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Scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (28 September 1994)

A scientific session of the General Physics and Astronomy Division of the Russian Academy of Sciences was held in the L P Kapitza Institute for Physical Problems on 28 September 1994. Three papers were presented:

(1) **V I Simonov** "Precision x-ray diffraction investigations of single crystals of HTSCs: Report on the 4th International Conference 'Materials and Mechanisms of Superconductivity of High-Temperature Superconductors' (July 1994, Grenoble, France)";

(2) **V B Timofeev** "Report on the XXII International Conference on Physics of Semiconductors (August 1994, Vancouver, Canada)";

(3) **R A Suris** "Report on the International Conference 'Superlattices, Microstructures and Microinstruments' (August 1994, Banff, Canada)".

An abridged version of the first paper is given below.

PACS numbers: 74.72.–h; 61.10.–i

Precision x-ray diffraction investigations of single crystals of HTSCs: Report on the 4th International Conference "Materials and Mechanisms of Superconductivity of High-Temperature Superconductors" (July 1994, Grenoble, France)

V I Simonov

The time lapse between the third conference in Japan and the fourth conference in France was extended to three years. This had its effect on the overloaded scientific program of the conference in Grenoble. The organising committee selected 120 reports and over 2000 posters. In each of the four poster sessions from 536 to 583 posters were presented. Clearly, each participant could only have taken in a small portion of this mass of information. Below an attempt is made (naturally a subjective one) to highlight the most interesting work in the field of structural investigations of HTSC crystals.

An overview of classical, organic (including fullerenes), and high-temperature superconductors can be clearly illustrated by the plots of J Jerome which were published in 1992. These plots are reproduced in Fig. 1. The curves for organic and high-temperature superconductors were the motivation for a search of new materials with higher T_c. In fact, in 1993 first one and then a series of new mercury-containing superconductors were synthesised.

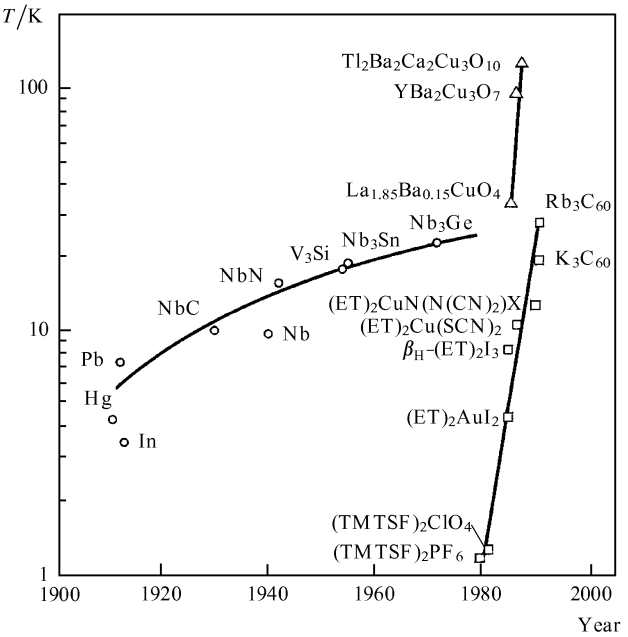

Figure 1. The advance of new materials towards a higher temperature region of normal-to-superconducting transition for classical, organic, and high-temperature superconductors according to the data of J Jerome (1992).

At present the record of $T_c = 135$ K, reliably established and reproduced in several laboratories, belongs to the compound $HgBa_2Ca_2Cu_3O_{8+\delta}$ from this series. Naturally, works on mercury-containing superconductors of the general chemical formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ received special attention. Structural studies were presented for compounds with n in the range from 1 to 6. E V Antipov, who is one of the co-authors of the first publication on the mercury-containing compounds, delivered the report on the new materials in the first plenary session.

Atomic models of the mercury-containing superconductors presented at the conference are similar, in the first approximation of isostructure, to Tl-phases of the series $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. However important distinctions between these two series of compounds were found. First of all they differ in the population densities of the oxygen positions in the Tl and Hg layers of structures, respectively, and also in the level of their structural disordering, patterns of isomorphic replacements, etc.

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I want to emphasise that most of the structural studies on mercury-containing superconductors were carried out for ceramic specimens. At the conference only a few results were reported and these were for single crystals of small size and poor quality. They did not always agree with the results for ceramic specimens. Precise structural studies of the Hg-phases of single crystals have yet to be carried out. They have been held up by the lack of single crystals of appropriate size and quality, although first reports that Hg-phases of such crystals had been obtained were delivered at the conference.

The next series of HTSCs which attracted particular interest at the conference was the series of cuprate compounds with carboxyl groups which replace square CuO_4 groups in particular positions: for example, as in the compound $(Cu_{0.5}C_{0.5})_2Ba_3Ca_3Cu_4O_{13}$ or $(Cu_{0.5}C_{0.5})_2Ba_3Ca_4Cu_5O_{15}$. The most impressive results for these compounds were obtained by atomic-resolution electron microscopy.

Precise structural investigations of crystalline HTSCs were performed for materials for which the technology of obtaining single crystals of x-ray diffraction quality and of appropriate size had been mastered. As an example of such investigations one can cite the results for thallium compounds.

The single crystals $TlBa_2LaCu_2O_7$ and $TlBa_2CaCu_2O_7$ have similar structure. The lanthanum phase does not reach a superconducting state whereas the calcium phase undergoes such a transition at $T_c = 80$ K. In the latter case it is important that up to 13 % atoms of Ca are replaced by atoms of Tl in their crystallographic positions. This fact implies that the formal valency of copper is exactly +2 in the normal state but increases to +2.43 in the superconducting state.

Precise structural investigations confirm this difference in the geometry of the cuprate layers. The atomic spacings Cu–O(1) are 0.056(1) Å shorter in the cuprate layer in the superconducting phase than those in the lanthanum phase. The spacing between Cu–O(2) and the apical oxygen is 2.451(7) Å in the normal phase and increases to 2.745(9) Å in the superconducting phase. The cuprate layers are less embossed in the superconducting phase (Fig. 2).

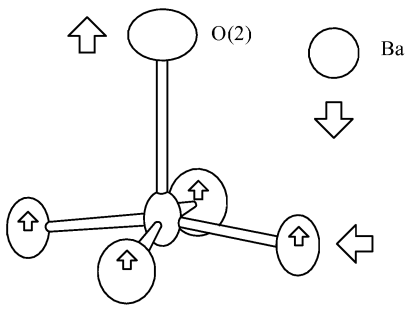

Figure 2. The change in the geometry of the cuprate layer in going from the normal compound $TlBa_2LaCu_2O_7$ to $TlBa_2CaCu_2O_7$ ($T_c = 80$ K).

It is interesting to compare these changes with the structures of cuprate layers of different specimens of single crystals of $Tl_2Ba_2CuO_6$ characterised by T_c in the range from 12.4 to 110 K. A clear dependence was established between T_c and the lattice constant c of the unit cell of the crystal. This parameter increases monotonically on increase in T_c. The main structural reason for such behaviour of c is that the spacing between Cu–O(2) and the apical oxygen is changed, as in the example quoted earlier. In several works it was established that up to 5–7 % atoms of Tl are isomorphically replaced by atoms of Cu in the Tl phases 2201.

Yet another important structural feature of Tl phases 2201 with different T_c is a deviation from stoichiometry relative to oxygen. An additional oxygen position with a low population density (about 9%) was established in this case in single crystals with $T_c = 30$ K in the double layers of Tl atoms. Detailed examination of the structure of a specimen with $T_c = 110$ K to this end did not reveal an additional oxygen. The change in the geometry of the cuprate layers with increasing T_c is the same in the case of the Tl phases 2201 as in going from a lanthanum compound to the superconducting calcium compound in the Tl phases 1212. Certainly, in the cuprate layers the copper is located in deformed octahedrons in phases 2201 as opposed to phases 1212.

At the conference debates continued on whether anomalies in the behaviour of structural parameters of single crystals of HTSCs can be registered by x-ray diffraction methods in the normal-to-superconducting transition of a crystal. Substantial anomalies were established in the vicinity of the temperature T_c in the behaviour of the parameters of thermal vibrations of those atoms whose chemical bonds in the crystal were most affected by the change in the electron structure occurring in the normal-to-superconducting transition. In this case parameters which characterise the anisotropy in the thermal vibrations of atoms behave differently.

In Fig. 3 the behaviour of the mean-square deviation from equilibrium is presented for the thermal motion of the atom O(1) from the cuprate plane of a single crystal $(Tl_{0.93}Cu_{0.07})_2Ba_2(Ca_{0.90}Tl_{0.10})Cu_2O_8$ before and after phase transition. Thermal vibrations of this atom are described by a triaxial ellipsoid. The shortest axis of the ellipsoid u_{11} is directed along the strong chemical bond Cu–O(1). The mean axis of the ellipsoid lies in the cuprate plane

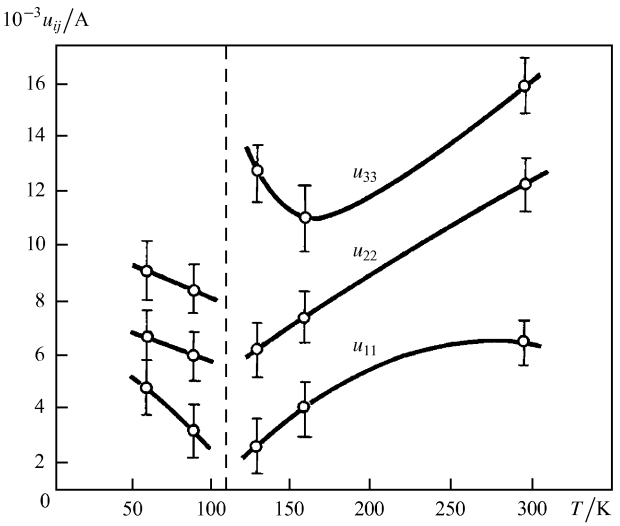

Figure 3. Anomalies in the behaviour of the anisotropic parameters of thermal vibrations of the atom O(1) from the cuprate layer in the compound $(Tl_{0.93}Cu_{0.07})_2Ba_2(Ca_{0.90}Tl_{0.10})Cu_2O_8$ in normal-to-superconducting transition ($T_c = 110$ K).

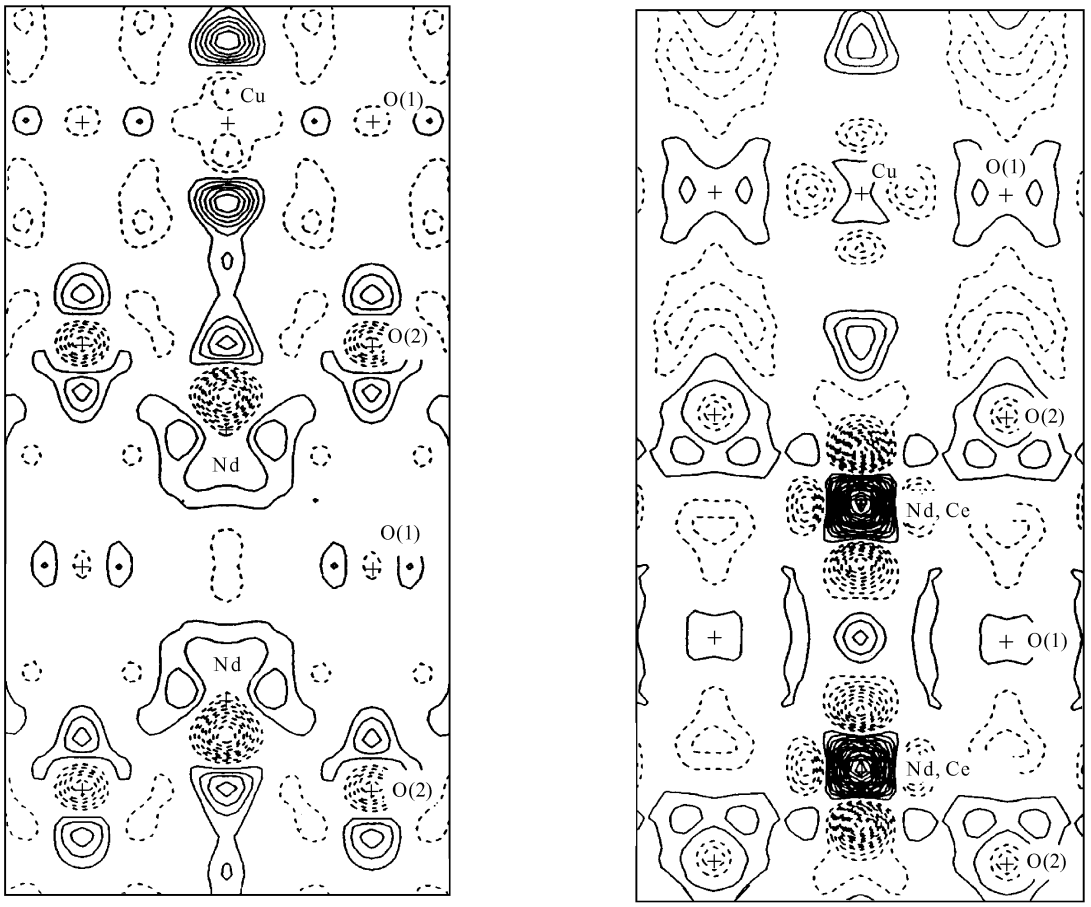

Figure 4. The cross-section (010) of three-dimensional distributions of the deformation electron density in the compounds Nd_2CuO_4 and $(Nd, Ce)_2CuO_4$.

and is perpendicular to the Cu–O(1) bond. The axis u_{33} which characterises the maximal amplitudes of vibrations is perpendicular to the cuprate plane.

Thermal vibrations of an atom in a crystal depend on the geometry and the strength of chemical bonds of the atom for a given temperature. The analysis of the behaviour of the parameters of thermal vibrations of atoms during the phase transition to the superconducting state makes it possible to deduce changes in the chemical bonds which, in turn, depend on the electron structure.

Precise structural studies also make it possible to identify small displacements of those atoms in the structure whose chemical bonds experience changes in the phase transition. Changes in the geometry of the structure of the cuprate layer in single crystal $(Tl_{0.93}Cu_{0.07})_2Ba_2(Ca_{0.90}Tl_{0.10})Cu_2O_8$ in the normal-to-superconducting transitions are similar to the scheme in Fig. 2.

A structural study of the spatial distribution of the valence electrons in atoms of a crystal is very complicated, since it is difficult to obtain reliable experimental data by x-ray diffraction methods. This problem can be solved by means of maps of the so-called deformation electron density. To this end it is necessary to find the differences between spatial distributions of experimental electron density retrieved from s-ray diffraction data and the computed electron density for free atoms (i.e. atoms not participating in chemical bonds) placed in the positions of atoms of the structure in question with the same thermal vibrations as atoms of the investigated crystal.

The maxima of electron density in the maps of deformation electron density indicate the sites in the structure where the valence electrons migrate when chemical bonds are formed. The regions of negative electron density in difference maps indicate the sites from which these electrons migrated. Naturally the integral of a three-dimensional map of deformation electron density over the lattice cell is zero.

Maps of deformation electron density provide direct information on the population densities of orbitals of atoms in various parts of the volume when a crystal is formed. In Fig. 4 examples of such maps are presented for a matrix crystal Nd_2CuO_4 and a cerium-doped single crystal $(Nd, Ce)_2CuO_{4-\delta}$.

Precise structural investigations of HTSCs are not yet complete. New reliable information on the dynamics of thermal motion of atoms in crystals of HTSCs and the behaviour of valence electrons in atoms in the course of normal-to-superconducting transition of a single crystal based on these investigations may be expected in the near future.

At the close of the conference it was announced that the 5th International Conference "Materials and Mechanisms of Superconductivity of High-Temperature Superconductors" will be held in the spring of 1997 in Peking. The organising committee promised to publish the proceedings of the conference in Grenoble in December 1994 in five issues of the journal *Physica C*.