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Superconducting Properties of the Family of Mercurocuprates and Role of Layered Structure

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The various phases of the homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ *were synthesized earlier using the program-controlled high pressure chamber. We observed that dependence of* $T_c(a)$, *where* a *is the in-plane lattice constant (and consequently oxygen content* δ*) have a typical bell-shaped character.* T_c *versus lattice constant has a similar bell-shaped curve for several values of* n, *with the maximum* T_c *value measured for* $n = 3$. *We have analysed this dependence (and of the formal copper valence) for different members of mercurocuprate family in terms of the phenomenological model of layered superconductors taking into account possible charge redistribution. The experimentally observed nonmonotonic bell-shaped dependence* $T_c(n)$ *was consistent with our model.*

There is considerable current interest in the properties of superconducting copper oxides. The mercurocuprate family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ is of special importance because it illustrated the fascinating features of HTSC and include the highest T_C value for the cuprates. Recently, there has been great progress in the synthesis of high quality samples.[1,2] The fabrication of the homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ has been performed using the high-pressure high-temperature synthesis which seems to be an efficient and workable method to produce high quality Hg-superconducting samples. The Hg–1223, Hg–1234, and Hg–1245 phases were synthesized using the program-controlled high pressure chamber with profiled anvil type of "konak" developed at HPPI. The temperature, pressure and oxygen content in the starting oxide mixture was found significantly affect the phase composition in the Hg–Ba–Ca–Cu–O system. By varying the oxygen content through changing the BaO/BaO_2 ratio, we obtained Hg–1223, Hg–1234, and Hg–1245 in the overdoped state. The heat treatments (nitrogen and oxygen flows) resulted in a change of T_c's from initial overdoped (118, 116,

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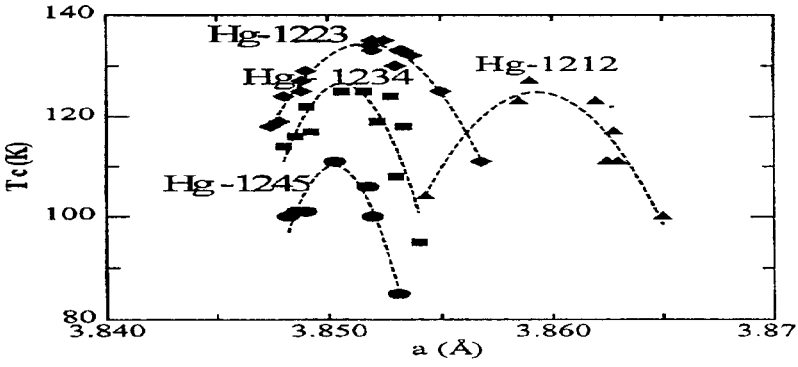

Fig. 1. Dependence of T_c on lattice distance a for $n = 2$–5.

and 100 K for Hg–1223, Hg–1234, and Hg–1245, respectively) to underdoped (102, 95, and 85 K) and, finally, to optimally-doped states (135, 125, and 111 K). The spatially of T_c vs. a-parameter (and, consequently, oxygen content) for these phases exhibit a bell-shaped behavior[1, 2] (Fig. 1).

Earlier we showed that a variation of the BaO/BaO_2 ratio in the initial oxide mixture was an important parameter, which influenced not only the extra oxygen content in the phase, but the phase formation as well.[1] For instance, the variation of x from 10.2 to 10.6 in the initial oxide mixture $HgBa_2Ca_3Cu_4O_x$ resulted in a drastic change of the phase composition of the as-prepared samples. We deduced from these experiments, that the heat treatments changed the carrier concentration from the overdoped state for the initial as-prepared compounds to underdoped phases (after treatments in nitrogen and then in oxygen) and, finally, to optimally-doped phases (after a treatment under 2000 bar oxygen pressure). Thus the doping state of mercurocuprates can be controlled by changing the oxygen content. The synthesis of $n = 1, 2, \ldots, 8$ of the Hg-based homologous series was performed by this and other techniques with $T_c = 97$ K for $n = 1$, $T_c = 127$ K for $n = 2$, $T_c = 135$ K for $n = 3$, $T_c = 126$ K for $n = 4$, $T_c = 110$–114 K for $n = 5$, $T_c = 96$–100 K for $n = 6$ and $T_c = 88$ K for $n = 7$. The concept of a homologous series,[3] which in the case of mercurocuprates play an especially important role, raise the natural question about the dependence of a superconducting critical temperature of this family of layered copper oxides from the number of pairs $(n-1)$ of CuO_2 and bare cation planes in the infinite layer block. In other words, because the members of each homologous series has the same charge-reservoir block[3] but a different number (n) of CuO_2 planes, our main interest is how T_c varies with (n). There seems to be a close relationship between the average copper valence and the phase produced in the high-pressure synthesis of mercurocuprates. This is

related with the oxidation of the CuO_2 layers. The formal copper valence for different members of mercurocuprate family is equal to $v_{Cu} = 2(n+\delta)/n$. The values of δ obtained from neutron scattering experiments lead to the conclusion that the extra oxygen content, and consequently the copper valence and lattice parameter depend on the number of CuO_2-layers and on heat treatment of the samples. Thus the correlation between the copper valence, lattice parameters and extra oxygen contents is important. In this report dependence T_c on the number n of CuO_2 planes in copper oxides is described in the framework of workable phenomenological model[4] and comparing with experimental data. The suitable phenomenological approach for calculation of T_c of layered cuprates has been proposed in Ref. 5. The physical idea was that there are distinct "active" elements in the multilayer structure. To each active element denoted l in the structure was associated a Ginsburg–Landau (GL) order-parameter field $\psi_l(r)$. Each of these $\psi_l(r)$ has some distinct "bare" transition temperature T_l^0 in that structure. We apply this line of reasoning for the mercurocuprate family. The free energy density was taken in Ref. 5 as a bilinear form in the modeled independent order parameters

$$f = \sum_i a_i(T)\,|\psi_i|^2 + \sum_{ij} v_{ij}\,|\psi_i - \psi_j|^2 \tag{1}$$

here v_{ij} is the coupling coefficient. This lead to relevant secular equation of the form

$$\|(a_i(T) + nv_{ij})\,\delta_{ij} - v_{ij}\| = 0 \tag{2}$$

According to Ref. 5, the transition temperature for an n-layer sample is determined as the maximum eigenvalue of the n-dimensional tridiagonal matrix. It is possible to consider a system composed of n identical layers, where all parameters are identical ($T_l^0 = T^0$ and $v_{ij} = v$). For this case the explicit expression[5] for T_c provides that the largest solution is $T = T^0$ and $T_c(n)$ is an increasing function of n with upper limit $T_c(n=\infty) = 141$ K. In the structural model we adopt in the present paper, a periodic layered system, whose unit cell contains two kinds (a and b) of layers ("active" elements) are considered ($1 \leqslant a \leqslant n$ and $1 \leqslant b \leqslant m$). Thus we can incorporate in our formulation the presence of two type of layers. There are a few possibilities to select inequivalent layers. It is well established that the CuO_2 layers are responsible for the superconductivity in cuprates and that the electrical properties are governed by a charge carrier density. In what follows, the layered structure of mercurocuprates is modeled by stack of n layers of type a (CuO_2-layers) and m layers of type b (charge-reservoir,

Hg–O-layers) in an elementary cell. Equation (3) is identical to the following expression

$$\det(TI - F) = 0;$$
$$F_{ij} = \left(T_i^0 - \frac{v_{i-1,\,i}}{a_i^0} - \frac{v_{i,\,i+1}}{a_i^0} \right) \delta_{ij} + \frac{v_{ij}}{a_i^0}\, \delta_{i,\,j\pm 1} \tag{3}$$

Equations (3) properly determine the critical temperature as a maximum solution $T_l^{\max}$ of this periodic $n-m$ layered system. The numerical solution of these equations with reasonable parameters show that T_c of the whole system is raised with the number n and reduced with the number m. This reflect the fact that the amplitudes of the order parameters for a-layers are larger that than those for b-layers. (It is necessary to say that present model could be refined to reduce the transition temperature of b-type layers practically to zero). The interplay of two order parameters of the two kind of active elements is one of the most important properties of the present phenomenological model. However, the model properties related to these effects do not give the observed "bell"-shaped form of $T_c(n)$. It is therefore necessary to take into account the interlayer effects of charge redistribution to fit the experimental data. It was supposed that in HTSC a charge redistribution may occur between the reservoir block and active block under various conditions like applied high pressure or with changing of composition, such as oxygen stoichiometry. The inequivalent layers model reveal essential feature arising from the sensitivity to the transition of one of the subsystems to the superconducting state so that n_h^l should rearrange when the system becomes superconducting. At the moment we do not have an effective microscopic mechanism which should explain the nature and provide amount of charge redistribution necessary for the model of Ref. 5 to account for the data. We adopt the following workable anzatz for the critical temperature T_a of an a-layer dependence on the number density of carriers of the form

$$T_a(x_c) = T_{a^0} \left(1 - \left[\frac{x_c - h_2}{h_1} \right]^2 \right)^{1/2} \tag{4}$$

where the carrier-number density x_c in a single layer is given by $x_c = x_{\text{out}}^b[cm + 2(1-c)]/(n+m)$ and x_{out}^b is the fraction of carriers which is provided by the outer b-layer adjacent to an a-layer per area while $x_{\text{in}}^b = c x_{\text{out}}^b$ $(c \leqslant 1)$ is the corresponding quantity provided by an inner b-layer. Here h_1 and h_2 are fitting parameters. To proceed further we use the following model estimations

$$T_b = \begin{cases} T_b^0(x_c/x_0), & 0 \leqslant x_c \leqslant x_0; \\ T_b^0, & x_c \geqslant x_0; \end{cases} \tag{5}$$

$$a_b^0(x_c) = \begin{cases} a_{b0} T_b^0 (x_c/x_0)^{1/2}, & 0 \leqslant x_c \leqslant x_0; \\ 2a_{b0} T_b^0 (x_0/(x_c + x_0)), & x_c \geqslant x_0; \end{cases} \tag{6}$$

Here $x_0 = m^* t_\perp / \pi h^2$ and $v = v_{ij}$ have no x_c dependence. With this simplification it is possible now to calculate the critical temperature.

We have calculated $T_c(n)$ with m fixed for $m = 1, 2, 3, 4$. The results of numerical calculations for $T_c(n)$ for $m = 3$ (Fig. 2) are shown as a broken solid line.

Thus, incorporating the charge interlayer redistribution, it is possible to restore the observable "bell"-shaped dependence even in the simplest version of the model and fit the experimental results well. This conclusion should be further established by considering the more general Lawrence–Doniach-type model for layered superconductors as well as more sophisticated description of charge redistribution. The GL and LD theories are much simpler then the microscopic theory and have a limited domain of validity. However, they give valuable insight into the general physical behavior and, moreover they give the important parameterizations of the system. In addition, for the mercurocuprates, we do not have a detailed phase diagram. This is partially related with the big difficulties of the fabrication and characterization of monophase samples. A detailed consideration of these questions as well as an extended version of our numerical calculations will be discussed elsewhere.

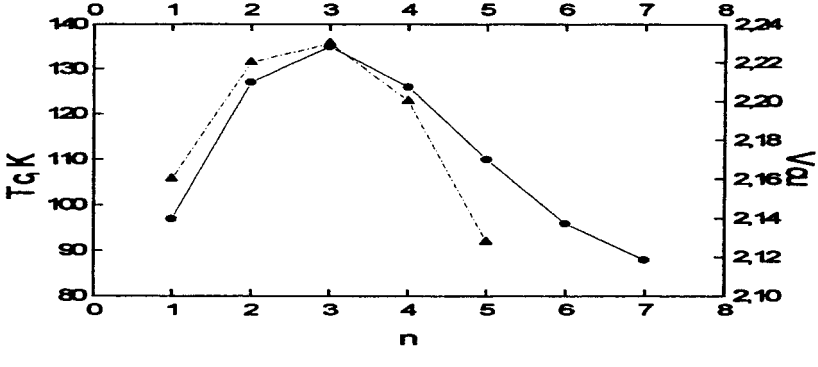

Fig. 2. Dependence of the superconducting critical temperature T_c and copper valence v_{Cu} on number of layers n. Full line is the critical temperature and dashed line is valence. Dependence of $T_c(n)$ was calculated with $m = 3$ fixed. The points are the experimental data. Parameters: $T_a^0 = 189.1$; $T_b^0 = 88.1$; $h_1 = 0.313$; $h_2 = 0.504$.

In summary, in this paper we have presented a simple phenomenological model which rationalizes reasonably the currently available experimental data for the mercurocuprate family.

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