Negative thermal expansion of HTSC-type structures: low temperature structure measurements on $Eu_{1+x}(Ba_{1-y}R_y)_{2-x}Cu_3O_{7-d}$ compounds and theoretical treatment

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The temperature dependences of the lattice parameters were investigated on the perovskite-like structures $Eu_{1+x}(Ba_{1-y}R_y)_{2-x}Cu_3O_{7-d}$ with Ba substitution by light rare earth, using x-ray diffraction techniques. A negative thermal expansion effect was observed and explained in detail.

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Background

Negative thermal expansion (NTE) has been known for some time in several compounds such as perovskite ferroelectrics [1] and layered superconductors [2]. Unusual lattice dynamics is responsible for this phenomenon. In such multilayer structures the lattice parameter in one of the crystallographic directions is much greater than the characteristic radius of interatomic interaction. This weakens the influence of regularity in the crystal atom distribution on the phonon spectrum and vibration properties of the crystal. Structures of this type take an intermediate state between crystals and disordered systems. We consider this effect for the HTSC perovskite-like system $Eu_{1+x}(Ba_{1-y}R_y)_{2-x}Cu_3O_{7-d}$ with Ba substitution by the light rare earth La. It was shown recently that the structural distortions in $Eu(Ba_{1-x}R_x)Cu_3O_{7+d}$ caused by a rare earth (R = La, Nd, Pr) on a Ba site include a crystallographic transition from orthorhombic to tetragonal symmetry, changes of the «buckling angle» at the CuO_2 plane layer, and changes in ionic bond lengths [3]. This results in suppression of high-temperature superconductivity in these compounds and a number of specific effects in the vicinity of the superconducting transition, which merit a comprehensive study. The present work is part of such a study.

Experimental part

Experiment details

We studied HTSCs with rare earth substitutions for Ba, corresponding to different levels of doping (concentration of carriers) [4] in order to check the attribution of volume changes at low temperatures (below the superconducting transition) to phase transitions. The crystal structure contains layers of Eu, CuO_2, BaO, CuO_{1-d}. Characterization of the samples has shown that procedure of their preparation provided perfect location of the substituting La atoms in Ba positions. A study of the neutron diffraction pat-
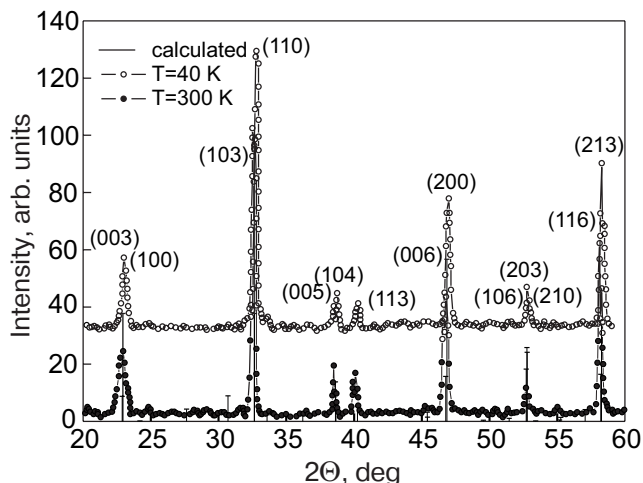
Fig. 1. X-ray diffraction patterns for $Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$.

terns (NDPs) above and below T_c, including measurements in magnetic field up to 4 T, was performed, together with the low temperature x-ray measurements. The x-ray spectra $I(\Theta)$ were registered on a DRON-2.0 diffractometer, using the Bragg−Brentano scheme of focusing (Θ−2Θ scheme). The complete spectra of the diffracted radiation were obtained, with a subsequent identification of the unit cell system and parameters. The accuracy of the intensity measurements was 0.5%. The lattice parameters were determined to accuracy within ± 0.01%. The error bars are shown on the measured curves. The DRON-2.0 diffractometer was also used in the cryogenic experiments: in this case a small-size cryostat for x-ray powder measurements in a temperature range 4.2−300 K was installed. In the experiment an x-ray tube with a copper anode was used ($\lambda_{CuK\alpha}$ = 1.54178 Å). The spectra were registered in the angle range $2\Theta = 20°−60°$.
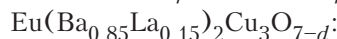
Experimental results

The typical measured diffraction patterns are shown in Fig. 1. The calculated lattice parameters are summarized in Table and illustrated by Fig. 2 for $Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$ as example. The space
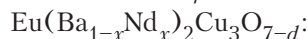
groups and discrepancy factors for these compounds are:

$EuBa_2Cu_3O_{7-d}$:

$Pmmm$, $R_p = 4.2$%, $R_{wp} = 5.4$%, $R_B = 6.2$% ;

$Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$:

$P4/mmm$, $R_p = 4.6$%, $R_{wp} = 5.6$%, $R_B = 6.4$% ;

$Eu(Ba_{1-x}Nd_x)_2Cu_3O_{7-d}$:

$Pmmm$, $R_p = 4.4$%, $R_{wp} = 5.6$%, $R_B = 6.2$% .

The data in Table show a weak orthorhombicity in the *Pmmm* structures.

Here we address ourselves to the problem of anisotropic negative expansion, illustrated by Fig. 2 for $Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$ as example. The same tendency is observed for the non-substituted compound $Eu_1Ba_2Cu_3O_{7-d}$, as our x-ray measurements revealed. The corresponding numerical data are presented in Table.

Discussion

Strong anisotropy of the thermal expansion when, at positive volumetric expansion, the lattice is compressed along any crystal axes (or planes), testifies, first of all, to strong anisotropy of the interatomic interaction.

The possibility of negative values of the linear thermal expansion coefficient (LTEC) along a direction of strong coupling of layered or chained structures (so-called «membrane effect») was first predicted by Lifshits [3] for strongly anisotropic compounds, the phonon spectra of which reveal the so-called bending vibrations with a quadratic dispersion law $\omega(k)$ at $k \to 0$. Later, negative values of the LTEC have been found (see, for example, [5]) for strongly anisotropic layered crystals containing modes with characteristic «quasi-bending» curvature in a long-wave length region of the vibration spectrum (for example, graphite), and for compounds (such as GaSe, GaS, InSe) in which the phonon spectra exibit either a weaker corresponding curvature or the latter is not revealed at
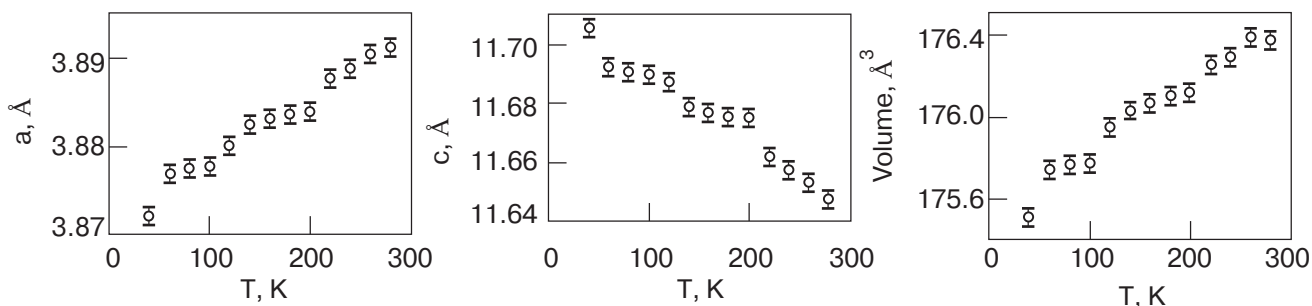

Fig. 2. Temperature dependence of the unit cell parameters for $Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$.

Table. The calculated lattice parameters of the perovskite-like structures $Eu_{1+x}(Ba_{1-y}R_y)_{2-x}Cu_3O_{7-d}$

T, K	a, Å			b, Å		c, Å			V, Å^3		
	$EuBa_2Cu_3O_{7-d}$	$Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$	$Eu(Ba_{1-x}Nd_x)_2Cu_3O_{7-d}$	$EuBa_2Cu_3O_{7-d}$	$Eu(Ba_{1-x}Nd_x)_2Cu_3O_{7-d}$	$EuBa_2Cu_3O_{7-d}$	$Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$	$Eu(Ba_{1-x}Nd_x)_2Cu_3O_{7-d}$	$EuBa_2Cu_3O_{7-d}$	$Eu(Ba_{0.85}La_{0.15})_2Cu_3O_{7-d}$	$Eu(Ba_{1-x}Nd_x)_2Cu_3O_{7-d}$
300	3.8313		3.8186	3.8900	3.8868	11.6699		11.5687	173.9254		171.7042
280		3.8912					11.6481			176.3690	
260		3.8905					11.6534			176.3858	
240	3.8305	3.8888		3.8893		11.6764	11.6571		173.9546	176.2876	
220		3.8877					11.6617			176.2574	
200		3.8839					11.6753			176.1182	
180	3.8295	3.8836		3.8873		11.6791	11.6761		173.8599	176.1030	
160		3.8830					11.6774			176.0682	
140		3.8824	3.8187		3.8904		11.6789	11.5851		176.0364	172.1114
120	3.8243	3.8800		3.8855		11.6838	11.6871		173.6133	175.9423	
100		3.8777					11.6894			175.7683	
80	3.8243	3.8775		3.8841		11.6862	11.6908		173.1325	175.7713	
60		3.8768					11.6930			175.7409	
40		3.8721	3.8184		3.8892		11.7064	11.5871		175.5159	172.0745

all. Recently, similar features were observed on advantageous superconductors like MgB_2. A more general analysis, based on microscopic consideration, of the reasons causing negative LTEC along directions of strong coupling in crystals with strong anisotropy of the interatomic interaction and elastic properties has been proposed in [6,7].

In such strongly anisotropic crystals the amplitude of the atomic vibrations along directions of weak coupling (perpendicular to layers or chains) is much higher than in directions of strong coupling. Displacement of atom along a direction of weak coupling leads to an increase in the distance between atoms within a layer (or chain) of magnitude Δl proportional to the square of this displacement. Consequently, within a layer a compressive force proportional to Δl arises, which is the reason for the anisotropic negative expansion alike the «membrane effect». We suggest the following microscopic description for these compressive forces.

If the potential energy Φ of a lattice is expanded in a number of components u_i of a small displacement of the atoms from equilibrium position up to the cubic term, then the temperature dependence of the principal values of the LTEC tensor $\alpha_{ii}(T)$ in view of translational invariance of the lattice are described by the following expression:

$$D_i \alpha_{ii}(T) = -\frac{1}{2} \sum_{\substack{\mathbf{r},\mathbf{r}' \\ k,l}} \Phi_{ikl}(\mathbf{r},\mathbf{r}') \langle u_k(\mathbf{r}) u_k(\mathbf{r}') \rangle_T, \quad (1)$$

where

$$D_i = \sum_{\mathbf{r}} \Phi_{ik}(\mathbf{r})|x_k|,$$

$$\Phi_{ik}(\mathbf{r}) = \Phi_{ik}(\mathbf{r} - \mathbf{r}') = \frac{\partial^2 \Phi}{\partial u_i(\mathbf{r}) \partial u_k(\mathbf{r}')}$$

are the elements of a force matrix,

$$\Phi_{ikl}(\mathbf{r}, \mathbf{r}') = \Phi_{ik}(\mathbf{r} - \mathbf{r}'', \mathbf{r}' - \mathbf{r}'') =$$

$$= \frac{\partial^3 \Phi}{\partial u_i(\mathbf{r}) \partial u_k(\mathbf{r}') \partial u_l(\mathbf{r}'')}$$

x_i are the components of the radius vectors $\mathbf{r}$ of the equilibrium positions of the atoms; the symbol $\langle u_i(\mathbf{r}) u_k(\mathbf{r}') \rangle_T$ is the correlator of the atom displacements, calculated in the harmonic approximation.

In considering effects nonlinear in the vibrations of a crystal lattice (see, for example, [8]) it is necessary to take into account anharmonicity only in the terms connected to the largest forces of interatomic interaction, while the potential energy of the weak forces of interlayer (or interchain) interactions, as well as noncentral forces, should be considered in the harmonic approach. Therefore in (1) it is possible to neglect the summands, containing correlators of the atomic displacements from different layers or chains, i.e., correlators of the $\langle u_x(\mathbf{r}) u_y(0) \rangle_T$ type. Besides, as in the majority of crystals the central interaction between atoms decreases with distance quickly enough, it is possible to neglect in (1) the summands, containing correlators between the second and more-distant neighbors of the same layer or a chain. Correlators of the $\langle u_\mu(\mathbf{r}) u_\mu(0) \rangle_T$ type for the nearest neighbors (the direction μ is chosen along the strong coupling) grow with temperature not faster than the root-mean-square displacement $\langle u_\mu^2(\mathbf{r}) \rangle_T$, and both these temperature dependences are similar (this follows, for example, from the expressions obtained in [9]). Therefore the behavior of the temperature dependence of the LTEC along a direction of strong coupling of a layered or chained crystal can be described by the rather simple expression:

$$\alpha_{||}(T) = \alpha_{\mu\mu}(T) = A \frac{\partial}{\partial T} \langle u_\mu^2 \rangle_T \left\{ \delta - \frac{\frac{\partial}{\partial T} \langle u_\perp^2 \rangle_T}{\frac{\partial}{\partial T} \langle u_\mu^2 \rangle_T} \right\}. \quad (2)$$

Here $\langle u_\perp^2 \rangle_T$ is the root-mean-square displacement of atoms along a direction of weak coupling, that is, $\langle u_\perp^2 \rangle_T = \langle u_c^2 \rangle_T$ for layered crystals (if ab is the plane of the layers) and $\langle u_\perp^2 \rangle_T = \langle u_a^2 \rangle_T + \langle u_b^2 \rangle_T$ for chained (with the chains built along the $\mathbf{c}$ axis). The parameters A and δ, appearing in (2) are obviously expressed in terms of the anharmonic constants $\Phi_{ikl}(\mathbf{r}, \mathbf{r}')$, but the explicit form of corresponding expressions is not presented here for reasons of space.

Let's analyze the temperature dependence of the quantity

$$\Delta(T) = \frac{\frac{\partial}{\partial T} \langle u_\perp^2 \rangle_T}{\frac{\partial}{\partial T} \langle u_\mu^2 \rangle_T}. \quad (3)$$

For strongly anisotropic crystals the quantities $\langle u_\perp^2 \rangle_T$ are not only much greater than $\langle u_\mu^2 \rangle_T$ but also at lower temperatures are outside of the classical limit. Thus, near the temperature $T_\perp$ (the temperature at which quantity $\langle u_\perp^2 \rangle_T$ approaches the classical limit) the function $\Delta(T)$ has a maximum, the size of which is proportional to $\exp(\gamma^{-1/2})$, where γ is the ratio of the weak interlayer or interchain interaction to the strong interaction along the layers or chains, respectively. Therefore, near this temperature the LTEC $\alpha_{||}$ is anomalously small and may have negative values.

The values of the temperatures of the maxima obtained in [6,7] for the quantities $\Delta(T)$ have shown good agreement with the temperatures of the minima on the measured dependences of the LTEC $\alpha_{||}(T)$ of strongly anisotropic layered crystals [5].

At once we should notice, that in [5–7] crystal structures were considered in which the strong anisotropy of interatomic interaction remains in the long-range order and manifests itself, in particular, in anisotropy of the elastic constants. In crystals such as 1–2–3 HTSC the anisotropy of the elastic constants is insignificant and, moreover, has the other sign, as the sound velocity along the layers is higher than in the direction normal to the layers [10]. At the same time, in such multilayered compounds the lattice period along the c axis is not only higher, than along axes a and b, but also substantially exceeds the characteristic radius of interatomic interaction. This leads to a weakening effect of the crystal structure regularity on the character of quasi-particle excitations. The spectral characteristics of such crystals display the features common to disordered systems. In particular, for the phonon spectra of multilayered structures the presence of quasi-local (weakly dispersed) modes [11–13] is typical. Consequently, the propagation of excitations along the c axis in such systems will be complicated in comparison with their propagation in the layers.

In multilayered lattices, even those for which the macroscopic characteristics are not distinguished by appreciable anisotropy (as, for example, HTSCs of the 1–2–3 type), the interaction between separate atoms or atomic groups can be strongly anisotropic. The «damped» propagation of the interaction between layers inherent in substances of the specified class may result in appreciable manifestation of such local anisotropy both in phonon spectrum [14] and in behavior of some vibrational characteristics, in particular the root-mean-square displacement of atoms from separate layers along various crystal directions.
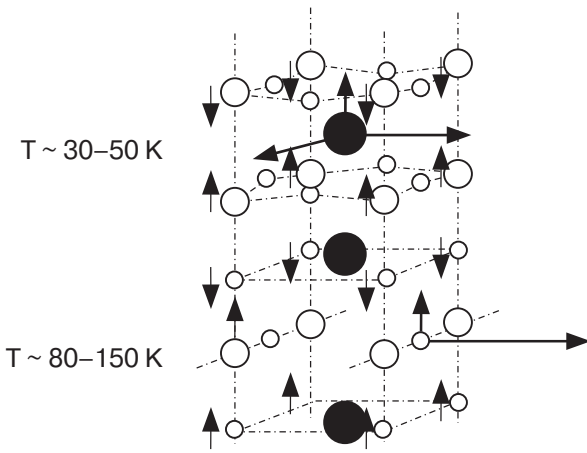
Fig. 3. Schematic presentation of the reasons of negative temperature expansion along the **c** axis in the $EuBa_2Cu_3O_{7-d}$ structure. The thick arrows indicate the comparative amplitudes of atomic vibrations in different crystallographic directions. The thin arrows demonstrate compression of the corresponding interlayer spacings.

Some multilayered HTSC, for example $Bi_2Sr_2CaCu_2O_x$, show the anisotropy of elastic constants inherent to layered crystals, and negative thermal expansion in the direction of the layers [15], which can be described by the formula (2). At the same time, for multilayered structures such as 1−2−3 HTSC, where the interlayer interaction between all layers is of the same order, and the intralayer interaction varies substantially from layer to layer. Local anisotropy of the «chain» type is characteristic for layers with weak intralayer interaction (a layer of the rare earth and a layer of Cu−O chains), that is, in these layers the root-mean-square displacements of the atoms in the layer plane are appreciably higher than the root-mean-square displacements of the same atoms in the direction normal to the layers and lie outside the classical limit at lower temperatures. Therefore there can exist temperature intervals, in which the interlayer distances $Cu_2O−Eu−Cu_2O$ and $BaO−CuO−BaO$ compress with temperature increase, which is the possible reason for the negative values of LTEC along the **c** axis (Fig. 3).

The temperature dependence of each spacing change can be described by some local thermal expansivity $\alpha_c^{(l)}(T)$ for which a relation of the form (2) is true, namely:

$$\alpha_c^{(l)}(T) = A \frac{\partial}{\partial T} \langle (u_c^l)^2 \rangle_T \{\delta^{(l)} - \Delta^{(l)}(T)\} , \quad (4)$$

where the index l numbers the atomic layers (R or CuO, respectively), and the functions $\Delta^{(l)}(T)$ are defined similarly to (3) by the addition of the index l for the corresponding root-mean-square displace-
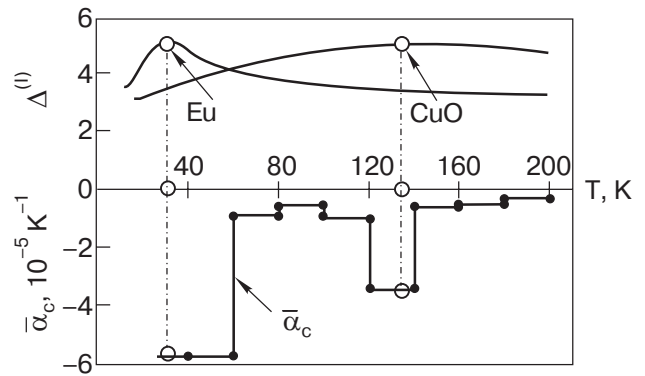

Fig. 4. Temperature dependences of the $\Delta^{(l)}(T)$ values for Eu and CuO layers of the compound $EuBa_2Cu_3O_7$ and the temperature dependence of the LTEC $\bar{\alpha}_c(T)$ averaged over temperature intervals between experimental points.

ments. Then $\langle (u_i^l)^2 \rangle_T$ ($i = a, b, c$) means either the root-mean-square displacement $\langle u_i^2 \rangle_T^R$ itself for the layers of rare-earth elements, or the half-sum $\frac{1}{2} \{\langle u_i^2 \rangle_T^{Cu} + \langle u_i^2 \rangle_T^O\}$ for the CuO layers.

Calculation of the temperature dependences $\Delta^{(l)}(T)$ was made by the method of J-matrices (see, for example, [16−18]). Necessary data on force constants are obtained on the basis of the data of [19−22].

Results of the calculation are presented in a Fig. 4 along with the temperature dependence of the average values of the LTEC along the **c** axis on each of the temperature intervals between the experimental points (see Table and Fig. 2):

$$\bar{\alpha}_c(T \in [T_i, T_{i+1}]) = \frac{2}{T_{i+1} - T_i} \frac{c(T_{i+1}) - c(T_i)}{c(T_{i+1}) + c(T_i)} .$$

Temperatures of maxima on curves $\Delta^{(l)}(T)$ get on intervals of the least values $\bar{\alpha}_c(T)$ where speed of reduction lattice parameter c is the greatest (see Table), partial replacement of Ba by La does not lead to appreciable change a phonon spectrum and oscillatory characteristics considered here). The good agreement of the results of calculation and experiment certainly testifies in favor of the mechanism offered here for the negative thermal expansion along the **c** axis in the considered compound, based on the crystal lattice dynamics in the quasi-anharmonic approach. At temperatures $T \leq 50$ K negative thermal expansion is caused by compression of interlayer spacings $Cu_2O \leftrightarrow Eu \leftrightarrow Cu_2O$, and at 80 K $\leq T \leq 150$ K by those of $BaO \leftrightarrow CuO \leftrightarrow BaO$ (see Fig. 3). At temperatures above 200 K an even faster linear decrease of the parameter c with temperature is observed, which is not explained by the proposed model (in the temperature range 260−280 K the crystal size decreases), as in this temperature range the quasi-harmonic lattice dynamics becomes in-applicable. It should be noted that

it follows from the experimental curves that at $T \leq$ ≤ 180 K the LTEC becomes practically zero. Thus testifies for independent mechanisms responsible for the negative thermal expansion at high (above 200 K) and low temperatures $T \leq 140$ K, as considered by us, or at least for a weak effect of the «high temperature» mechanism on the thermal expansion at $T \leq 180$ K. The results do not show any significant contribution of the BaO layers to the negative expansion.

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