygen ions for the analysis of the dynamics of noncentral ions is the direct correlation between the increase in the frequencies of completely symmetric Ag vibrations of (0 4) sites and the increase in T_c in several high T_c superconductors with the 1-2-3 lattice.[10]

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