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Invited

Current Status of Developments of Oxide Superconductors

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The discoveries of a series of the high critical temperature oxide superconductors are reviewed. The physical properties of these materials have been essentially uncovered. Efforts to fabricate practical materials out of 90K-class oxide superconductors have been initiated quite extensively. So far the thin film fabrication has been relatively successful in obtaining the sufficient critical current, hence the phase of development seems to be entering the one to demonstrate the proto-type devices.

I. Discovery of High Tc Superconductors

The following six successive break throughs in finding the new materials have led us to the present excitement in the wide spread fields both of basic and applied researches of superconductivity.

1) Indication of the presence of high Tc superconductivity, up to 35 K, in a mixed phase system of Ba-La-Cu-O by IBM Zurich group (Apr.-Oct. 1986).[1,2]

2) Confirmation of the superconductivity in the same system and the subsequent identification of the superconducting phase as $(La_{1-x}Ba_x)_2CuO_4$ by Univ. of Tokyo group (Nov.-Dec. 1986).[3,4]

3) Substitution of the component ions to create a higher Tc material $(La_{1-x}Sr_x)_2CuO_4$ of 40K-class by Univ. of Tokyo Group (Dec. 1986).[5]

4) Substitution of the component ions to create even a higher Tc Y-Ba-Cu-O system of 90K-class by Alabama-Houston univ. group (Feb. 1987).[6]

5) Determination of the phase and crystal structure of $Ba_2YCu_3O_7$(Mar.-Apr.1987)[7-10]

6) Discovery of magnetic superconductors of the same 90K class as $Ba_2LnCu_3O_7$ with Ln = every rare earth elements except Pr and Ce. (Mar. 1987)[11-14]

Although, reports of finding higher Tc superconductors with Tc's up to 50 have been presented, they still await reliable experiments.

II. Properties of the high Tc Oxide Superconductors.

Various properties are similar for the 40K and 90K-class oxides and will be summarized for the 90K-class materials.

1) The crystal structure is basically of perovskite type. Ba and Y (Ln) are preferentially sited to form layers of Ba to Sandwitch the one of Y, resulting in a triple-layer structure. Oxygen ions on the Y plane are essentially missing. On the Cu-O layer between the two adjacent Ba layers, oxygen ions are preferentially depleted to create inequivalent unit cell parameters a and b as shown in Fig. 1.

2) The low carrier density of p-type in the range of $5\times10^{21}cm^{-3}$ as indicated by the

Hall measurements (Fig. 2) and plasma edge observation in the near infrared region reflectivity (Fig. 3). This low density of carriers seems to raise potential barriers at interfaces due to the weak screening of the interface charges. Also it should affect the device characteristics when the material is used as the non-equilibrium superconducting devices as well as proximity effect transistors.

3) A moderate value of the density of states at the Fermi energy N(0) as indicated by specific heat measurements (Fig. 4)[15] and Pauli paramagnetism. In Fig. 4 is illustrated a relationship between Tc and the electronic specific heat coefficient ± which is in proportion with N(0). The N(0) values of the high Tc oxides are in the range 1-2 states$\cdot$eV$^{-1}\cdot$Cu-atom$^{-1}\cdot$spin^{-1} which are in the typical range of the d-band metal superconductors, athough they become smaller when compared per volume. They are slightly larger than expected from band calculations.[16]

4) Apparently large electron-correlation interaction as suggested by the temperature dependence of the thermo-electromotive force (Fig. 5). Because of this, the superconductivity is closely situated in the neighborhood of Mott-Hubbard type metal-to-insulator transition as well as of magnetism.

5) A large superconducting gap Δ. In the case of BCS superconductors, the factor $2\Delta/kTc$ is expected to be 3.52. The recent tunneling measurements mostly find this factor in the range 4 to 7, indicating the superconductivity in the strong coupling region[17], although it is still controvertial. This large factor as well as the high Tc make the gap much larger than that of the conventional superconductors, almost by a factor of ten. This should lead the electronic devices to be used in the much higher voltage region. But the energy consumption per switching should increase accordingly. Since the superconducting condeasation energy is propotional to $N(0)\Delta^2$, the present material should have a much larger difference in the free energy change associated with the superconducting transition.

6) A strong anisotropy observed e.g. for upper critical field Hc_2 up to several times[18] and the critical current Jc up to 100 times.[17] This may cause some inconvenience for the device application, but may be more seriously for the polycrystalline wire application.

7) Very short coherence length ξ_0 in the range of 1nm to several nm.[18] This is due mainly to the large gap parameter and the narrow band width. The small ξ_0 value is regarded to require a more uniformity e.g. in the thickness of the ultra-thin insulating film for the J-J device.

8) An extremely large variation of oxygen content. The oxygen deficiency δ may vary from ca. 0 to 1 when the formula is expressed as $Ba_2YCu_3O_{7-\delta}$ as shown in Fig. 6.[19] Because of this, the material needs to be slow cooled for acquisition of sufficient oxygen to minimize the adverse effect of oxygen deficiency on the superconducting properties. The oxygen is depleted preferentially along b-axis as shown in Fig. 7.[20]

9) A phase transition from tetragonal to orthorhombic structure takes place in association with the decrease in the oxygen deficiency. Above 500°C, this transition occurs at $\delta \sim 0.3$. At lower temperatures, the orthorhombic structure persists over $0 \lesssim \delta \lesssim 0.7$.

10) Weak Josephson coupling characteristics are observed in the polycrytalline specimen

as well as along the c-axis in the nearly single crystalline specimens.[19] This is probably associated with grain boundaries or sub-boundaries but needs further studies for the clear explanation.

11) The material tends to react with water and carbon dioxide in the atmosphere which deteriorates the superconducting properties and hence should be avoided.

III. Perspectives in the Application.

As far as the electronic applications are concerned, the first goal, a high enough Jc, has been achieved. Hence the demonstration of the high performance proto-type devices are being the next target. For the polycrystalline wires, low Jc is still a problem to be overcome by a significant improvement.

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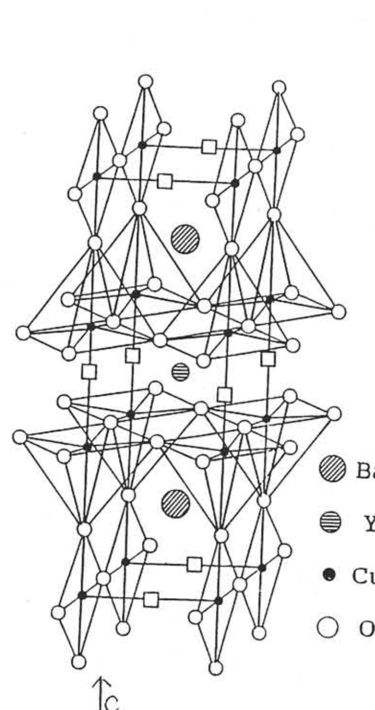

Fig. 1 Crystal structure of $Ba_2YCu_3O_7$.

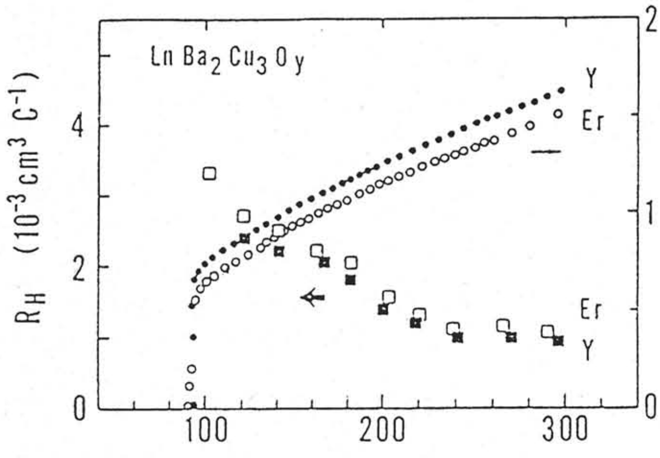

Fig. 2 Temperature dependence of the resistivity and the Hall coefficient for $Ba_2YCu_3O_7$ together with $Ba_2ErCu_3O_7$.

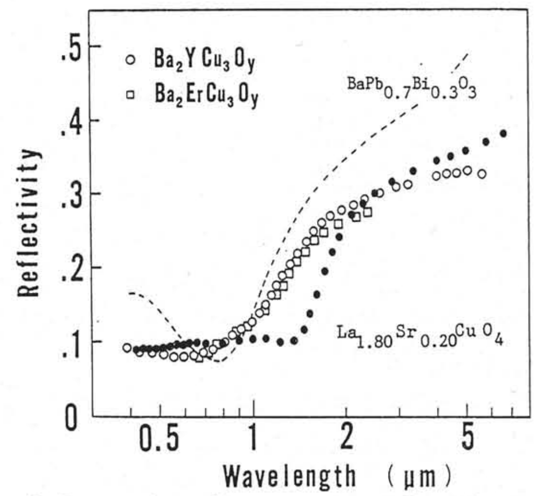

Fig. 3 Optical reflectivity of $Ba_2YCu_3O_7$ compared with the other oxide Super-conductors.

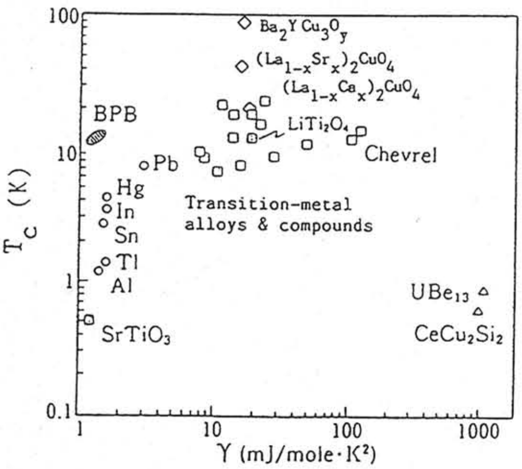

Fig. 4 Relationship between electronic specific heat coefficient Y and Tc for various superconductors.

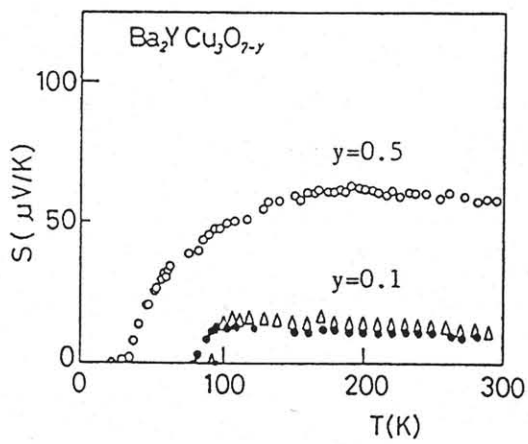

Fig. 5 Temperature dependence of the Seebeck coefficient for $Ba_2YCu_3O_{7-y}$ with various nonstoichiometry y.

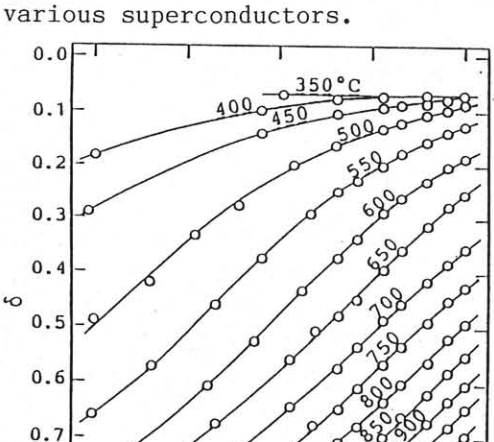

Fig. 6 Equilibrium oxygen deficiency δ in $Ba_2YCu_3O_{7-\delta}$ as a function of temperature and oxygen pressure.

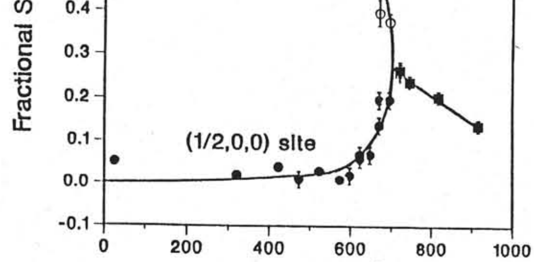

Fig. 7 Fractional site occupancy of oxygen on (0, 1/2, 0) site along b-axis and on (1/2, 0, 0) site along a-axis.