Role of Layered Structure for Superconducting Critical Temperature of the Mercurocuprates.

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Abstract

The physics of the mercurocuprate family was studied from the crystal structure point of view. A phenomenological approach determining the critical temperatures for homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ depending of number of layers n was developed. Dependence of T_c vs. a- parameter (and consequently, oxygen content δ) have an universal "bell"-shaped character. The similar "bell"-shaped character has a number of layers dependence of $T_c(n)$ with the maximum at $T_c(n = 3)$. We have analysed dependence of a superconducting critical temperature of mercurocuprates and of the formal copper valence for different members of mercurocuprate family in terms of a phenomenological model of layered superconductors. The redistribution of charge was taken into account. This lead to observable nonmonotonic "bell"-shaped dependence of $T_c(n)$ and provides a quantitative explanation of the experiments. It was shown that the correlations between the copper valence, lattice parameters and extra oxygen contents are the essential factors in the physical behaviour and HTSC characterization of the mercurocuprates.

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РОЛЬ СЛОИСТОЙ СТРУКТУРЫ МЕРКУРОКУПРАТОВ ДЛЯ ТЕМПЕРАТУРЫ СВЕРХПРОВОДЯЩЕГО ПЕРЕХОДА.
Изучалась физика высокотемпературных ртутных сверхпроводников с точки зрения особенностей их кристаллической структуры. Рассмотрение критической температуры перехода для семейства

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$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ в зависимости от n проводилось в рамках феноменологического подхода. Зависимость T_c vs. a (и следовательно, от содержания кислорода δ) имеет универсальный колоколообразный характер. Подобный характер имеет также зависимость $T_c(n)$ с максимумом при $T_c(n = 3)$. Для объяснения этой зависимости использовалась феноменологическая модель слоистых сверхпроводников с учетом перераспределения заряда. Это позволило получить количественное согласие с наблюдаемой немонотонной колоколобразной зависимостью $T_c(n)$. Показано, что корреляция между параметрами решетки, валентностью, степенью окисления и числом слоев повидимому имеет существенное значение для температуры сверхпроводящего перехода.

1 Introduction

There is considerable current interest in the properties of superconducting copper oxides. The studies of the mercurocuprate family of high-temperature superconductors (HTSC) has been the object of special interest during last years after their discovery [1], [2]. Particular importance is the question of interrelation of crystal structure and superstructure and superconductivity and the role of anisotropy in layered superconducting cuprates. Mercurocuprates have a pronounced layered structure and have raised once again the problem of how a structure of these materials affect their properties. 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 of these layers. The homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ is of special interest because it culminates the fascinating features of HTSC and are still most high-Tc representatives of cuprates [3],[4]. One of the most important issue for mercurocuprate family is to understand the exact role of layered structure and most important parameters that govern the highest value of transition temperature of these materials. Recently, there has been great progress in synthesis of high quality samples [5]- [8] and detailed structural studies [9]- [11].
The structure of the family of mercurocuprates can be viewed [12], [13] as consistent of $Ca_{n-1}Cu_nO_{2n}$ block and the $Hg-O_\delta$ block which play a role of reservoir of charge. The fabricating of 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 the efficient and workable method to produce high quality Hg-superconducting samples [5] - [8]. The synthesis of $n = 1, 2...8$ of the Hg-based homologous series was performed by this and other techniques with Tc =97 K for $n = 1$, Tc = 127 K for $n = 2$, Tc = 135 K for $n = 3$, Tc = 126 K for $n = 4$, Tc =110-114 K for $n = 5$, Tc = 96-100 K for $n = 6$ and Tc = 88 K for $n = 7$ (see Table 1 (c.f. [8]). The experimental results on the dependence of

Table 1 .

n	1	2	3	4	5	6	7
T_c, K	97-98	127	135	125-126	110-114	96-100	88
δ	0.08	0.22	0.28-0.35	0.4(1)	0.32(2)	-	-
a, A	3.880	3.8580	3.852	3.847	3.8523(4)	3.8533	3.847-851

the critical temperature on the number of layers n presented on Fig.1. On the Fig.2 the dependence of the T_c on the lattice distance a for $n = 1-5$ members of family is presented.

The highest superconducting transition temperature at ambient pressure was observed for the third ($n = 3$) of Hg-based copper-mixed oxide series $HgBa_2Ca_2Cu_3O_{8+\delta}$(Hg-1223) with Tc (onset) at 135 K after which a saturation seemed to be reached (see Fig.1 , Fig.3). This feature of the highest Tc for $n = 3$ is analogous to that occurred in the $Tl-$ and $Bi-$based series. Unfortunately, mercurocuprates have been produced, are as a rule, not in their optimum doping state. This requires some additional treatment to achieve their highest temperature. There are an important differences between the mercurocuprates and the thallium analogues. One of the main differences is that connected with the partially occupied oxygen sites in the region between CuO_2 planes, occupancy for which in mercurocuprates is very small. Thus the doping state of mercurocuprates can be controlled by changing the excess oxygen content [14], [15]. It is also important to note that for the mercurocuprate family the unilayer, bilayer, trilayer etc. dependence of physical properties show a different behavior as regards to anisotropy (two- or three dimensional nature) [16], [17].

The concept of a homologous series [4] , which in the case of mercurocuprates play an especially important role, raise the natural question about 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 another words, because of one member of one homologous series has the same charge-reservoir block [4] but the number of CuO_2 planes (n) is different, the main interest is dependence $T_c(n)$ [18], [19].

There seems to be a close relationship between the average copper valence and the phase produced in the high-pressure synthesis of mercurocuprates [2]. This is related with the oxidation of the CuO_2 layers. According to Ref. [2] the formal copper valence for different members of mercurocuprate family is equal to $v_{Cu} = 2(n + \delta)/n$. The averaged copper valence $< v_{Cu} >$ is the tunable parameter [20] that characterizes the synthesis of different phases and favour the low member of the family for high copper valences while high members are only obtained with low average copper valence. The values of δ obtained from neutron scattering experiments lead to conclusion that the extra oxygen content, and consequently the copper valence and lattice parameter depend on the number of CuO_2-layers (Fig.3) and on heat treatment of the samples.

The $T_c(n = 1, 2)$ can be changed by reducing or oxidasing treatments, contrary to the $T_c(n = 3)$ which is not so strongly influenced by high pressure oxygen treatment. This may reflect the important fact that in $Hg - 1223$ structure, the distribution of charges between the two type of CuO_2-layers seems to be different. Such a structural specific feature which include the interplay of two "active" elements of different kind could be responsible for this behaviour. In the simplest case it could be the planes and the chains but as regards to the inequivalent CuO_2 layers in multilayer structure the inner and outer CuO_2 layers can have different charge carrier density. Thus the correlation between the copper valence, lattice parameters and extra oxygen contents becomes then important (Fig.4). These circumstances should be keeping in mind when discussing the number of layer dependence of $T_c(n)$ [13].

In the present paper we will analyse the physics of the optimally doped layered mercurocuprate family from the structural point of view. The superconducting transition temperature dependence from the number n of CuO_2 planes in copper oxides will be described in the framework of workable phenomenological model and compared with experimental data.

2 Layered superconductors models

The problem of theoretical calculating of the superconducting critical temperature of layered superconductors in the context of copper oxides has been investigated previously to explain the variation of T_c with the number n of adjacent CuO_2 planes, present in the various superconducting copper oxide compounds. The approach based on a two dimensional model for electronic structure of a CuO_2 sheet has been proposed very early in Refs. [21], [22]. It was related with the statement that a 2D electronic band always shows a logarithmic singularity in the density of states. For n sheets, the density of states in two dimensions was proposed to be $N = nN_0$ and the effective electron-phonon interaction $\lambda = n\lambda_0$. The law $T_c(n) = T_0 \exp -1/\sqrt{n\lambda_0}$ has been derived. This formula even for a such oversimplified model was valid only for small n's. An another mean-field approach was proposed in Ref. [23], where it was insisted that the average spacing between the CuO_2 layers and not merely the number of layers per unit cell determine the critical temperature. A more sophisticated and detailed theory was proposed in Ref. [24] which give the monotonic increase of $T_c(n)$ and upper limit for mercurocuprate family $T_c(n = \infty) = 153$ K. Very recently the interlayer effects in Hg-based cuprates under high pressure for samples with n = 1 - 6 sublayers in the unit cell was considered in Ref. [25]. The theory of the interlayer tunneling of holon pairs has been used and applied for $n > 4$ cases and agreement and disagreement with experimental results was analyzed. D.T.Jover et al [26] have considered the mercurocuprates up to $n = 4$ on the basis of the model approach of charge redistribution of holes among the various CuO_2 layers [27]. They found out that for $n \geq 3$ this distribution is highly nonhomogeneous. This can lead to observable nonmonotonic n dependence of $T_c(n)$ as was discussed in details in Ref. [25].

As already mentioned, the different members of the mercurocuprate family are found to ehxibit different optimal superconducting transition temperatures which increase up to the third member, after T_c decreases. According to Ref. [2] an important and general structural feature of the mercurocuprates is that the apical $Cu-O$ distances are larger then the corresponding distances in the other cuprates and the Cu and O atoms forming the CuO_2-layers are coplanar. These structural features could be responsible for the highest transition temperature, however a satisfactory overall picture of the nature of this high-Tc behaviour is still in the process of evolution. Unfortunately, we have, at the present time, no generally accepted and complete formal theory of HTSC. The essence of the problem is in the inherent interaction (and coexistence) between charge and spin degrees of freedom which are coupled in a very nontrivial self-consistent way [28]. Since the honest theoretical treatment of the all above mentioned problems is very complicated, perhaps, it is instructive to look again at the physics involved from a phenomenological point of view.

3 Phenomenological Models

The phenomenological approach to layered copper oxides was developed by many authors. The consideration of inequivalent layers in the phenomenology of cuprates was done in Ref. [29] in terms of proximity effect [30] between the superconducting and insulating layers forming the unit cell of various copper oxides. The model accounted for observed positive curvature in the temperature dependence of the $H_{c2}^{\perp}$ and do not tackled the calculation of transition temperature. Subsequently, different authors have used several distinct approaches to realize this idea of inequivalent layers. It is interesting to note that notion of distinct "active" elements in the structure (type of plane, or chain) in layered cuprates was formulated in the very beginning stage of the studies of these materials even with some exotic model statements that adjacent Cu-O layers have negative Josephson coupling [31], forcing the order parameter to change sign from one layer to the next. The phenomenological approach for calculation of transition temperature of layered cuprates has been proposed in Ref. [32]. The physical idea was that there are distinct "active" elements in the multilayer structure. To each active element denoted l in the structure is 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. The full GL theory is a generalization to coupling order parameters of the seminal work of Lawrence and Doniach (LD) [33]. The LD theory is valid for disturbances in which ψ_l varies slowly on the scale of s and close to T_c. The approach of Ref. [32] have demonstrated that for polytype multilayer copper oxide systems it is possible to obtain the increasing $T_c(n)$,where n is polytype number $n = 2, 3...\infty$, with upper limits for T_c. In this paper we apply this line of reasoning (with suitable modifications) for the mercurocuprate family.

In order to model the layered structure of the mercurocuprates, we use the LD model, which consists of superconducting sheets separated by a distance s, with a Josepson coupling between the sheets. The GL functional is

$$F = \sum_l \int d^2x \Big(\frac{\hbar^2}{2m} | \left(\nabla_l - i\frac{2e}{\hbar c}\vec{A}_l \right) \psi_l|^2 + \frac{\hbar^2}{2Ms^2}|\psi_l - \psi_{l+1}|^2 + a_l|\psi_l|^2 + \frac{1}{2}b_l|\psi_l|^4 \Big) \tag{1}$$

where m and M are the effective masses in the $a-b$ plane and along the c axis, respectively, $a_l = a_l^0(T/T_l^0 - 1)$. The simplified version of GL theory consider the competing order-parameter fields as spatially homogeneous and the temperature region just near the critical temperature. In the normal state, $T > T_c$ all order parameters are zero. For $T < T_c$ some order parameters $\psi_l \neq 0$ for minimum free energy. Near T_c, if the coherence length perpendicular to the layers extends over many layers then the system acts as a bulk anisotropic superconductor.

The free energy density was taken in Ref. [32] as a bilinear form in the spacially independent order parameters

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

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

$$||(a_i(T) + nv_{ij})\delta_{ij} - v_{ij}|| = 0 \tag{3}$$

According to Ref. [32], the transition temperature for an n-layer sample is determined as the maximum eigenvalue of the n-dimensional Jacobi (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 [32] 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. The first and n-th layers of type a have the same order parameter ($1 \leq a \leq n$ and $1 \leq b \leq m$). Thus we can incorporate in our formulation the presence of two type of layers. The equation (3) is identical to the following expression

$$\det(TI - F) = 0; \tag{4}$$
$$F_{ij} = (T_i^0 - \frac{v_{i-1,i}}{a_i^0} - \frac{v_{i,i+1}}{a_i^0})\delta_{ij} + \frac{v_{ij}}{a_i^0}\delta_{i,j\pm 1}$$

Equations (3) and (4) 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. This interplay of the two order parameters of the two kind of active elements is one of the most important properties of the present phenomenological considerations.

Nevertheless, the model properties related to these effects do not give the observable "bell"-shaped form of $T_c(n)$. It is therefore of considerable interest to take into account the interlayer effects of charge redistribution to fit the experimental data.

4 The Charge Redistribution

The charge carriers in active CuO_2 planes are the fundamental degrees of freedom which are primarily responsible for the essential physics. The problem how doping will modify the charge and spin distribution of the system is not well understood for HTSC [28]. Contrary to the insulating behaviour the doped systems still are not completely understood and create a number of controversy [27], [34]. This confirm the statement that the question about true nature of carriers in the copper oxides are one of the central in the field and are still open. It was emphasized in Ref. [34] that the distribution of charge among the CuO_2 layers should be understood in order to describe adequately the variation of T_c with the number of CuO_2 layer per unit cell in layered cuprates with three or more CuO_2 planes.

The carrier concentration n_h is an crucial factor determining the critical temperature $T_c(n_h)$ [25], [26]. 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. In the multilayer structures there are a possibility of charge redistributing between the layers within a unit cell thus leading to models of "inequivalent" CuO_2 layers. The inequivalent layer models reveal essential physics 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. In the considered here the case of the mercurocuprate family with $n \geq 3$ it are the holes in inner and outer CuO_2 planes for which charge redistribution transfer with the "reservoir" block seemed could be different.

In addition, it was pointed out [35] that the electromagnetic response of the layered superconductors can have a peculiar behavior related to the specific of the interlayer charge transfer . One of the most important properties of the cuprate superconductors is that the frequency of the plasma with c-axis polarization is very low. An detailed analysis of the mercurocuprates in this respect will clarify the behavior of dielectric function and interlayer charge transfer in this family (c.f. [36]).

In our present work, ignoring at the first stage the subtleties of the delicate problem of the exact charge redistribution 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

$$T_a(x_c) = T_{a^0}\Big(1 - [\frac{x_c - h_2}{h_1}]^2\Big)^{1/2} \tag{5}$$

where the carrier-number density x_c in a single layer is given by $x_c = x^b_{out}[cm + 2(1-c)]/(n+m)$ and x^b_{out} is the fraction of carriers which is provided by the outer b-layer adjacent to an a-layer per area while $x^b_{in} = cx^b_{out}$ $(c \leq 1)$ 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 :

$$T_b = \begin{cases} T^0_b(\frac{x_c}{x_0}), & 0 \leq x_c \leq x_0; \\ T^0_b, & x_c \geq x_0; \end{cases} \qquad a_b(x_c) = \begin{cases} a^0_b T^0_b(\frac{x_c}{x_0})^{1/2}, & 0 \leq x_c \leq x_0; \\ 2a^0_b T^0_b \frac{x_0}{x_c + x_0}, & x_c \geq x_0; \end{cases} \tag{6}$$

Here $x_0 = m^* t_\perp / \pi\hbar^2$ and $v = v_{ij}$ have no x_c dependence (c.f. [33]).
With these simplifications it is possible now to calculate the critical temperature. There are the following free model parameters:
(i) n and m which determine the structure;
(ii) x^b_{out} and c which determine x_c;
(iii) x_0 and T^0_b which determine T_b;
(iv) a^0_a, a^0_b and v.

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.5) are shown as a 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.

5 Conclusions

In summary, in this paper we have presented a simple phenomenological model which rationalizes reasonably the currently available experimental data for the mercurocuprate family. We discussed the main structural features of layered mercurocuprates and gave the physical interpretation and plausible arguments on the role and significance of structural anisotropy and interlayer effects in this family. It was shown that within the LD-weak -link type model the observable behavior could not be explained without an additional invoking to the incorporating of the interlayer charge redistribution. Within the framework of the our combined model the experimentally observed nonmonotonic "bell"-shaped dependence $T_c(n)$ was traced back to the experimental one with reasonable accuracy. Therefore, in spite of the rather crude nature of our phenomenological model approach, the results presented here show that our threatment is quantitatively applicable to the layered mercurocuprate family. From the another side, our analysis favours an approach which are describable in terms of the generalized LD model with suitable charge redistribution corrections. This conclusion should be further substantiated by considering the more general GL model for layered superconductors as well as the more sophisticated description of the charge redistribution. A detailed consideration of these questions as well as an extended version of our numerical calculations will be discussed elsewhere.

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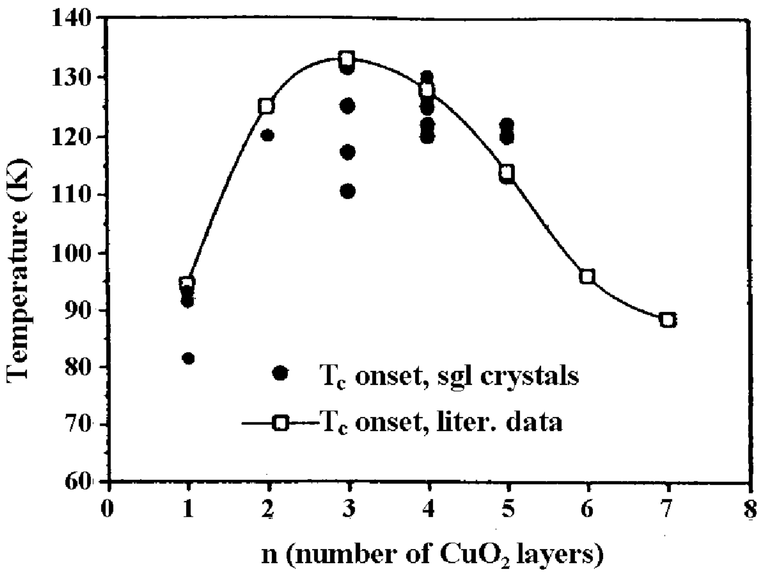

Fig. 1: Dependence of the superconducting critical temperature on number of layers n from Ref. [19].

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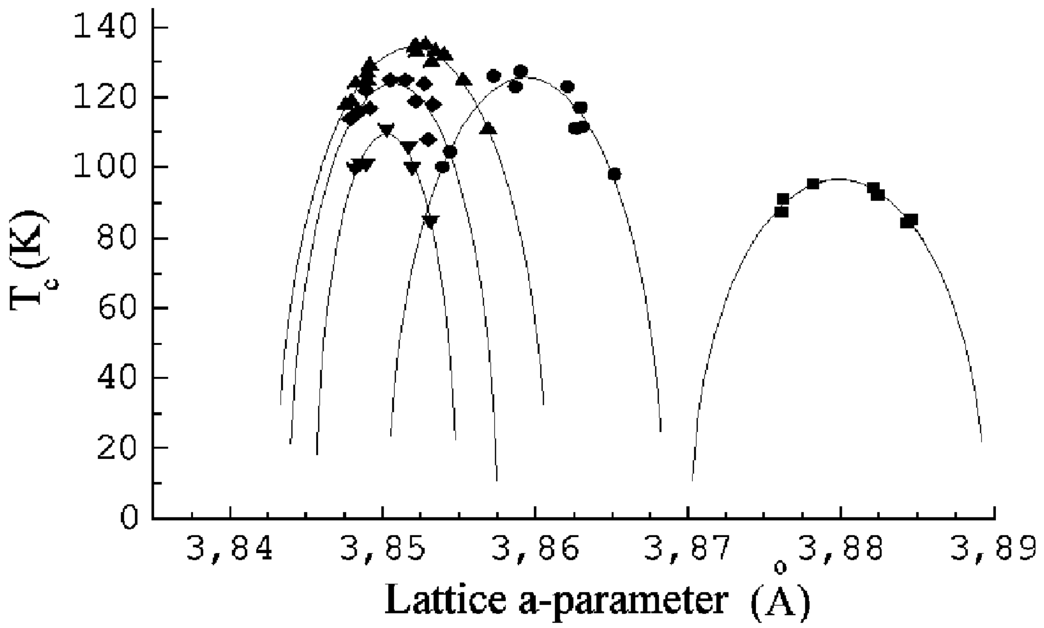

Fig. 2: Dependence of the superconducting critical temperature on lattice distance a for $n = 1 - 5$. ⊓ - n =1; • - n = 2; △- n=3; ⋄ - n = 4; ▽ - n = 5; (c.f. [8])

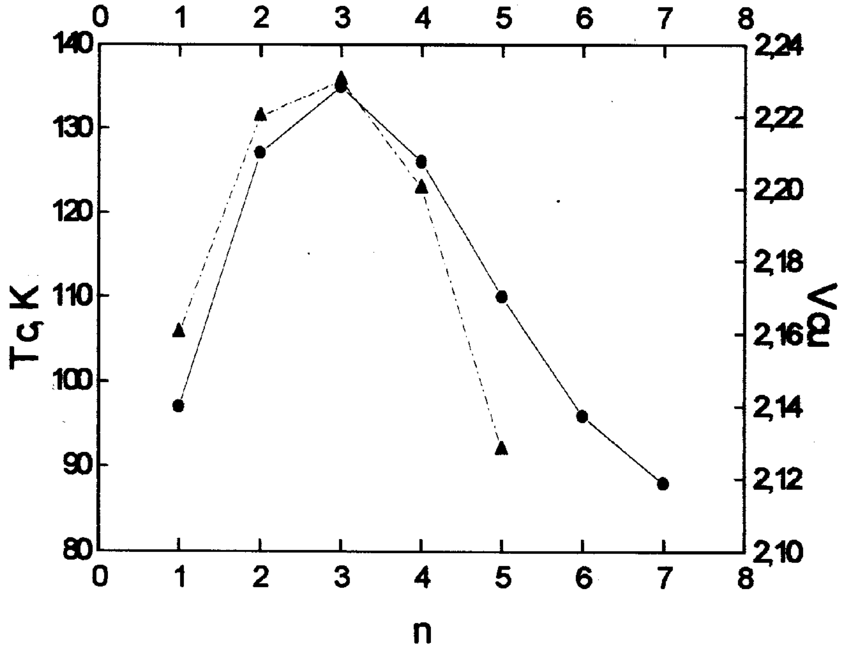

Fig. 3: Dependence of the superconducting critical temperature and copper valence on number of layers n according to data from Table 1. Full line is the critical temperature and dashed line is valence.

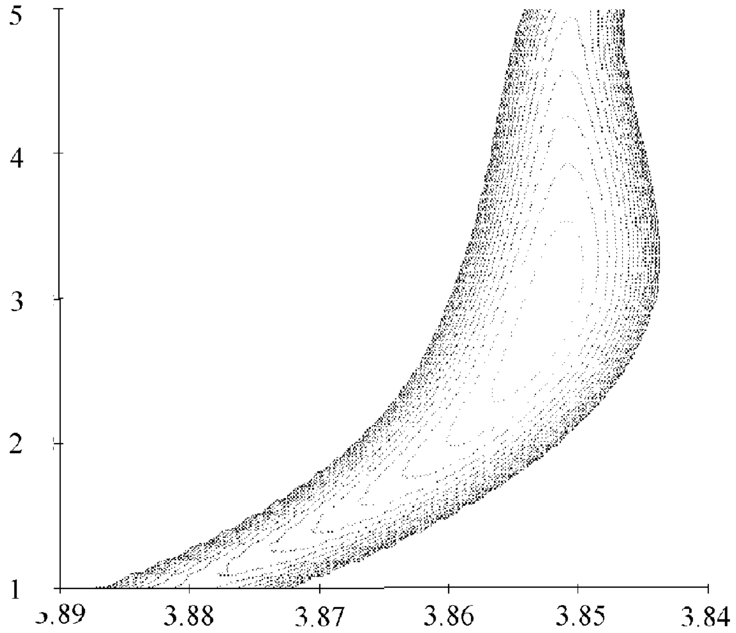

Fig. 4: Lines of the equal values of T_c versus n and a.

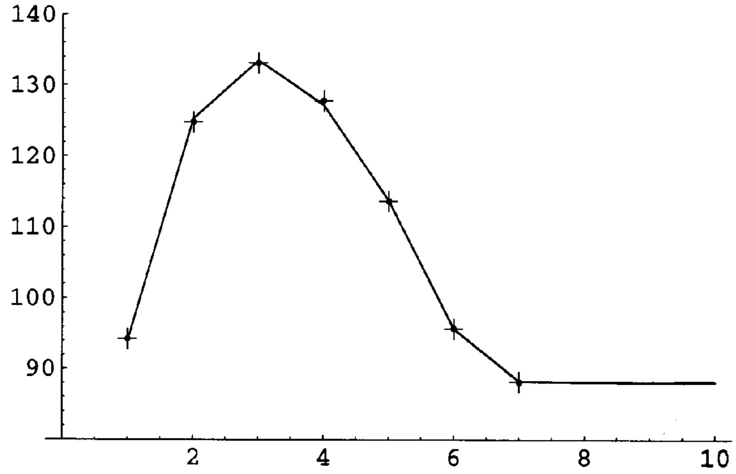

Fig. 5: Dependence of superconducting critical temperature $T_c(n)$ with $m = 3$ fixed. Parameters: $T_a^0 = 189.1$; $T_b^0 = 88.1$; $h_1 = 0.313$; $h_2 = 0.504$.