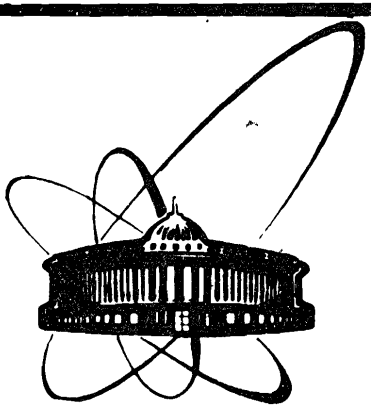

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DISORDERED BINARY ALLOY MODEL FOR OXIDIC SUPERCONDUCTOR $Ba(Pb,Bi)\ O_3$

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$BaPb_{1-x}Bi_xO_3$ (BPB), the solid solution of Perovskite-type oxides $BaPbO_3$ and $BaBiO_3$ [1], belonges to the same group as the new high-temperature metallic oxidic superconductors. Today it is obsolete to say about "exotic" superconductivity [2] in this material. Nevertheless, the main properties of BPB, namely relatively high-temperature superconductivity in the composition range $0.05 \leq x \leq 0.3$ ($T_c \sim 13K$ at $x \sim 0.25$) as well as a metal-semiconductor transition at $x \sim 0.35$ are not explained yet. In the very recent paper [3] the authors claim that neither this value T_c nor the normal state properties of BPB have been understood on the basis of a band model plus an electron-phonon interaction. Rice and Sneddon have proposed interesting charge disproportionation model [2]. It is suggested that when x becomes small the k-space (BCS) pairing occurs instead of the real space pairing. This ionic model also presumed the distortions of the breathing-type which would discriminate neighbouring Bi sites (Pb sites) and lead to a charge disproportionation into Bi^{3+} -Bi^{5+} ionic states. In paper [4] the qualitative arguments have been given why the breathing mode cannot contribute to the electron-phonon coupling constant λ because the Fermi surface for $x < 0.35$ is not large enough to allow the wave vector of the breathing mode to connect any pair of points on the Fermi surface. It seems likely that the neutron [5] as well as optical [6] experimental studies do not confirm the disproportionation model. The optical data [6] contradict the Mattheiss-Hamann band calculations carried out for BPB. The situation is ambiguous also due to recent APW band structure calculations performed for BPB in [7] where the Mattheiss-Hamann results have been criticized too. The most recent attempts [8,9] to reinforce the Rice-Sheddon model [2] have not been successful [7]. Another very speculative approach to explain the metal-semiconductor transition in BPB has been proposed in paper [10], however, without considering the superconducting properties. Thus at present the situation is rather obscure.

The aim of the present paper is to develop a self-consistent microscopic theory of the superconductivity in BPB alloy series with a proper explicit treatment of the electron-phonon and Coulomb interactions within a relatively simple and

realistic disordered binary alloy model. Let us assume that the solid solution $BaPb_{1-x}Bi_xO_3$ 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. Let us write the total Hamiltonian of our model for a given configuration of atoms in an alloy as

$$H = H_e + H_{e-i} + H_i .$$

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

$$H_e = \sum_{i\sigma} \epsilon_i n_{i\sigma} + 1/2 \sum_{i\sigma} U_i n_{i\sigma} n_{i-\sigma} + \sum'_{ij\sigma} t_{ij} a^+_{i\sigma} a_{j\sigma} . \qquad (1)$$

Here $n_{i\sigma} = a^+_{i\sigma} a_{i\sigma}$ and $a^+_{i\sigma}$ ($a_{i\sigma}$) creates (annihilates) the conduction electron in Wannier state $|i>$ with spin σ. The t_{ij} are the intersite hopping matrix elements and ϵ_i and U_i are the random "energy levels" and intrasite Coulomb integral, respectively. These random quantities taking on the values ϵ_A, ϵ_B and U_A, U_B depending on the type of atoms occupying site i. The electron-phonon interaction Hamiltonian is written (see /11/ for definitions)

$$H_{e-i} = \sum_{ij} \sum_{\alpha\sigma} T^{\alpha}_{ij} (u^{\alpha}_i - u^{\alpha}_j) a^+_{i\sigma} a_{j\sigma} . \qquad (2)$$

Here u^{α}_i is the α-th component of the displacement of an ion at the i-th site. The last part of the Hamiltonian represents the ion subsystem and in the harmonic approximation we use here is given by

$$H_i = \sum_n \frac{P_n^2}{2M_n} + 1/2 \sum_{nm} \sum_{\alpha\beta} u^{\alpha}_n \Phi^{\alpha\beta}_{nm} u^{\beta}_m . \qquad (3)$$

The dynamical matrix $\Phi^{\alpha\beta}_{nm}$ is in general a random quantity too. In this paper we assume for simplicity that the spin effects play no role, and hence $<a^+_{i\sigma} a_{i\sigma}> = n_i$.

The relatively high transition temperature of BPB makes one think that a strong coupling theory of superconductivity is useful for such a case. Eliashberg's theory gives an integral equation whose solution yields T_c. It enables us to investigate the electronic and lattice properties of the system in both the normal and superconducting states. The micro-

scopic self-consistent theory for strong coupling superconductivity in disordered transition metal alloys has been developed in paper /12/. The configurational averaging procedure in /12/ has been performed in the coherent potential approximation (CPA). Using this theory for the present disordered binary alloy model of BPB we can write down the analytical expressions for the explicit concentration dependence of the electron-phonon coupling constant

$$\lambda(x) = \sum_{\alpha} \bar{t}^2 \frac{a^2_{\alpha}}{a^2} \{ x \Re_A(E_f) \tilde{D}^{\alpha}_A [x \Re_A(E_f) + \tfrac{1}{4}(1-x) \Re_B(E_f)] + \qquad (4)$$

$$+ (1-x) \Re_B(E_f) \tilde{D}^{\alpha}_B [(1-x) \Re_B(E_f) + \tfrac{1}{4} x \Re_A(E_f)] \} / \Re(E_f)$$

and the Coulomb pseudopotential

$$\mu = \Re(E_f) U_{eff} [1 + \Re(E_f) U_{eff} \ln \frac{w}{\theta}]^{-1} . \qquad (5)$$

In the above formulae $\Re_A$, $\Re_B$, $\Re$ mean the partial and total densities of states on the Fermi level Ef, θ is of the order of the Debye temperature of an alloy, w is the alloy band width, $\bar{t}$ is the averaged nearest neighbour hopping integral, a is the distance between neighbouring atoms and $\tilde{D}^{\alpha}_i$ is

$$\tilde{D}^{\alpha}_i = -\frac{2}{\pi} \int d\omega \frac{\mathrm{Im}\, D^{\alpha}_i(\omega + i\epsilon)}{\omega} , \qquad i = A, B .$$

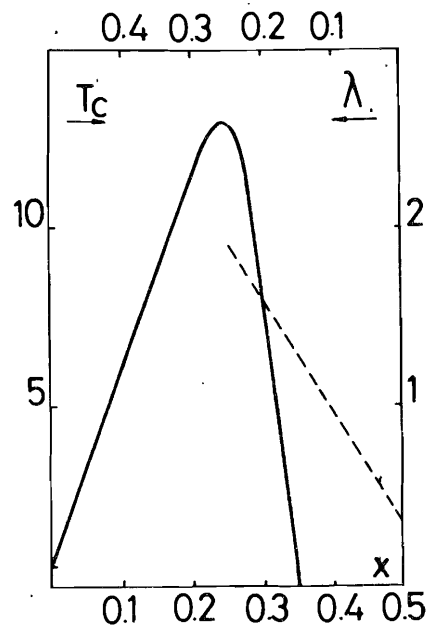
Here $D_{A(B)}(\omega)$ means conditionally averaged phonon Green function /12/. Contrary to the theory which has been developed in paper /13/, in our self-consistent approach the electron-phonon and Coulomb interactions have been taken into account explicitly. The Yoshioka-Fukuyama attractive Hubbard interaction /13/ does not constitute a truly correct starting point for a theory of superconductivity in BPB. The true interaction between electrons, that leads to the Cooper-pair instability, is the real electron-phonon interaction which in the strong coupling theory is represented by a complex, frequency-dependent Eliashberg interaction. The attempts to mimic this interaction by an attractive Hubbard interaction may be reasonable, if any, for the weak-coupling (BCS) case.

In all the numerical estimations to follow, expression (4) for λ has been used in conjunction with famous formulae for T_c of the strong-coupling theories /14/. The typical values of the parameters we use here are: the Debye temperature $\theta \sim 170 \div$

$\div$ 200K; the density of states $\mathcal{N}(E_f) \sim 0.1$ eV^{-1}; the site energy difference $\delta_o = \epsilon_A - \epsilon_B = 0.1 \div 0.9$ eV; the bandwidth $w \sim 4$ eV and the Coulomb pseudopotential $\mu\,(x \lesssim 0.25) \sim 0.11 \div 0.12$. Before proceeding, it should be mentioned that the Eliashberg strong coupling theory introduces the very important, electron-phonon spectral function. The meaning of the electron-phonon spectral function is that it counts at fixed frequency Ω, how many phonons with $\omega(q) = \Omega$ are there, and weights each phonon by the strength and number of electron transitions from $\vec{k}$ to $\vec{k} + \vec{q}$ across the Fermi surface which this phonon can participate in. It is rather crude approximation to ignore the whole phonon spectrum and consider only a single "relevant" or "vital" phonon mode which seems to provide an essential contribution to the superconductivity. Nonetheless, in the light of paper [15] the single-mode strong-coupling theory seems to be quite workable. The reason why such a theory can work for BPB is that the system has an unusually high transition temperature and that it indicates that the optical phonon contributions to λ lead to such a substantially increasing T_c. At present it is unclear which phonon mode definitely plays a vital role. Furthermore, we have no definite experimental information on crystal structure yet [16]. It is thus theoretically logical to fit the relevant frequency. The suitable candidates are: 1) the so-called "tilting" mode attributed to rotational vibration of the oxygen octahedra; 2) modes which are connected with ferroelectric displacements of Pb, Bi atoms; 3) breathing mode displacements of O atoms. The comparison of the theory with experiments is made difficult by the fact that the neutron [17] and optical [6, 10] experiments give contradictory results. Thus, there seems to be a severe contradiction between the estimations of "vital" phonon mode in literature [2,4,7-10,13,18,19] in the temperature range 60$\div$600K. In the approach used in the present paper, on intuitive grounds we can suppose that the relevant phonon mode

$$\mathrm{Im}\, D(\omega + i\epsilon) \sim \delta(\omega - \Omega)$$

must be about a Debye frequency $\Omega \lesssim 150 \div 250$K. The figure shows the results of numerical calculations. The solid line is calculated T_c versus concentration x and the dashed line is the calculated electron-phonon coupling parameter. It is worth emphasizing that the calculations were done for $x \lesssim 0.25$. For $x > 0.25$ there are reasons to believe the Coulomb interaction rapidly increases. Such an increasing most likely leads to the appearance of the Mott-Hubbard gap and drastic increasing of the Coulomb pseudopotential μ. Thus, the superconductivity in this region rapidly disappears. This kind of behaviour need a more refined theory beyond the Hartree-Fock approximation for the Coulomb term.



In summary, the qualitative and partly quantitative microscopic theory of the strong-coupling superconductivity in BPB has been presented. The analysis is based on a Hamiltonian explicitly exhibiting short-range Coulomb repulsion and electron-phonon interaction. It should be exphasized that this theory is far from exact. The literal application of this theory to BPB can be questioned on many grounds. Nonetheless, the relatively simple description of the superconductivity in BPB suggests that a useful physical model has been overlooked. If the present analysis is reasonable it means that the electron-phonon pairing mechanism is quite reliable for BPB. This brings up the question of searching for an isotopic effect in superconducting BPB, because one of the most suggestive tests for electron-phonon coupling in conventional superconductors is the isotope effect. Taking into account the negative result of searching for the isotope effect in Y-Ba-Cu-O system [20] it will be very interesting to compare the situation for a more simple but very similar BPB system.

Next we mention the paper [21] where the determination of valence of Cu in superconducting $La_{2-x}(Sr,Ba)_xCuO_4$ system has been done. The results indicate the coexistence of Cu II and Cu III states in these compounds. This kind of behaviour would be more likely described in the framework of the present or modified [3] binary alloy model.

And lastly, before finishing it is necessary to make a remark concerning the interpretation of the normal state resistance of the BPB. Many years ago Fisk and Lawson [22] suggested that the temperature dependence of the normal state electrical resistivity could be used to categorize many compounds and elements with respect to their superconductivity. They

pointed out that most superconductors with great resistance ratio have the positive temperature coefficient of resistivity $dR/dT > 0$. Exceptions occur when the scattering is dominated by impurity of vacancies. In this cases $dR/dT < 0$ and $NbN_{0.9}$ exemplifies this behaviour. The proper treatment of the electron-phonon scattering and strong potential scattering in the binary alloy model we use here leads to the conclusion that in the system with the strong disorder the temperature coefficient of resistivity is negative [23] . Hopefully, the insights derived from such a study [23] can be extended with minor modifications to BPB system. Clearly, more work is required for both theory and experiment on this question.

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Модель неупорядоченного бинарного сплава для оксидного сверхпроводника $Ba(Pb,Bi)O_3$

Для описания металлооксидной сверхпроводящей керамики $Ba(Pb,Bi)O_3$ предложена модель бинарного сплава $A_{1-x}B_x$ с учетом сильной связи электронов и фононов. В рамках теории сильной связи Элиашберга, обобщенной для случая сплава, найдена зависимость от концентрации x параметра электрон-фононного взаимодействия $\lambda(x)$ и критической температуры $T_c(x)$.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1987

Kuzemsky A.L. E17-87-593

Disordered Binary Alloy Model for Oxidic Superconductor $Ba(Pb, Bi)O_3$

The disordered binary substitutional alloy $A_{1-x}B_x$ model has been proposed for the description of the normal and superconducting properties of $Ba(Pb,Bi)O_3$ superconducting metallic oxidic compound. The equations for strong coupling superconductivity in disordered alloys have been used. 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.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1987