Anomalous behavior of thermal vibrations of atoms as a result of the phase transition of $Tl_2Ba_2CaCu_2O_8$ single crystals to the superconducting state

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An x-ray diffraction analysis reveals that structural parameters of a $(Tl_{0.93}Cu_{0.07})_2Ba_2 \cdot (Ca_{0.88}Tl_{0.12})\ Cu_2O_8$ single crystal with $T_c = 100$ K behave in an anomalous way as a result of a phase transition to the superconducting state. The anomalous temperature dependence is seen particularly clearly in parameters of thermal vibrations of atoms. It thus becomes possible to draw conclusions about the changes in the valence state and the chemical bonds (i.e., the electronic structure) of atoms in the crystal upon the phase transition. Substantial changes in the phonon spectrum in the course of this phase transition are indicated.

The method of x-ray diffraction has been used for many years to study first-order phase transitions in ferroelectrics, solid electrolytes, and other crystalline materials. This analysis method can reliably establish the nature of the atomic restructuring which occurs in the course of these transitions, and it allows one to compare this restructuring with the physical properties of the crystals before and after the phase transition. Structural studies of first-order phase transitions provide the most reliable information for establishing the relationships between atomic structure and physical properties of single crystals.[1–3]

A second-order phase transition in its pure form is not related to an atomic restructuring in a crystal. However, a change in the electronic structure of a compound affects the nature of the chemical bonds of the atoms in the crystal, so it should have a direct influence on the characteristics of thermal atomic vibrations. Precise structural studies make it possible to work from x-ray or neutron-diffraction data to determine the thermal vibrations of each of the basic (crystallographically independent) atoms of the structure; the anisotropy and anharmonicity of these vibrations are taken into account here. In other words, structural studies of second-order phase transitions in crystals provide a wealth of information on the local behavior of each of the basic atoms of the structure in the course of the transition. Shevyrev *et al.*[4] have shown, for the $KMnF_3$ crystal, of cubic symmetry with the barium titanate structure, that an analysis of the thermal motion of the atoms over a temperature interval of tens of degrees, before the temperature at which a displacive phase transition occurs, provides information on whether a transition occurs and on the nature of this transition to the tetragonal phase. A Fourier transformation of the parameters of the ther-

mal atomic motion, found with allowance for the anharmonic components, puts the distribution in crystal space of the probability density for an atom at a given spatial point in the course of its thermal motion. Analysis of such distributions provides information on which atoms will undergo displacements, and in which directions, in the course of the forthcoming phase transition. In this letter we are reporting a study of the behavior of structural properties of a single crystal of the thallium superconductor $(Tl_{0.93}Cu_{0.07})_2Ba_2 \cdot (Ca_{0.88}Tl_{0.12})Cu_2O_8$ as it undergoes a transition to a superconducting state at $T_c = 110$ K. The structural data from Refs. 5 and 6, obtained at temperatures of 296, 160, and 60 K, have been supplemented with some structural refinements based on x-ray diffraction, of the same crystalline sample, at 130 and 90 K. The single crystal of the 2212 Tl phase was grown, and its conductivity studied, at the Institute of Solid State Physics, Russian Academy of Sciences.[5] The symmetry of the crystal is tetragonal before and after the phase transition; its space group is $I4/mmm$; and its lattice constants at room temperature are $a = 3.852(2)$ and $c = 29.290(6)$ Å . One distinguishing feature of this structure is the occurrence of isomorphic substitutions. The Tl atoms occupy their primary site in the structure to an extent of 93%. The electron-density patterns indicate that 7% of the vacancies are filled by much lighter atoms. These are most probably Cu atoms. Up to 12% of the sites of the Ca atoms are filled statistically by Tl atoms. A second distinguishing feature of the structure is a disorder (a displacement from the fourfold symmetry axis) of the Tl atoms and of the O3 oxygen atoms bound to them. These displacements lower the local symmetry to orthorhombic, without changing the average tetragonal symmetry of the crystal.

The basic conclusions reached in an analysis of the behavior of structural properties of $Tl_2Ba_2CaCu_2O_8$ single crystals upon the transition to the superconducting state are as follows. The volume of the unit cell of the crystal decreases as the crystal is cooled in the customary way for thermal deformation, and this volume does not react (at the accuracy of our measurements) to the phase transition to the superconducting state. The lattice constants $a = b$ of the tetragonal cell shrink rapidly near the phase transition. The primary cause of this shrinkage is an anomalous shortening of the Cu–O1 interatomic distances in the cuprate plane, which is evidence of a strengthening of the corresponding chemical bonds when the crystal goes superconducting. There is a simultaneous decrease in the corrugation of the CuO_2 lattice. The behavior of the volume V is offset by a slowing of the decrease in the lattice constant c near $T_c = 110$ K (Fig. 1). It is difficult to analyze the situation regarding the Tl atoms because of their statistical disorder in the structure. The Ba atoms react to the phase transition in an extremely noticeable way. These atoms move closer to the cuprate lattice. Figure 2a shows a fragment of the structure and the directions in which the Ba and O1 atoms move in the course of the phase transition (a complete figure of the structure is given in Ref. 6).

However, the topic of greatest interest is the behavior of the characteristics of the thermal vibrations of the atoms of the structure when the single crystal goes superconducting. Figure 2b shows the mean square displacements of the Ba and Cu atoms from their equilibrium positions in the course of the thermal vibrations before and after the phase transition. Since the experimental points closest to T_c are ± 20 K

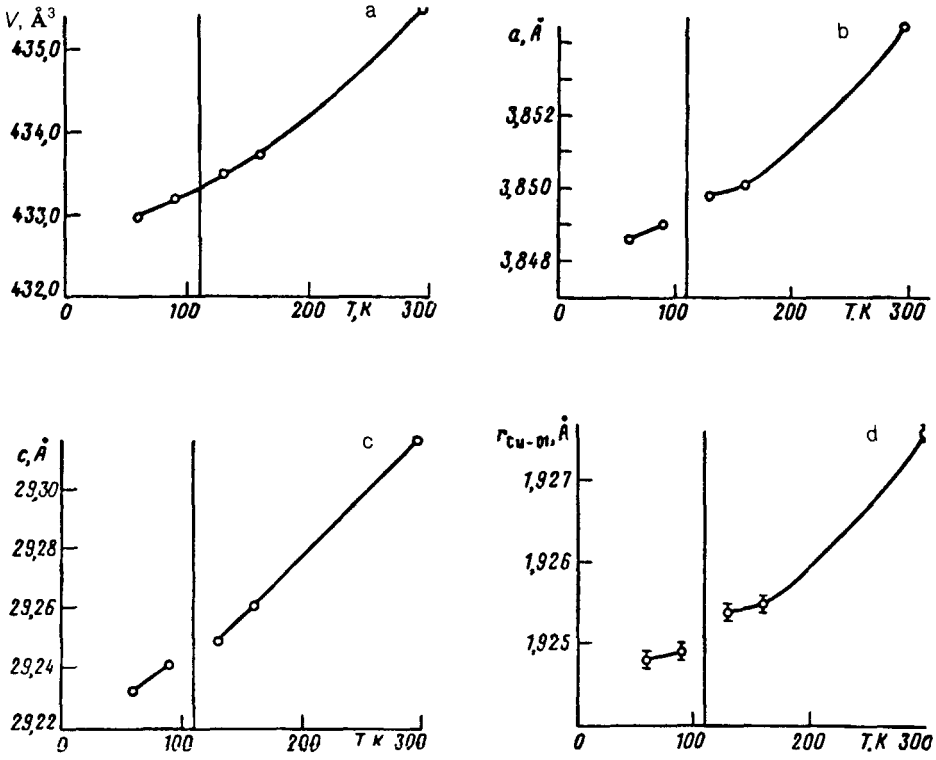

FIG. 1. Temperature dependence of the volume of the unit cell, V, of the lattice constants $a=b$ and c, and of the Cu–O1 interatomic distance in the cuprate network of a $Tl_2Ba_2CaCu_2O_8$ single crystal. The vertical line is the superconducting transition temperature, $T_c=110$ K.

away, all that we can say with confidence is that there is an anomalous behavior of these properties near the transition to the superconducting state. The Ca atoms are fixed at the symmetry center and in fact serve as origin for a description of the structure. With regard to the Tl atoms, we note that their disorder causes a strong correlation between their static displacements and the thermal parameters, hindering a reliable determination of the latter.

Being the lightest atoms in this compound, the oxygen atoms yield the least accurate information from the x-ray diffraction studies. The standard deviations of the oxygen parameters are considerably larger than the corresponding standard deviations for the heavy atoms. This comment applies, in particular, to the parameters of the thermal vibrations of these atoms. Figure 2c shows characteristics of anisotropic thermal vibrations of an O1 atom from the cuprate network. The position of this atom in the structure can be determined more reliably than that of any other oxygen atom. The smallest amplitudes of the thermal vibrations of the O1 atoms, u_{11}, are naturally directed along –Cu–O1–Cu– bonds. The amplitudes u_{22}, of intermediate magnitude, are perpendicular to these bonds and lie in the cuprate plane. The largest amplitudes,

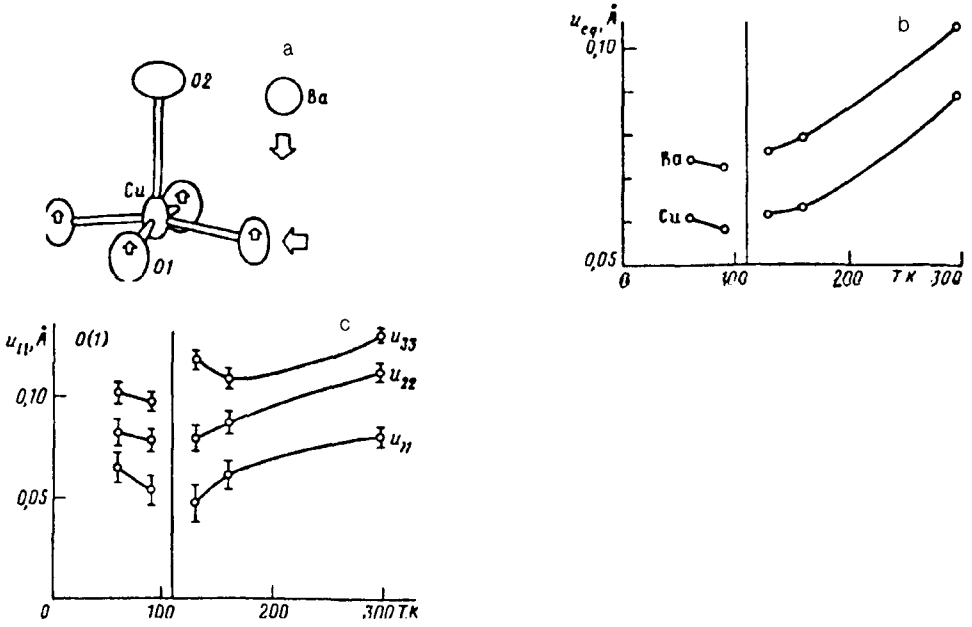

FIG. 2. a—The structural fragment which undergoes the greatest changes upon the transition of the single crystal to the superconducting state; b—temperature dependence of the parameters of thermal vibrations of the Ba and Cu atoms shown in this structural fragment, in the isotropic approximation; c—the same, but with allowance for the anisotropy of the O1 atoms.

u_{33}, are perpendicular to the cuprate plane. All these parameters exhibit an anomalous behavior near the phase-transition temperature.

The sharp changes in the parameters of the atomic thermal vibrations when the crystal goes superconducting indicate that the phonon spectrum plays an important role in this phase transition. Unfortunately, we were unable to find in the literature any study of the behavior of the parameters of thermal atomic vibrations upon the transition of classical superconductors of the $(Ge,Nb)Nb_3$ type to the superconducting state. The need for such studies is obvious: They would provide additional information on the extent to which the superconductivity mechanisms in classical superconductors and high-T_c superconductors are similar and dissimilar. There is every reason to assume that an analysis of the behavior of the parameters of thermal atomic vibrations in the course of second-order phase transitions will provide extremely meaningful local information on the mechanisms for such transitions.

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