ACCURATE X-RAY STRUCTURAL INVESTIGATIONS OF SINGLE CRYSTALS OF HIGH-Tc MATERIALS

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ABSTRACT. The atomic structure of HTc-superconducting single crystals was refined using X-ray diffraction methods:  
1. Different degree of ordering in Sr atom distribution over La sites and Tc dependence on it were revealed in La-phases.  
2. Oxygen atom ordered arrangement was determined in Y-phases with various oxygen content. Orthorombic local symmetry of single crystals was detected in the so-called tetragonal superconducting Y-phases.  
3. The changes of structural parameters during the superconducting phase transition were established in Tl2Ba2CaCu2O8.  
4. Distribution of valence electrons in space was obtained for Nd2CuO4.

1. Introduction

In 1911 the Dutch physicist G. Kamerling-Onnes discovered in the course of a study of the behaviour of electrical resistance of mercury upon temperature lowering that for T < Tc = 4.15 K the resistance dropped down to zero. It was shown later that at the critical temperature Tc a second-order phase transition occurs. This new state was called the superconducting state. Then Kamerling-Onnes observed that the application of a strong magnetic field eliminated the superconductivity. A fundamental property of superconductors – the Meissner effect – was discovered only 22 years later. The experiments conducted by W. Meissner and R. Oxenfeld, in which an appropriate sample was pushed from the magnetic field, proved that the external field does not penetrate the bulk of the superconducting material. The physical reason for the Meissner effect is as follows. Nonattenuating currents arise in the surface layer of a superconductor hundreds of angstroms thick under the effect
of an external magnetic field. These currents compensate for the external field inside the sample. The theoretical understanding of superconductivity was being developed rather slowly. It was only in 1934 that the brothers F. and G.Londons suggested the first version of the phenomenological theory of electrodynamic properties in superconductors. In 1937 L.D.Landau predicted the structure of an intermediate state in superconductors which was later determined experimentally by A.I.Shal'nikov and co-workers. The generalized phenomenological theory of superconductivity was founded by V.L.Ginzburg and L.D.Landau in 1950. Based in their behaviour in a magnetic field superconductors can be divided into two groups: first- and second-order superconductors. In the former, superconductivity in the entire bulk is destroyed by a magnetic field. The latter superconductors were described in 1952 by A.A.Abrikosov. These superconductors are characterized by two different values of the critical magnetic field. At intermediate values of an external magnetic field a second-order superconductor is pierced by the Abrikosov swirls whose density increases with the field and the superconductivity is retained only beyond these swirls. The superconducting state is a quantum state of a macroscopic object. According to the theory, the magnetic flux piercing a superconducting ring with nonattenuating current is quantized. This effect was observed experimentally for the first time in 1961 and enabled the determination of the charge of the particles that are current carriers in superconductors. This charge was twice as large as the charge of an electron. This observation is in conformity with the effect of formation of stable pairs by electrons with opposite spins in a crystal lattice, which was predicted by L.Cooper in 1956. It is these Cooper pairs that are carriers of nonattenuating current in superconductors.

A rigorous microscopic theory of superconductivity was developed in 1957-1958 in the works of J.Bardeen, L.Cooper, G.Schrieffer and, at the same time, by N.N.Bogolyubov. It is based on the following. Electrons of a Cooper pair, which exchange phonons with the lattice, are attracted and form a particle with a zero spin. These particles obey Bose-Einstein statistics. Bose condensation of such particles and their superfluidity takes place in these superconductors. Since each particle carries a 2e charge, superfluidity of a quantum electronic liquid leads to superconductivity.

In the period 1911-1985 superconductivity was found experimentally in dozens of pure metals and in hundreds of various alloys and intermetallic compounds. An unrivalled superconductor was Nb$_3$(Ge$_{0.8}$Nb$_{0.2}$) with $T_c = 23.2$ K. The structure of these crystals is shown in Fig.1. Superconductivity was discovered in some strongly doped