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TWO-COMPONENT ALLOY MODEL FOR BISMUTHATE CERAMICS

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The disordered binary substitutional $A_{1-x}B_x$ alloy model has been proposed for the description of the normal and superconducting properties of bismuthate ceramics Ba(Pb,Bi)O_3. The Eliashberg-type equations for the strong coupling superconductivity in strongly disordered alloys have been used to describe the superconducting properties. The relevant configurational averaging has been performed in the framework of CPA. The concentration dependence of electron–phonon coupling constant $\lambda(x)$ and transition temperature $T_c(x)$ has been calculated.

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$BaPb_{1-x}Bi_xO_3$ (BPB), the solid solution of perovskite-like oxides $BaPbO_3$ and $BaBiO_3$ belongs to the same group as the new high-T_c oxide superconductors.[1–7] In spite a lot of efforts,[5–10] the main properties of BPB, namely moderately high-temperature superconductivity in the composition range $0.05 \leq x \leq 0.3$ ($T_c = 13$ K at $x = 0.25$) as well as a metal–semiconductor transition at $x = 0.35$ are not well understood yet. Quite recently[11] the new family of quaternary intermetallic $LnNi_2B_2C$ compounds has been shown to display superconductivity with $T_c = 16.6$ K for $LuNi_2B_2C$, which, besides that studies of their physical properties are still in the early stages, suggest that electron–phonon coupling is responsible for the superconductivity.

The natural question arise how to describe these kinds of moderately high-temperature superconductivity on the basis of microscopic electron–phonon model (c.f. Ref. 12)

The most important feature of BPB is that the carrier density is more than one order of magnitude smaller (2×10^{21} cm^{-3}) than those for usual metal or for intermetallic alloy superconductors, and that, nonetheless, T_c is relatively high. Such a low-carrier density makes the system interesting from general point of view, because of its compatibility with $Ba_{1-x}K_xBiO_3$ suggests the same type of superconducting mechanism. Furthermore, several interesting properties of BPB thin films relevant to device applications have been observed. For example, a highly sensitive optical detector using $Ba_{0.7}Bi_{0.3}O_3$ thin film has been described.[13] Optical

signals create quasiparticles and induce changes in the superconducting energy gap. These changes are measured by tunnel junctions which are formed along the grain boundaries in the BPB polycristalline thin film. Consequently, this BPB detector is well suited in infrared spectrometer and optical-communications systems applications.

The BPB system has been studied intensively during recent decade.[14–16] The important step was the formulation of charge disproportionation model(CDM).[17,18] It was suggested that when x becomes small in the k-space, BCS pairing occurs instead of real space pairing. This ionic model also presumed the distortion of the breathing-type which would discriminate neighboring Bi sites (Pb sites) and lead to a charge disproportionation into Bi^{3+}–Bi^{5+} ionic states. There are experimental problems in measuring the disproportionality of charges.[8,9] Nevertheless, from the valence concept point of view,[19] CD model are quite well posed. Furthermore, for $BaBiO_3$ the relatively clear evidence for two different octahedral sites have been observed.[8] The band structure calculations[14,15] and the photoemission[9] and optical measurements not well corresponds each other. However, the isotope effect[6,7] was found to be large, indicating that phonons participate in the formation of pairs. Quite recently the metal–insulator transition in bismuthates has been studied[4] within a Holstein molecular model and the previous speculative approach[5] to metal–semiconductor transition in BPB was substantially refined.

The aim of the present paper is to develop a self-consistent microscopic theory of the superconductivity in bismuthates with a proper explicit treatment of the electron–phonon and Coulomb interactions within a relatively simple workable model. This model is based on our detailed studies of the microscopic description of the electron–phonon interaction in strongly disordered binary substitutional alloys[20] and the derivation of the self-consistent equations of the superconductivity for such a system.[21]

The main assumption is that the solid solution BPB is, in certain sense, the disordered binary substitution alloy $A_{1-x}B_x$, where the octahedron $PbO_6(PbO_3)$ is assigned to the A atom ("pseudoatom") and $BiO_6(BiO_3)$ to the B atom (c.f. Ref. 22). Let us write the total Hamiltonian of our disordered binary alloy model for a given configuration of atoms in an alloy as

$$H = H_e + H_{e-i} + H_i \tag{1}$$

The first term is the electronic part of the Hamiltonian given by

$$H_e = \sum_{i\sigma} \epsilon_i n_{i\sigma} + \frac{1}{2} \sum_{i\sigma} U_i n_{i\sigma} n_{i-\sigma} + \sum_{ij\sigma}{}' t_{ij} a^+_{i\sigma} a_{j\sigma} \,. \tag{2}$$

where $n_{i\sigma} = a^+_{i\sigma} a_{i\sigma}$ and $a^+_{i\sigma}(a_{i\sigma})$ creates (annihilates) the conduction electron in Wannier state $|i\rangle$ with spin σ. The t_{ij} are the intersite hopping terms and ϵ_i and U_i are the random "energy levels" and intrasite Coulomb integral, respectively.

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These random quantities taking on the values $\epsilon_{A(B)}$ and $U_{A(B)}$ depending on the type of atoms occupying site i. This part of the total Hamiltonian is called the random Hubbard model.[23] There are plenty of implicit experimental evidences, especially from neutron scattering, that the octahedrons A and B have different z-size. This fact justify the present model picture.

The electron–phonon interaction term H_{e-i} is written in the spirit of the Modified Tight-Binding Approximation(MTBA).[24,25]

$$H_{e-i} = \sum_{ij} \sum_{\alpha\sigma} T_{ij}^{\alpha}(u_i^{\alpha} - u_j^{\alpha}) a_{i\sigma}^{+} a_{j\sigma} \,, \tag{3}$$

where u_i^{α} is the αth component of the displacement of an ion at ith site and the T_{ij}^{α} are given by[20,21]

$$T_{ij}^{\alpha} = \frac{q_0^i + q_0^j}{2} t_{ij} \frac{R_j^{\alpha} - R_i^{\alpha}}{|\mathbf{R}_j - \mathbf{R}_i|} \,. \tag{4}$$

The Slater coefficient q_0^i describes an exponential $\exp(-q_0^i r)$ decrease of the tight-binding electron wave functions. It takes on the value $q^{A}(q^{B})$ when the atom at site i is of A(B) type. Here the distance $\mathbf{R}_j - \mathbf{R}_i = \mathbf{R}_{ji}$ is the relative position vector of two ions at sites i and j.

The last term of the Hamiltonian, H_i represents the ion subsystem and in the harmonic approximation we use here has the form

$$H_i = \sum_n \frac{P_n^2}{2M_n} + \frac{1}{2} \sum_{nm} \sum_{\alpha\beta} u_n^{\alpha} \Phi_{nm}^{\alpha\beta} u_m^{\beta} \,. \tag{5}$$

The dynamical matrix $\Phi_{nm}^{\alpha\beta}$ is in general a random quantity too. This disordered binary alloy model describes the physical situation in bismuthates quite analogous to the two-sublattice Néel model in high-T_c copper layered oxides. The CDW vacuum in BPB plays the same role as antiferromagnetic vacuum in two-dimensional plains in copper oxides. By introducing our two component alloy model (1) for BPB we make the same type an approximation for the true vacuum as we did when replace the true vacuum in CuO_2 planes by classical Néel vacuum.

The relatively high transition temperature of BPB makes one think that a strong coupling theory of superconductivity is appropriate for the case. The microscopic self-consistent theory for strong coupling superconductivity in strongly disordered transition metal alloys has been developed by us[21] on the basis MTBA electron–phonon Hamiltonian.[20] This Eliashberg-type theory gives a system of integral equations which solutions yields T_c. It enables us to investigate the electronic and lattice properties of the system in both normal and superconducting states. This subject is too extended to be discussed as a whole in the present context. We write down here the final expression for Eliashberg-type electron–phonon spectral function[21]

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$$\overline{\alpha^2(\omega)F(\omega)} = 2\sum_{\alpha}\bar{t}^2\frac{a_\alpha^2}{a^2}\Big\{x^2q_{\mathrm{A}}^2N_{\mathrm{A}}^2(E_{\mathrm{F}})\Big[-\frac{1}{\pi}\mathrm{Im}\,D_{\mathrm{A}}^{\alpha}(\omega+i\delta)\Big] + \frac{1}{4}xy(q_{\mathrm{A}}+q_{\mathrm{B}})^2N_{\mathrm{A}}(E_{\mathrm{F}})N_{\mathrm{B}}(E_{\mathrm{F}}) + \Big[-\frac{1}{\pi}\mathrm{Im}\,D_{\mathrm{A}}^{\alpha}(\omega+i\delta) - \frac{1}{\pi}\mathrm{Im}\,D_{\mathrm{B}}^{\alpha}(\omega+i\delta)\Big] + y^2q_{\mathrm{B}}^2N_{\mathrm{B}}^2(E_{\mathrm{F}})\Big[-\frac{1}{\pi}\mathrm{Im}\,D_{\mathrm{B}}^{\alpha}(\omega+i\delta)\Big]\Big\}\frac{1}{N(E_{\mathrm{F}})}, \tag{6}$$

$$N(E_{\mathrm{F}})U_{\mathrm{eff}} = \left\langle\frac{U_iN_i^2(E_{\mathrm{F}})}{N(E_{\mathrm{F}})}\right\rangle,$$

where $N_i(E_{\mathrm{F}})$ and $N(E_{\mathrm{F}})$ denote, respectively, the partially and totally averaged electron densities of states at the Fermi level. The configurational averaging procedure in (6) has been performed in the coherent potential approximation (CPA) (c.f. Ref. 3). Using this expression for the present disordered binary alloy model of BPB (1) we can write down the analytical expressions for the explicit concentration dependence of the electron–phonon coupling constant

$$\lambda(x) = \sum_{\alpha}\bar{t}^2\frac{a_\alpha^2}{a^2}\Big\{xN_{\mathrm{A}}(E_{\mathrm{F}})\bar{D}_A^{\alpha}\Big[xN_{\mathrm{A}}(E_{\mathrm{F}}) + \frac{1}{4}(1-x)N_{\mathrm{B}}(E_{\mathrm{F}})\Big] + (1-x)N_{\mathrm{B}}(E_{\mathrm{F}})\bar{D}_{\mathrm{B}}^{\alpha}\Big[(1-x)N_{\mathrm{B}}(E_{\mathrm{F}}) + \frac{1}{4}xN_{\mathrm{A}}(E_{\mathrm{F}})\Big]\Big\}\frac{1}{N(E_{\mathrm{F}})} \tag{7}$$

and the Coulomb pseudopotential

$$\mu = N(E_{\mathrm{F}})U_{\mathrm{eff}}\left(1 + N(E_{\mathrm{F}})U_{\mathrm{eff}}\ln\frac{W}{\Theta}\right)^{-1}, \tag{8}$$

where $\bar{D}$ is the conditionally averaged phonon Green Function[21] and W is the alloy band-width, $\bar{t}$ is the averaged nearest neighbor hopping integral, a is the distance between neighboring atoms and Θ is of the order of the Debye temperature of an alloy. The main sense of Eqs. (6) and (7) is that the true interaction between electrons, that leads to the Cooper pairing in BPB is real electron–phonon interaction which in the strong-coupling theory is represented by a complex, frequency dependent Eliashberg-type interaction. In all the numerical expressions to follow, expression (7) for $\lambda(x)$ has been used in conjunction with well known set of formulae for T_c of the strong-coupling theories.[26] The fitting was done with the typical values of parameters in the following intervals: the Debye temperature $\Theta \sim 170$–220 K; the density of states $N(E_{\mathrm{F}}) \sim 0.1$ eV; the band-width W $\sim 3-5$ eV and the Coulomb pseudopotential $\mu(x \leq 0.25) \sim 0.11-0.13$.

Before proceeding, it should be mentioned that the Eliashberg strong coupling approach introduces the very important notion, namely the electron–phonon spectral function (EPSF)[25] (in the present theory (6)). The physical meaning of the

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EPSF is that it counts at fixed frequency Ω, how many phonons with $\omega(q) = \Omega$ are there, and weight each phonon by the strength and number of electron transition from $\mathbf{k}$ to $\mathbf{k}+\mathbf{q}$ across the Fermi surface which this phonon can participate in. It was argued earlier,[27] on the basis of qualitative arguments, that the breathing mode cannot contribute to the electron–phonon coupling constant λ, because the Fermi surface, as author believe, for $x \leq 0.35$ is not large enough to allow the wave vector of the breathing mode to connect any pair of points on the Fermi surface. Our point is that the final answer can be obtained on the basis Eliashberg-type approach only. The expression (6) show how complicated is the reconstructed EPSP in disordered binary alloy in comparison with the one component sample. Since the honest numerical computations of the EPSF even for pure transition metals[25] are very complicated, perhaps it is instructive to look again at the physics involved. Let us consider the possibility to operate with one "relevant" mode. It is rather crude approximation to ignore the whole phonon spectrum and consider only a single relevant or "vital" phonon mode which sesms to provide an essential contribution to the superconductivity. Nonetheless, in the light of very detailed microscopic description of the electron and phonon subsystems within alloy model, the single-mode strong coupling theory seems to be workable to some extend. At present it is not definitively clear which phonon mode plays a vital role. It is thus theoretically logical to fit the relevant frequency. The suitable candidates are:

(i) the so-called "tilting" mode attributed to rotational vibration of the oxygen octahedra;
(ii) modes which are connected with ferroelectric displacement of Pb, Bi atoms;
(iii) breathing mode displacements of O atoms.

The comparison of the theory and experiments is made difficult by the fact that the neutron and optical experiments not fully agree and are incomplete. Thus, there seems to be a severe contradiction between the estimations of "vital" phonon mode in the temperature range 60 – 600 K. In the approach used in the present paper, on the practical grounds we can suppose that the relevant phonon mode Ω

$$\operatorname{Im} D(\omega + i\delta) \sim \delta(\omega - \Omega) \tag{9}$$

must be about a Debye frequency: $\Omega \sim 150 - 300$ K. This mode very probable should be the breathing-type. The Fig. 1 shows the results of our numerical estimations. The solid line is calculated T_c versus concentration x and the dashed line is the calculated electron–phonon coupling parameter. The estimations were done for $x \leq 0.25 - 0.3$. For higher concentrations there are reason to believe that the Coulomb interaction increases rapidly. Such an increasing most likely leads to the appearance of the Mott–Hubbard gap(c.f. Ref. 4) and to the drastical increasing of the Coulomb pseudopotential μ. Thus, the superconductivity in this region will disappear rapidly. This kind of behaviour need a more refined theory within our model (1) to go beyond the Hartree–Fock approximation for the Coulomb term we used here.

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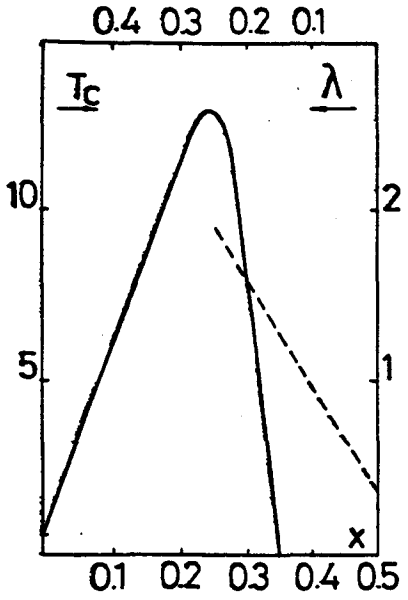

Fig. 1. Numerical results for the concentration dependence of the superconducting temperature T_c and electron–phonon mass enhancement coefficient λ

In summary, the qualitative and partly quantitative workable microscopic theory of strong-coupling superconductivity in BPB ceramics has been proposed. The analysis is based on the Hamiltonian explicitly exhibiting short-range Coulomb repulsion and electron–phonon interaction in alloy. The last point is rather remarkable and is the main advantages of the approach we suggest. We believe that it bear the real physics of BPB ceramics. The chemical theoretical arguments[19] support the clever idea of disproportionalization.[28] The main objections to this idea is that experimentally, say in neutron scattering,[8] we do not obtain the ultimate evidence for clear (3^+)–(5^+) disproportionalization. Nevertheless, the careful analysis of the experimental technique show why it is "masked" and the fate of this instructive idea should not depend ultimately on experimental finding, at least at the present time. To summarize, the results presented here confirm the fact that it is possible to construct realistic workable electron–phonon microscopic model within modified tight-binding approximation. It is shown that the EPSF in two component alloy model of the "pseudoatoms" of different sizes is modified strongly. By suitable choice of fitting parameters it is possible to describe the concentration dependence of T_c in the superconducting region. We believe that the approach we suggest gives some real insight into better understanding of the properties of BPB and the similar type of substances. Clearly, more work is required for both theory and experiment on these materials with moderately high-T_c to clarify ultimately the microscopic model of superconductivity.

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