Mechanism for superconductivity suppression in the tetragonal phase of $YBa_2Cu_3O_{7-y}$

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A phenomenological description proposed here relates the relative magnitudes of the lattice constants, their orientation with respect to the cell-tripling direction for the parent phase, the suppression of superconductivity in the tetragonal phase, and the symmetry of the superconducting state of solid solutions based on $YBa_2Cu_3O_{7-y}$. © *1995 American Institute of Physics.*

1. In this letter we wish to show that several disconnected results which have been established in research on the properties of solid solutions based on $YBa_2Cu_3O_{7-y}$ can be explained by a common phenomenological approach which starts from the following three generally recognized facts: 1) The structure of $YBa_2Cu_3O_{7-y}$ can be thought of as a derivative of a perovskite-like parent phase with symmetry O_h^1 and a lattice constant $d_c \sim c/3$, $\sim a$, $\sim b$ (Ref. 1). Here a, b, and c are the lattice constants of $YBa_2Cu_3O_{7-y}$. The structure of this parent phase may arise because of a disorder of the Y^{3+} and Ba^{2+} ions in the $YBa_2Cu_3O_{7-y}$ structure[1] and because of small displacements of all the atoms which make the structure more cubic. 2) The actual structure of $YBa_2Cu_3O_{7-y}$ can be obtained from the structure of the parent phase by a lowering of its symmetry described by the two nonequivalent order parameters $\boldsymbol{\mu}\{\mu_1,\mu_2,...,\mu_6\}$ and $e\{e_1,e_2\}$. Physically, μ_1 represents linear combinations of probabilities for the filling of a regular system of $1(b)$ points in O_h^1 by Y or Ba atoms. These linear combinations are characterized by the star vector $\mathbf{K}^{(1)}=1/3\mathbf{b}_1$, where $\mathbf{b}_1$ is an O_h^1 reciprocal-lattice vector.[2] The components of $\mathbf{e}$ describe a longitudinal deformation of the cubic cell of the parent phase: $e_1 \sim 2u_{zz}-u_{xx}-u_{yy}$, $e_2 \sim \sqrt{3}(u_{xx}-u_{yy})$, where u_{ik} are components of the strain tensor. 3) The pairing of charge carriers in $YBa_2Cu_3O_{7-y}$ leads to a state in which the angular momentum of the pairs is 2 (this is d-wave pairing).[3] Even in the parent phase, this angular momentum must be partially frozen by the cubic crystal field, and the order parameters describing the superconducting state may have four or six components. We assume that the superconducting state of $YBa_2Cu_3O_{7-y}$ is described by the four-component order parameter[3] $\boldsymbol{\eta}\{\eta_1,\eta_2,\eta_2^*,\eta_1^*\}$.

The symmetry properties of the interactions between the order parameters play a major role in the description of the properties of $YBa_2Cu_3O_{7-y}$ offered below. We will describe the effect of each order parameter on the properties of $YBa_2Cu_3O_{7-y}$ in Landau's theory of phase transitions. For a qualitative description of experiments it is sufficient to assume that the interactions between the order parameters are so weak that it is legitimate to construct a perturbation theory based on the following hierarchy of interactions. The energy responsible for the ordering of the yttrium and barium ions is much

greater than the energy responsible for the ferroelastic transition, and the latter is in turn much larger than the energy responsible for the high-T_c superconducting state. This fourth hypothesis is required only to simplify the results of the calculations presented below. It allows us to omit from the theoretical results the weak inverse effect of the high-T_c superconducting state, described by η, on the elastic subsystem, described by $\mathbf{e}$, and also the effect of the strains $\{e_1 e_2\}$ on the equilibrium ordering of the Y and Ba, described by $\mu_1^{(0)}$.

2. The Landau potential of this model can be written as the sum of five terms:

$$\Phi = \Phi_{\text{ord}} + \Phi_{\text{int}}^{(1)} + \Phi_{\text{el}} + \Phi_{\text{int}}^{(2)} + \Phi_S . \tag{1}$$

The only important result of an analysis of Φ_{ord} is that this term allows orderings described by

$$1)\ \boldsymbol{\mu}_1^{(0)}\{\mu_1=\mu_2,\mu_3=\mu_4=\mu_5=\mu_6=0\}\ \text{ and }\ 2)\ \boldsymbol{\mu}_2^{(0)}\{\mu_1\neq\mu_2,\mu_3=\mu_4=\mu_5=\mu_6=0\},$$

which correspond to a tripling of the lattice constant of the parent phase along the z axis (the fourfold axis C_4, O_h^1). In the phase with $\mu_1=\mu_2$ the order is strict and corresponds to the composition $YBa_2Cu_3O_{7-y}$; for $\mu_1 \neq \mu_2$, there is the stoichiometric composition $Y(B_{1-x}Y_x)_2Cu_3O_{7-y}$ (Ref. 2). The two states may border each other along the line of transitions, but a transition from them to the parent phase is possible only as a first-order phase transition, except at the critical point.

In a Landau potential describing the interaction of the order and the elastic subsystem it is sufficient to consider only the term of lowest order in e_1 and μ_k:

$$\begin{aligned}\Phi_{\text{int}}^{(1)} = {} & \alpha_1\{e_1[2(\mu_1^2+\mu_2^2)-\mu_3^2-\mu_4^2-\mu_5^2-\mu_6^2]-\sqrt{3}e_2(\mu_3^2+\mu_4^2-\mu_5^2-\mu_6^2)\} \\ & \times\alpha_2\{(e_1^2-e_2^2)(\mu_1^2+\mu_2^2)+(\mu_3^2+\mu_4^2)(-e_1^2+e_2^2+2\sqrt{3}e_1e_2) \\ & +(\mu_5^2+\mu_6^2)(-e_1^2+e_2^2-2\sqrt{3}e_1e_2)\}.\end{aligned} \tag{2}$$

The part of potential (1) responsible for the ferroelastic transition is a function of two invariants, $I_1=e_1^2+e_2^2$, and $I_2=e_1^3-3e_1e_2^2$:

$$\Phi_{\text{el}}(e_1,e_2)=E_{\text{el}}(I_1,I_2)=a_1I_1+P_{\text{el}}(I_1,I_2). \tag{3}$$

If there is no actual ferroelastic transition, we can ignore P_{el} in Φ_{el} in (3). The interaction between the order and the deformation of the crystal, (2), then describes a noncharacteristic deformation of the unit cell of the parent phase which makes the cell tetragonal in accordance with the symmetry determined by the order $\boldsymbol{\mu}_1^0$. The ferroelastic order parameter $\mathbf{e}$ itself can, according to the form of I_1 and I_2, induce three different phases, which differ in the longitudinal deformation of the unit cell of the parent phase. In the $\mathbf{e}_1^{(0)}$ and $\mathbf{e}_2^{(0)}$ phases we have $e_2=0$ and $e_1>0$ or <0. These two tetragonal distortions of the cell of the parent phase differ in the sign of the tetragonality. For $\mathbf{e}_1^{(0)}$ we have $c_T>a_T=b_T$, while for $\mathbf{e}_2^{(0)}$ we have $c_T<a_T=b_T$, where c_T is the size of the cell of the parent phase along the fourfold axis, whose direction we denote by $\mathbf{n}$. The orientation of $\mathbf{n}$ with respect to the direction $(\mathbf{z})$, along which the cell of the parent phase multiplies, determines the interaction α_1 in (2). Let us assume $\alpha_1<0$; then we have $e_1>0$, and an orientation of $\mathbf{n}$ along the cell-multiplication direction is favored from the energy stand-

point. If the crystal instead goes into a ferroelastic phase characterized by a squashed cell, the orientation $\mathbf{n} \perp \mathbf{z}$ has the advantage in terms of energy. In this case, of course, the cell becomes orthorhombic because of the interaction introduced by α_2 in (2), since the relations $\mu_1 \neq 0$, $\mu_2 \neq 0$, $e_1 \neq 0$, and $\mathbf{e}_1 \perp \mathbf{n}$ lead to $e_2 \neq 0$. This result can be seen most conveniently by rewriting (2) in a coordinate system more convenient for this orientation of $\mathbf{n}$: a system which is rotated an angle $2\pi/3$ in the space of the elastic order parameter $\{e_1 e_2\}$. The new coordinates in real space correspond to a rotation of the $\mathbf{n}$ axis through $\pi/2$, $e_1^* \sim (2u_{yy} - u_{zz} - u_{xx})$ and $e_2^* \sim (\sqrt{3}(u_{zz} - u_{xx})$:

$$\Phi_{\text{int}}^1 = -\alpha_1 \{e_1^* [2(u_3^2 + \mu_4^2) - \mu_5^2 - \mu_6^2 - \mu_1^2 - \mu_2^2] + e_2^* \sqrt{3}(\mu_5^2 + \mu_6^2 - \mu_1^2 - \mu_2^2)$$
$$+ \alpha_2 \{(e_1^{*2} - e_2^{*2})(\mu_1^2 + \mu_2^2) + (\mu_3^2 + \mu_4^2)[-e_1^{*2} + e_2^{*2} + 2\sqrt{3} e_1^* e_2^*]$$
$$+ (\mu_5^2 + \mu_6^2)[-e_1^{*2} + e_2^{*2} - 2\sqrt{3} e_1^* e_2^*]\}. \qquad (2')$$

As before, the ground state in the $\mathbf{n} \perp \mathbf{z}$ phase corresponds to one of the states characterized by $\mu_1 \neq 0$, $\mu_2 \neq 0$, $\mu_3 = \mu_4 = \mu_5 = \mu_6 = 0$. We see from (2′) that we have $e_1^* \neq 0$ and $e_2^* \neq 0$. Because of α_2 we have $e_2 \neq \pm \sqrt{3} e_1$; i.e., the transition from $e_1 > 0$ to $e_1 < 0$ in the presence of $\boldsymbol{\mu}$ leads to a phase of orthorhombic symmetry. In $(Y_{1-x}Ln_x)(Ba_{1-x}Me_z)_2Cu_3O_{7-y}$ solid solutions the $\mathbf{n} \| \mathbf{z}$ phase corresponds to a tetragonal phase T, while $\mathbf{n} \perp \mathbf{z}$ corresponds to an orthorhombic phase T, and $\mathbf{n} \perp \mathbf{z}$ corresponds to an orthorhombic phase P1 (Ref. 1). Here Ln is a lanthanide, and Me is a divalent or trivalent metal replacing barium.

According to (3), between the ferroelastic phases $\mathbf{e}_1^0$ and $\mathbf{e}_2^0$ on the phase diagram there is a phase $\mathbf{e}_3^0$, in which the ferroelastic deformation itself renders the cubic cell of the parent phase orthorhombic ($e_1^0 \neq 0$ and $e_2^0 \neq 0$). The orientation of the largest lattice constant of the ferroelastic orthorhombic phase itself ($\mathbf{n}^1$) with respect to the $\mathbf{z}$ axis changes in accordance with (2′), switching from $\mathbf{n}^1 \| \mathbf{z}$ to $\mathbf{n}^1 \perp \mathbf{z}$. Because of energy selection of the ferroelastic domain of the parent phase, this change in orientation can occur without the formation of a phase of monoclinic symmetry through a mixture of phases. The intermediate orthorhombic phase (P2) is observed on all phase diagrams of $YBa_2Cu_3O_{7-y}$-based solid solutions.[1,5,6]

3. The superconducting state of the parent phase is described by the four-component order parameter $\boldsymbol{\eta}(\eta_1; \eta_2; \eta_2^*; \eta_1^*)$, whose imaginary and real components form a basis for the E_g representation of the O_h^1 group.[4] In this case the potential Φ_S depends on the three invariants, $i_1 = |\eta_1|^2 + |\eta_2|^2$, $i_2 = |\eta_1|^2 \cdot |\eta_2|^2$, and $i_3 = (|\eta_1|^2 - |\eta_2|^2)^3 - 3(|\eta_1|^2 - |\eta_2|^2)(\eta_1 \eta_2^* + \eta_2 \eta_1^*)^2$:

$$\Phi_S(\boldsymbol{\eta}) = F_S(i_1, i_2, i_3) \equiv a_1 i_1 + a_2 i_1^2 + b_1 i_2 + b_2 i_2^2 + c_1 i_3 + c_2 i_3^2 + P_S(i_1, i_2, i_3). \qquad (4)$$

The potential in (4) allows the existence of seven superconducting phases of different symmetries, in three of which a second-order transition can occur:[4] Phase 1), $\{\eta_1; +i\eta_1; -i\eta_1^*; \eta_1^*\}$, is compatible with the cubic crystal symmetry of the parent phase. Phase 2), $\{0; \eta_2; \eta_2^*; 0\}$, and phase 3), $\{\eta_1; 0; 0, \eta_1^*\}$, are compatible with tetragonal symmetry. The transition temperature is set by the condition $a_1 = 0$, and the selection of phases is determined by the signs of b_1 and c_1. Figure 1 shows the intersection of the phase diagram in the space a_1, b_1, c_1 with an $a_1 = \text{const} < 0$ plane. We see that a large

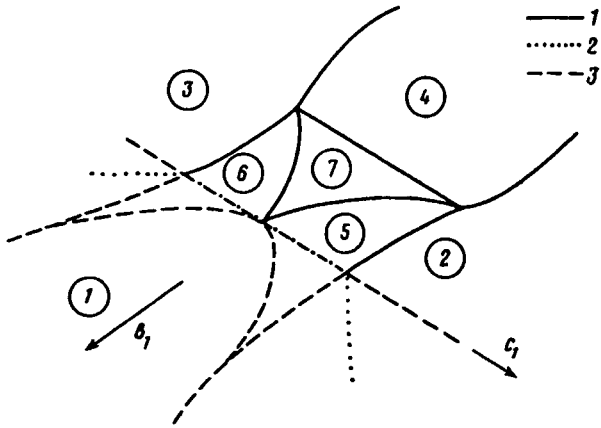

FIG. 1. Positions of the high T_c superconducting states of the parent phase induced by η in the b_1c_1 plane under the condition $a_1=\text{const}<0$ in accordance with $\phi_s(\eta)-P_s$[see (4)]. The numbers in circles specify the phases. Solid lines—Lines of second-order transitions; dotted lines—equilibrium lines; dashed lines—instability boundaries of the phases of various symmetries.

area on this cross section is occupied by phase 4), $\{\eta_1, \eta_1 \exp i\varphi, \eta_1^* \exp(-i\varphi), \eta_1^*\}$, which is compatible with only orthorhombic symmetry, like the phase with lowest symmetry of the high-T_c superconducting state, 7), $\{\eta_1, \eta_2, \eta_2^* \eta_1^*\}$. Symmetry forbids a line of second-order transitions from the normal state (N) to phases 4) and 7) and also to anti-isostructural phases 5) and 6), which are characterized by $\eta_1=\xi_1 \exp i\Omega$ and $\eta_2=-i\xi_2 \exp i\Omega$. Phases 5) and 6) are compatible with only a tetragonal crystal structure; phase 5) corresponds to $\xi_1>\xi_2$, and phase 6) to $\xi_1<\xi_2$. An important point is that the transition between phase 1 and any other high-T_c-superconducting phase is always of first order.

In a first approximation, the effect of the elastic order parameter on the high-T_c superconducting state is described by three independent invariants in $\Phi_{\text{int}}^{(2)}=\delta_1 j_1+\delta_2 j_2+\delta_3 j_3$, where

$$
\begin{aligned}
j_1&=e_1(|\eta_1|^2-|\eta_2|^2)-e_2(\eta_1\eta_2^*+\eta_2\eta_1^*),\\
j_2&=(|\eta_1|^2-|\eta_2|^2)(e_1^2-e_2^2)+2(\eta_1\eta_2^*+\eta_2\eta_1^*)e_1e_2,\\
j_3&=e_1[(|\eta_1|^2-|\eta_2|^2)^2-(\eta_1\eta_2^*+\eta_2\eta_1^*)^2]+2e_2(|\eta_1|^2-|\eta_2|^2)(\eta_1\eta_2^*+\eta_2\eta_1^*).
\end{aligned}
\tag{5}
$$

We assume that the condition $b_1 \geqslant 0$ holds in the $YBa_3Cu_3O_{7-y}$ parent phase and that high-T_c superconducting phase 1) is realized. The anisotropy of the gap operator in phase 1) near T_c is $\Delta \exp i\Omega=\eta[1/\sqrt{3}(2k_z^2-k_x^2-k_y^2)+i(k_x^2-k_y^2)]$. According to the tetragonal symmetry of the actual structure, phase 1) is described as an anisotropic $S(2z^2-x^2-y^2)+id(x^2-y^2)$ state. In the tetragonal structure, this state can form as a result of no less than two second-order transitions.[7] In the case of orthorhombic symmetry of the crystal, state 1) is simply an anisotropic S state, and it can easily arise through a single second-order transition. The interactions between the ferroelastic order parameter

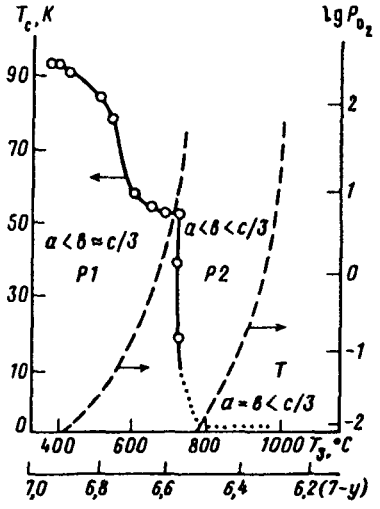

FIG. 2. Typical behavior of the temperature of the transition of $YBa_2Cu_3O_{7-y}$ to the high-T_c superconducting state for various relations among the lattice constants a,b, and c, compiled from results in Refs. 1, 5, and 6. Here T_3 is the temperature at which the test samples are annealed. Dashed lines—Boundaries between phases; dotted line—no quantitative data are available.

and η do not split the transition from N to phase 1), but they do renormalize the transition temperature in accordance with a replacement of the equality $a_1=0$ by

$$a_1=-e_1\delta_1(1-\cos^2\varphi e_2^2/e_1^2)^{1/2}, \tag{6}$$

where $\varphi=\Omega_1-\Omega_2$ is the phase difference between η_1 and η_2.

In the case $\delta_1>0$ in the tetragonal phase with $c/3>a=b$, a transition to a superconducting state can thus be completely suppressed. Furthermore, in a tetragonal structure we have $e_2=0$ and $\cos\varphi=0$. In the orthorhombic phase, with $c/3>b>a$, the transition temperature begins to move away from zero as the differences $b-a$ and $c-b$ change, because of the relations $e_1\sim 0$ and $e_2\neq 0$. Here we have $\varphi_3\neq\pi/2$ because of the δ_3 interaction which we have introduced. The T_c superconducting state 1) acquires the symmetry of state 4) in the orthorhombic phase, since we have $\varphi\neq\pi/2$. This change, however, occurs because of weak interactions of fourth order in the components of η. Phases 1) and 4) are also different in the orthorhombic phase: A line of isostructural phase transitions runs between them. The primary influence on T_c, however, is exerted by the change in the sign of e_1 in (6) because of the ferroelastic phase transitions described by (3). To clarify the comparison with experiment, we show in Fig. 2 some typical experimental results on the behavior of T_c in $YBa_2Cu_3O_{7-y}$ for various relations among a,b, and $c/3$.

There is also a direct interaction of η and μ. In the phases characterized by $\mu_3=\mu_4=\mu_5=\mu_6=0$ the direct interaction is described by

$$\Phi_{\text{int}}^{(3)}=g(|\eta_1|^2-|\eta_2|^2)(\mu_1^2+\mu_2^2). \tag{7}$$

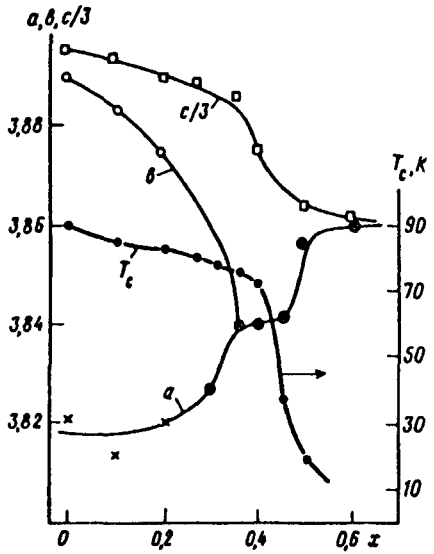

FIG. 3. Behavior of the lattice constants a,b, and $c/3$ and the transition temperature T_c for $YBa_{2-x}La_xCu_3O_{7-y}$ according to Ref. 9.

This interaction may prove important in solid solutions in which Ba is replaced by a lanthanide, since the deformation of the unit cell of the parent phase is frequently small in the ordered phase of $YBa_{2-x}Ln_xCu_3O_{7-y}$. From the phenomenological standpoint, $|\delta_1 e_1|$ is on the same order of magnitude as $g(\mu_1^2+\mu_2^2)$. The direct interaction of the anisotropic superconducting state with the ordering of the barium and lanthanide ions also lowers the temperature of the transition to the high-T_c superconducting state in accordance with

$$a_1 = -g(\mu_1^2+\mu_2^2)[(1+\delta_1 e_1/g(\mu_1^2+\mu_2^2))^2 - \delta_1^2\cos^2\varphi e_2^2/(g^2(\mu_1^2+\mu_2^2)^2]^{1/2}. \quad (8)$$

If $e_2=0$ and $e_1<0$, the effect of interaction (7) is weakened according to (8). Figure 3 shows an example of a suppression of the high- T_c state by the direct interaction between the superstructure and η ; this figure was constructed from the data of Ref. 9.

We would like to conclude with two clarifying comments.

1. Our hypothesis that there can be a disorder of the differently charged ions[1] Y^{3+} and Ba^{2+} no longer looks implausible when we recall that a similar disorder of S^{2-} and I^{1-} ions above 519 K is observed in Ag_3SI, of Al^{3+} and Si^{4+} ions above 523 K in $Na_{1-x}K_xAlSi_3O_8$, etc. There is also evidence of a disorder of Y^{3+} and Ba^{2+} directly in the form of phases of the $Y(Ba_{1-x}Y_x)_2Cu_3O_{7-y}$ type in the system of solid solutions based on $YBa_2Cu_3O_{7-y}$ (Ref. 1).

2. The generally accepted assumption[1,4] of a perovskite-like parent phase of $YBa_2Cu_3O_{7-y}$ was criticized in Ref. 7. The differences which follow from the choice of a cubic parent phase[7] are important for our purposes in the present letter. These differ-

ences are manifested in the nature of the diffusion of oxygen, in the channeling of heavy ions, in the existence of an ordered "limiting" composition $Y(Ba_{1/2}Y_{1/2})_2Cu_3O_7$ (Refs. 1 and 7), etc.

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