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SOFT MODES AND STRUCTURAL PHASE TRANSITIONS IN La_2CuO_4

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First discovered high temperature superconductors $La_{2-x-y}Re_yMe_xCuO_4$ (Re - rare earth, Me=Ba,Sr,Ca) have a rather complex phase diagram. In the compound $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ a number of structural phase transitions (SPT) is observed with synchrotron x-ray powder diffraction measurements [1]. In the range x<0.15 there is a sequence of SPT of the second order which occur with decreasing temperature: high temperature tetragonal phase (HTT) → low temperature orthorhombic (LTO) → low temperature orthorhombic 2 (LTO2) → low temperature tetragonal (LTT), raising of the symmetry taking place in the last transformation. There are only two SPT at x above 0.15, the first is of the second order, the other one is of the first order: HTT→LTO→LTT.

Symmetry analysis of transformations from HTT structure is carried out in [2]. SPT is driven by the soft modes which correspond to the irreducible representation of two - armed star of wave vectors $\vec{q}_{1,2}=\frac{\pi}{a}(\pm1,1,0)$. The irreducible representation of the wave vector group being one dimensional, there is one phonon branch with two degenerate soft modes ($\omega(\vec{q}_1)=\omega(\vec{q}_2)$) owing to the existence of the fourfold rotational z-axis in HTT phase. At the temperature of transformation from HTT phase into a low-temperature phase the mode frequency becomes zero, driving the static tilt rotation of octahedra CuO_6 around axis (-1,1,0) (mode $\omega_1=\omega(\vec{q}_1)$) and (1,1,0) (mode $\omega_2=\omega(\vec{q}_2)$). All the three low-temperature phases arise as a result of the coherent superposition of these rotations. Let us introduce "frozen" normal coordinates Q_1 and Q_2 which are proportional to the amplitudes of octahedra tilting in the polar representation

$$Q_1=Q\cos\phi,\qquad Q_2=Q\sin\phi, \tag{1}$$

where ϕ denotes the angle between the direction of the resulting rotation lying in the x-y plane and (-1,1,0) axis, Q is amplitude of this rotation. In paper [2] the invariants of the irreducible representations are presented in terms of which the free energy of the crystal is constructed: $I_1=Q_1^2+Q_2^2$, $I_2=Q_1^2Q_2^2$, and also the most general coupling of macroscopic strains and the soft modes is considered.

In order to describe the sequence of SPT J.D. Axe et al. have proposed the following simplified thermodynamic potential [3],[4]

$$F=A(Q_1^2+Q_2^2) + u(Q_1^2+Q_2^2)^2 + v(Q_1^4+Q_2^4) + w(Q_1^8+Q_2^8) + \\ + \frac{1}{2}c\eta^2 + d\eta(Q_1^2-Q_2^2) \ , \tag{2}$$

where $A=\frac{1}{2}a(T-T_3)$, u, v, w, c, d – are the model parameters dependent on a temperature in a general case, $\eta=\varepsilon_{xy}$ – shear strain in HTT phase. The last two terms are the energy of static deformations and the coupling energy of the phonon amplitudes and the macroscopic strain, respectively.

The strain η can be eliminated from the equilibrium condition under the stress-free condition $\frac{\partial F}{\partial \eta}=0$

$$\eta=-\frac{d}{c}(Q_1^2-Q_2^2) \ . \tag{3}$$

So the macroscopic strain is zero, if $Q_1^2=Q_2^2$.

Substituting the relation (3) into (2) and using the polar representation (1) one can rewrite eq. (2) only in terms of Q and ϕ:

$$F(Q,\phi)=f(Q) + \alpha(Q)\cos 4\phi + \beta(Q)\cos 8\phi \ , \tag{4}$$

where $f(Q)= AQ^2 + (u + \frac{3}{4}v - \frac{1}{4}\frac{d^2}{c})Q^4 + \frac{59}{64}wQ^8$,

$\alpha(Q)= \frac{1}{4}(v - \frac{1}{4}\frac{d^2}{c})Q^4 + \frac{13}{16}wQ^8$, $\beta(Q)= \frac{1}{64}wQ^8$.

Using the following relations $\frac{\partial F}{\partial \phi}=0$, $\frac{\partial F}{\partial Q}=0$ and positive definition of the matrix of the second derivatives one can obtain equilibrium values of Q and ϕ.

At $T>T_3$ we have $Q^2=0$, and, hence, $Q_1^2=Q_2^2=0$ (HTT phase). With de-

creasing temperature SPT of the second order takes place provided the parameters satisfy the following restriction at $T=T_3$

$$4u + 3v - \frac{d^2}{c} \pm (v - \frac{d^2}{c}) > 0 \ . \tag{5}$$

Below T_3 the parameter Q is not equal to zero, and ϕ determines the low symmetry phase. In the case of $\beta>0$ there are three low symmetry phases in general:

i) at $\alpha<-4\beta$ we have $\phi=0(\mathrm{mod}\ \frac{\pi}{2})$ which corresponds to LTO phase ($Q_1^2\neq0$, $Q_2^2=0$, or the other domain $Q_1^2=0$, $Q_2^2\neq0$),

ii) at $\alpha>4\beta$ we have $\phi=\frac{\pi}{4}(\mathrm{mod}\ \frac{\pi}{2})$ – LTT phase ($Q_1^2=Q_2^2\neq0$),

iii) and at $|\alpha|<4\beta$ the direction of the rotation axis gradually changes from $\phi=0$ to $\phi=\frac{\pi}{4}$: $\phi=\frac{1}{4}\arccos(-\frac{\alpha}{4\beta})$ – LTO2 phase ($Q_1^2\neq Q_2^2\neq0$), see Fig.1.

The sequence of the low symmetry phases depends on whether $\alpha(Q(T))$ is an increasing or decreasing function of temperature, in turn, this is determined by the values of the model parameters and its dependence on a temperature.

It should be pointed out that transformation LTT-LTO2 is of the second order in spite of the fact that both Q_1 and Q_2 are not equal to zero at the transition temperature. For this SPT one can introduce new phonon amplitudes $Q_1'=\frac{1}{\sqrt{2}}(Q_1-Q_2)$ and $Q_2'=\frac{1}{\sqrt{2}}(Q_1+Q_2)$. Q_1' is equal to zero in the LTT phase, while in LTO2 it is not. Hence, Q_1' is the order parameter for this transformation.

In the case $\beta<0$ intermediate phase LTO2 becomes unstable and a jump in values of parameters ϕ and η occurs at the transformation LTO-LTT. In the region $|\alpha|<|4\beta|$ the free energy has local minimums at both the $\phi=0$ (LTO) and $\phi=\frac{\pi}{4}$ (LTT). A phase corresponding to absolute minimum of this two minimums is stable, only local one is metastable. So, in compound $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ coefficients w (eq. (2)) and β (eq. (4)) change their signs at x=0.15.

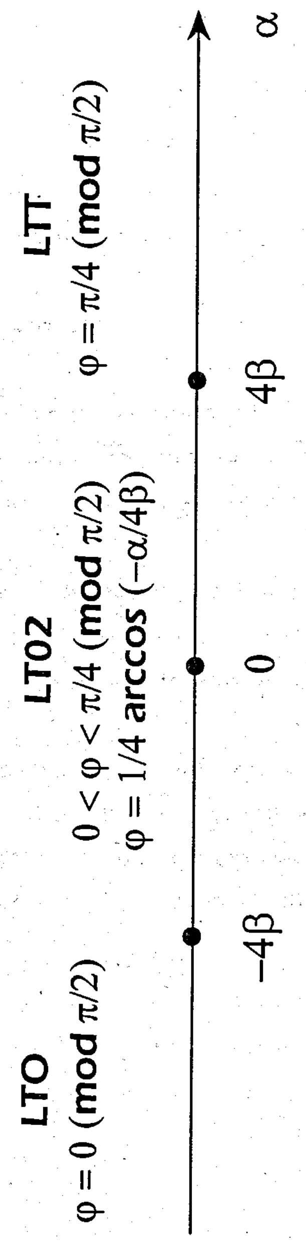

Fig.1. The sequence of the three low temperature phases versus α (see eq.4).

The temperature dependence of the generalized susceptibility $\chi_\phi=\left(\frac{\partial^2 F}{\partial \phi^2}\right)^{-1}$ has been calculated by J.D. Axe [4] by means of the potential (4). However experiments give a direct observation of not the generalized susceptibility but of the soft mode frequencies, and our paper deals with the calculation of dependence of these frequencies on the temperature.

The second derivatives $\chi_i^{-1}=\frac{\partial^2 F}{\partial Q_i^2} \propto \omega_i^2$ (i=1,2) yield susceptibility χ_i determining fluctuations of the amplitude Q_i and allow us to evaluate the soft modes ω_1 and ω_2.

For optic vibrations at the characteristic soft mode frequencies the strain cannot follow fluctuations of the primary order parameters, hence, the order parameter susceptibilities are elastically clamped. In order to obtain the soft mode frequency dynamics in this case one should differentiate eq.(2) and only after that substitute the equilibrium value of η (3) into acquired expression [7].

For convenience one can express order parameter susceptibilities in terms of $\frac{\partial^2 F}{\partial \phi^2}$ and $\frac{\partial^2 F}{\partial Q^2}$ provided the relations at equilibrium $\frac{\partial F}{\partial \phi}=0$ and $\frac{\partial F}{\partial Q}=0$ are held. Here we derive

$$\omega_1^2 \propto \frac{\partial^2 F}{\partial Q_1^2} = \frac{\partial^2 F}{\partial Q^2}\cos^2\phi - \frac{\partial^2 F}{\partial Q \partial \phi}\sin 2\phi + \frac{\partial^2 F}{\partial \phi^2}\frac{\sin^2\phi}{Q^2}\ ,$$
$$\omega_2^2 \propto \frac{\partial^2 F}{\partial Q_2^2} = \frac{\partial^2 F}{\partial Q^2}\sin^2\phi + \frac{\partial^2 F}{\partial Q \partial \phi}\sin 2\phi + \frac{\partial^2 F}{\partial \phi^2}\frac{\cos^2\phi}{Q^2}\ . \qquad (6)$$

Rewriting eq. (2) in polar representation (1) and using equilibrium conditions we note that $\frac{\partial^2 F}{\partial Q \partial \phi}$ is equal to zero in all phases except of LTO2, $\frac{\partial^2 F}{\partial Q^2}=0$ only at $T=T_3$ (i.e., at the temperature of SPT from HTT phase), and

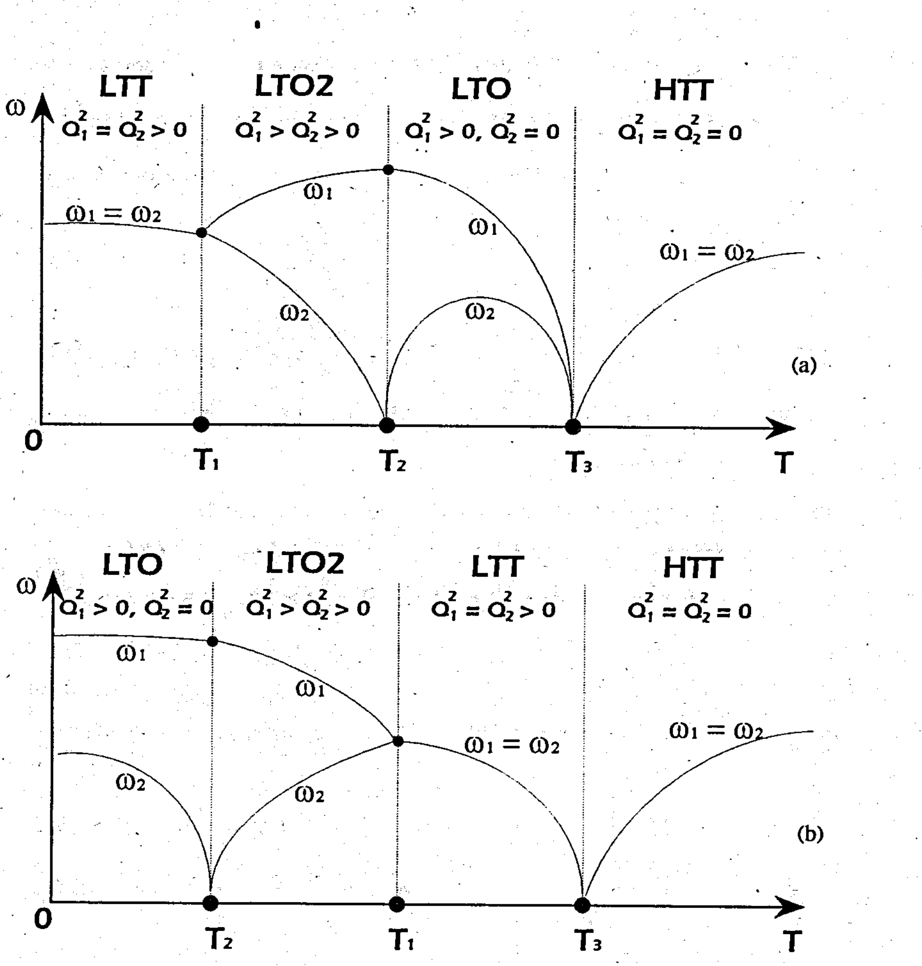

Fig.2. Temperature dependence of the soft mode frequencies $\omega_1=\omega(\vec{q}_1)$ and $\omega_2=\omega(\vec{q}_2)$ ($\vec{q}_{1,2}=\frac{\pi}{a}(\pm1,1,0)$) for the different sequences of phases. In LTT phase the modes are degenerate due to the fourfold screw z-axis. At the temperature of the transformation LTO2-LTT the soft mode frequencies are not equal to zero.

$$\frac{\partial^2 F}{\partial \phi^2} = \begin{cases} 0, & \text{in HTT,} \\ -16(\alpha+4\beta)\ , & \text{in LTO,} \\ -\frac{4}{\beta}\left[(4\beta)^2-\alpha^2\right]+2\frac{d^2}{c}Q^4(1+\frac{\alpha}{4\beta})\ , & \text{in LTO2,} \\ -16(-\alpha+4\beta)+4\frac{d^2}{c}Q^4\ , & \text{in LTT,} \end{cases} \qquad (7)$$

where the last terms in angle second derivatives for LTO2 and LTT phases appear due to the fact that the order parameter susceptibilities are considered to be elastically clamped. So, $\frac{\partial^2 F}{\partial \phi^2}$ is equal to zero at temperature of any transformation mentioned above with the exception of LTO2-LTT transition.

From the latter equations one can obtain inverse susceptibilities for HTT phase

$$\chi_1^{-1}= \chi_2^{-1}= \frac{1}{2}\ \frac{\partial^2 F}{\partial Q^2}\quad ,$$

for LTT phase

$$\chi_1^{-1}= \chi_2^{-1}= \frac{1}{2}\ \left(\frac{\partial^2 F}{\partial Q^2} + \frac{\partial^2 F}{\partial \phi^2}\ \frac{1}{Q^2} \right)\quad ,$$

for LTO (domain $Q_1^2\neq0$, $Q_2^2=0$)

$$\chi_1^{-1}= \frac{\partial^2 F}{\partial Q^2}\ ,\ \chi_2^{-1}= \frac{\partial^2 F}{\partial \phi^2}\ \frac{1}{Q^2}\quad ,\ \chi_1^{-1} > \chi_2^{-1}\ ,$$

and for LTO2 a rather complex dependence, but for domain $Q_1^2>Q_2^2>0$

$$\chi_1^{-1} > \chi_2^{-1}\quad .$$

The results are displayed in Figs. 2(a) and 2(b). One should stress two features of the soft mode behaviour. Firstly, at the temperature of the transformation LTO2-LTT the soft modes are not equal to zero, as well as the inverse generalized susceptibility χ_ϕ^{-1} is not equal to zero. Secondly, the modes are degenerate in the LTT phase owing to the existence of the fourfold screw z-axis.

If the parameter w (see eq.2) is very small and positive, then the LTO2 region T_1-T_2 diminishes strong and the abrupt change of the soft mode frequencies takes place in this range. In the case w<0 there is no intermediate LTO2 phase, and hence, ω_1 and ω_2 experience a jump, and the first order transition is realized.

In order to verify the results obtained here for the soft mode behaviour single crystals of La_2NiO_4 or Pr_2NiO_4, which have been investigated in [5], [6] and have demonstrated the same SPT sequence, can be used, as to prepare a single crystal of solid solution Nd and Sr in La_2CuO_4 required for the inelastic neutron scattering experiments is a complicated technical problem.

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Мягкие моды и структурные фазовые переходы в La_2CuO_4

С помощью термодинамического потенциала, предложенного Д.Д.Экс и др. [3], рассматривается последовательность структурных фазовых переходов $HTT(D_{4h}^{17}) \to LTD(D_{2h}^{18}) \to LTO2(D_{2h}^{10}) \to LTT(D_{4h}^{16})$ в допированном La_2CuO_4. Рассчитывается температурная зависимость мягких мод $\omega(\vec{q}_1)$ и $\omega(\vec{q}_2)$, отвечающих за рассматриваемые структурные фазовые переходы. Показано, что в *HTT* и *LTT* фазах эти моды вырождены, причем при переходе $LTO2 \to LTT$ частота этих мод не обращается в нуль. Рассматривается также теоретически возможная последовательность структурных фазовых переходов $HTT \to LTT \to LTO2 \to LTO$.

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Cherny A.Yu. E17-94-242

Soft Modes and Structural Phase Transitions in La_2CuO_4

The structural sequence $HTT(D_{4h}^{17}) \to LTD(D_{2h}^{18}) \to LTO2(D_{2h}^{10}) \to LTT(D_{4h}^{16})$ in doped La_2CuO_4 is considered with Landau-type thermodynamic potential proposed by J.D. Axe et al. [3]. Temperature dependence of the soft mode frequencies $\omega(\vec{q}_1)$ and $\omega(\vec{q}_2)$ associated with instability of these phases is calculated, the modes in *HTT* and *LTT* phases are found to be degenerate. It is shown that the mode frequencies are not equal to zero at the temperature of transformation $LTO2 \to LTT$. Inverse sequence $HTT \to LTT \to LTO2 \to LTO$ which is possible theoretically is also treated.

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

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