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1989 Jpn. J. Appl. Phys. 28 L112

(http://iopscience.iop.org/1347-4065/28/1A/L112)

JAPANESE JOURNAL OF APPLIED PHYSICS
VOL. 28, NO. 1, JANUARY, 1989, pp. L 112–L 115

Metal-Insulator Transition in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ System

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(Received November 22, 1988; accepted for publication December 15, 1988)

Metal-insulator transition driven by the change of the carrier concentration was investigated in the 80 K superconductor $Bi_2Sr_2CaCu_2O_{8+y}$. The carrier concentration was controlled by the substitution of yttrium for calcium. Experimental results from structural, transport, and magnetic studies are discussed in comparison with other high-temperature superconductor systems, $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$.

KEYWORDS: metal-insulator transition, $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$, electronic phase diagram

High-temperature superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ turn into insulators with decreasing hole concentration. The antiferromagnetisms were established in the insulating phases, La_2CuO_4 and $YBa_2Cu_3O_6$, by μSR[1,2] and neutron[3,4] experiments. Theories which stress magnetic interaction in the high-temperature superconductors are supported by the antiferromagnetisms in the insulating phases of superconductors. For 80 K superconductor $Bi_2Sr_2CaCu_2O_{8+y}$ we reported that $Bi_2Sr_2YCu_2O_{8+y}$ might be the corresponding insulating phase.[5] Recent μSR experiment by Nishida et al.[6] found magnetic order in $Bi_2Sr_2YCu_2O_{8+y}$ at room temperature. In this paper, we report on the characteristics of the metal-insulator transition in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system.

Samples used in the experiments were prepared by solid-state reaction. Powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO were mixed thoroughly with the ratio of Bi:Sr:Ca+Y:Cu=2:2:1:2 and prefired at 800°C for a few hours. Then the temperature was increased in one or two steps to the final temperature. The final temperature settings were chosen as 860°C for $x=0$ and 900°C for $x=1$, increasing gradually with x. We sustained the final temperature for more than 100 hours with a few intermediate grindings. In the initial stage of the reaction, another phase with $c\sim24$ Å is partly formed which transforms into $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ with $c\sim30$ Å by prolonged firing.

Structural properties were studied by powder X-ray diffraction and electron diffraction experiments. The electron diffraction was performed by a H-9000 (Hitachi) TEM operating at 300 kV. Electrical resistances were measured by the conventional dc four-probe method. Hall effects were measured in a field of 5 Tesla generated by a split-type superconducting magnet. The magnetic field was fixed in the persistent-mode and the samples were rotated 180 degree to subtract the contribution from the resistance part. Magnetic susceptibilities were measured by a pendulum-type magnetometer under a field of 1.18 Tesla. Formal copper valencies were analyzed by an iodometry method.

Figure 1(a) shows the lattice constant variatlon with x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$. As we have reported, the lattice of the end member $Bi_2Sr_2YCu_2O_{8+y}$ is orthorhombic. The orthorhombic distortion is evident in the powder X-ray pattern by the splitting of (2,0,0) and (0,2,0) for $x\geqq0.7$. For $x=0.6$ and $x=0.5$, however, these peaks are observed only as one broadened peak. So we determined the difference of a and b only from the excess width of this peak. For samples with $x\leqq0.4$, we could not determine the equality of a and b from the powder X-ray patterns. Other single crystal X-ray diffraction analyses[7,8] have claimed that $Bi_2Sr_2CaCu_2O_{8+y}$ is slightly orthorhombic. In fact, there is no reason why lattice constants a and b should be equal in the presence of the modulated structure only in the b-axis, so we believe that the lattice of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system is orthorhombic for all values of x.

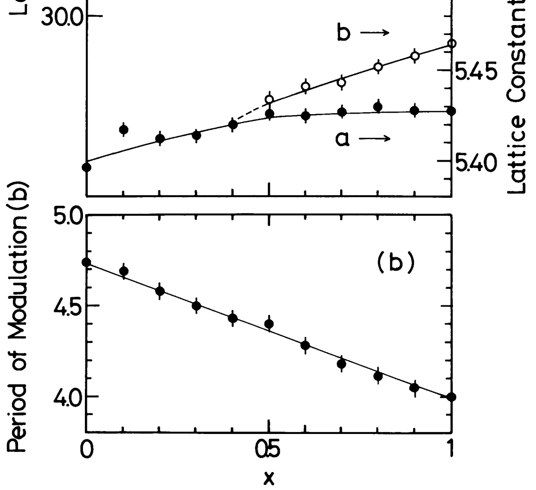

Fig. 1. Lattice constants (a) and lattice modulation period (b) variations with x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$.

Electron diffraction patterns show the presence of lattice modulation in the b-axis for all of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. The period of the modulation, which is about 4.74b in $Bi_2Sr_2CaCu_2O_{8+y}$, varies continuously to 4.0b in $Bi_2Sr_2YCu_2O_{8+y}$ as shown Fig. 1(b). Onoda et al.[9] found the lattice modulation in $Bi_2Sr_2CaCu_2O_{8+y}$ is so strong that it could be seen in the powder X-ray pattern. The continuous change of the modulation period in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system is also evident in the X-ray powder diffraction pattern. Four-fold modulation in $Bi_2Sr_2YCu_2O_{8+y}$ might seem to be inconsistent with our earlier report that the modulation in $Bi_2Sr_2YCu_2O_{8+y}$ is eight-fold.[5] Actually, the electron diffraction on $Bi_2Sr_2YCu_2O_{8+y}$ clearly shows the presence of the spots which correspond to eight-fold modulation. These spots clearly appear only in $Bi_2Sr_2YCu_2O_{8+y}$ and slightly in $Bi_2Sr_2Ca_{0.1}Y_{0.9}Cu_2O_{8+y}$. The intensities of the eight-fold spots are weaker than those of the four-fold ones. Therefore, we think that the period of the main modulation in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system changes from 4.74b to 4.0b continuously, and weak eight-fold modulation is superposed only very near to $Bi_2Sr_2YCu_2O_{8+y}$.

Figure 2 shows the temperature dependence of the resistivity for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. Metallic conduction for smaller x samples turns into insulative conduction for samples with x larger than 0.6. The transition temperature (T_c) for $Bi_2Sr_2CaCu_2O_{8+y}$ is slightly lower than that for $x=0.1$. One of the reasons for T_c in $x=0$ being lower than that in $x=0.1$ may be the difference in crystal quality. Actually, X-ray powder diffraction patterns show that the quality of $Bi_2Sr_2CaCu_2O_{8+y}$ is not as good as that of $x=0.1$. As many people have reported,[10,11] one can obtain a better crystal and higher T_c with a sharper transition in a sample prepared by starting with the strontium to calcium ratio of about 1.5:1.5 rather than 2:1. A rather sharp decrease in T_c is seen for $x=0.4$. Resistivity does not go to zero for x larger than 0.6. For the insulating samples, the temperature dependence of the resistance is consistent with the variable range hopping formula in two-dimension $R \propto \exp(-(T_0/T)^{1/3})$ in a certain range of temperature.[12] Similar temperature dependence has been reported by Yoshizaki *et al.*[13]

Temperature variations of the Hall coefficients are shown in Fig. 3. The sign of the Hall coefficient is positive as in other high-temperature superconductors,[14,15] and slightly temperature dependent. The ratio of the Hall coefficient at room temperature and 100 K is 1.5 at most, which is about 3 in case of $YBa_2Cu_3O_7$.[15] The temperature dependence of the Hall coefficient is less pronounced as x is increased. We think that the extraordinary large temperature dependence of the Hall

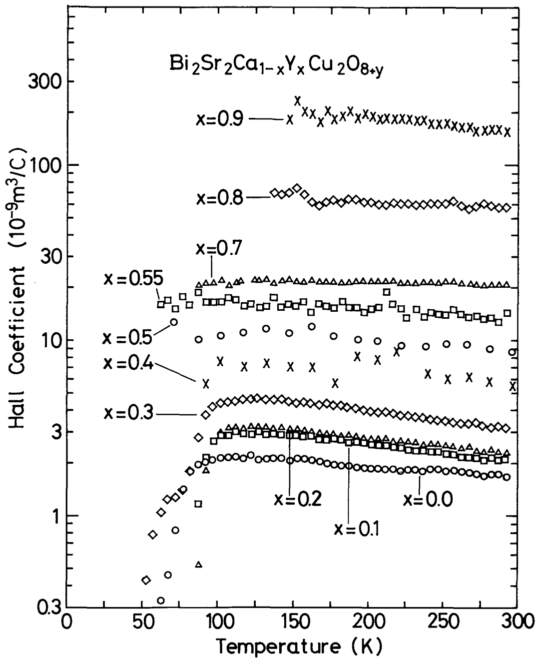

Fig. 3. Temperature dependences of the Hall coefficients for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system measured under the field of 5 Tesla.

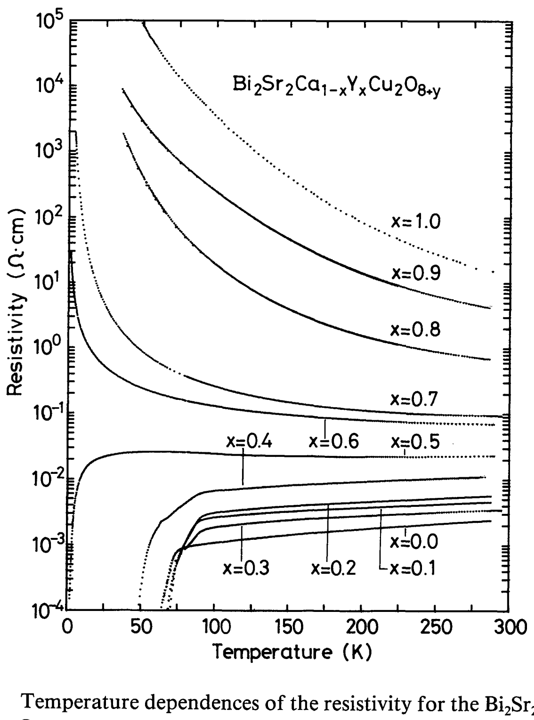

Fig. 2. Temperature dependences of the resistivity for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system.

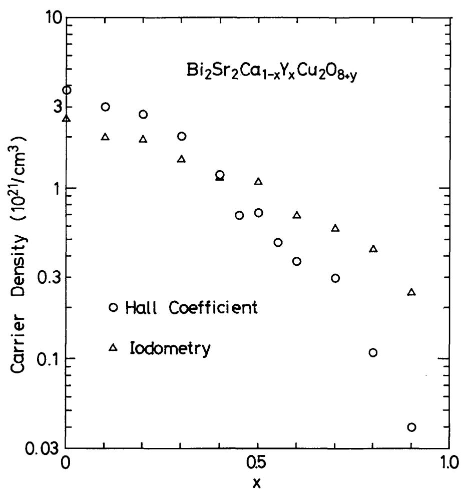

Fig. 4. Variation of the carrier concentrations with x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ determined by the Hall coefficient and the iodometry method.

coefficient in $YBa_2Cu_3O_{7-y}$ is related to the CuO chain, which is not present in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. Carrier concentrations (n_H) calculated from the Hall coefficient assuming the simple relation $n_H=1/eR_H$ are shown in Fig. 4 together with those deduced from the chemical analysis by an iodometry method (n_I) on the assumption that each Cu^{3+} gives one hole. Here, we assumed the valency of bismuth as +3 and ignored the presence of a secondary phase. n_H is slightly larger than n_I in samples with smaller x. However, as x is increased, n_H decreases more rapidly than n_I indicating mobile carriers are dying in the insulating region.

Figure 5 summarizes the temperature dependence of the magnetic susceptibility for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. The magnetic susceptibilities for $x \geqq 0.8$ show sharp peaks at 13 K. However, it was clarified that these peaks were due to an impurity phase, $Y_2Cu_2O_5$.[5,16] In the fully yttrium-substituted sample, the molar ratio of $Y_2Cu_2O_5$ is estimated at about 9%. If we subtract the contribution from $Y_2Cu_2O_5$, susceptibilities are almost the same for samples with x larger than 0.6 at room temperature. As we go from the metallic phase to the insulating one, the susceptibility at room temperature decreases and the slope $d\chi/dT$ increases. This tendency is very similar to what is observed in other superconducting systems.[17] The positive slope of the susceptibility in the insulating phase is interpreted as trace of a broad maximum at a higher temperature which results from a short-range antiferromagnetic correlation in the CuO_2 planes.

Carrier concentration in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system is governed not only by the yttrium content but also by the oxygen content. In case of $Bi_2Sr_2CaCu_2O_{8+y}$, the amount of excess oxygen was reported $y \sim 0.2$.[11] If we assume the chemical formula $Bi_2Sr_2YCu_2O_{8+y}$, y should be 0.5, taking account of the fact that there is almost no Cu^{3+}.[5] However, it is not certain crystallographically how much excess oxygen can be incorporated in the lattice. Though the presence of $Y_2Cu_2O_5$ as an impurity indicates that the real composition is slightly different from $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$, the oxygen content must increase to some extent with increasing yttrium content to neutralize the electronic charge. The lattice modulation is thought to be strongly coupled with the excess oxygen and the cation distribution. In fact, in $Bi_2Sr_2CaCu_2O_{8+y}$, distribution of the site occupation of the cations is indicated by a high-resolution electron microscope image.[8] In $Bi_2Sr_2YCu_2O_{8+y}$, similar distribution of the site occupation of the cations coupled with the excess oxygen would make the four-fold lattice modulation stable.

In a recent μSR experiment, Nishida *et al.*[6] found magnetic ordering in a fully yttrium-substituted sample of $Bi_2Sr_2YCu_2O_{8+y}$ at room temperature. This magnetic order is most likely to be an antiferromagnetic one considering its magnetic susceptibility. An electronic phase diagram can be drawn for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ analogous to that for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$. Figure 6 shows the electronic phase diagram for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. We define T_c as the temperature where the resistance drops to 50 % of the normal state resistance. The top and bottom of the line with the closed circles indicate the temperature where the resistance drops to 90 % and 10 % of the normal state resistance, respectively. Susceptibility measurements as well as resistivity measurements show that the onset temperatures of the superconductivities are about 85 K for all superconducting samples except for $x=0$. A rather abrupt decrease in T_c is seen above $x=0.4$. Both of these facts indicate that there is a large spatial fluctuation of the composition in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system, which causes the distribution of T_c.

The correlation between T_c and hole concentration in the CuO_2 planes has been established in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$.[19,20] The marked decrease of T_c for $x=0$ offers an interesting question whether there are excess holes in $Bi_2Sr_2CaCu_2O_{8+y}$. The average copper

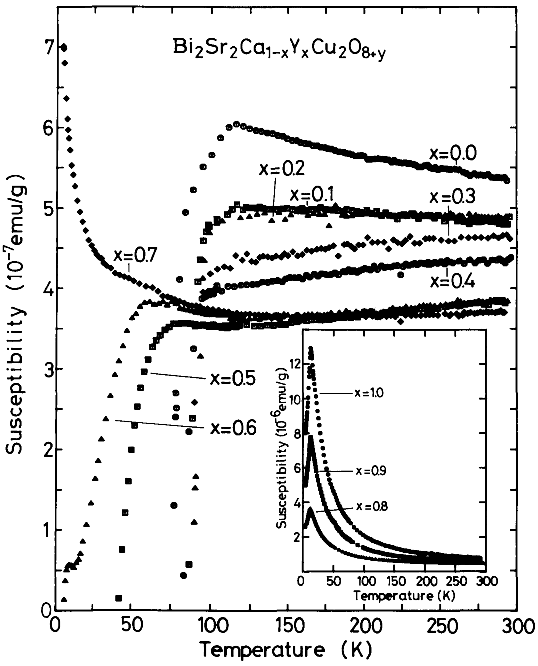

Fig. 5. Temperature dependences of the dc magnetic susceptibility for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system measured under the field of 1.18 Tesla. Inset shows the data for $x \geqq 0.8$, where peaks from the impurity phase $Y_2Cu_2O_5$ are evident.

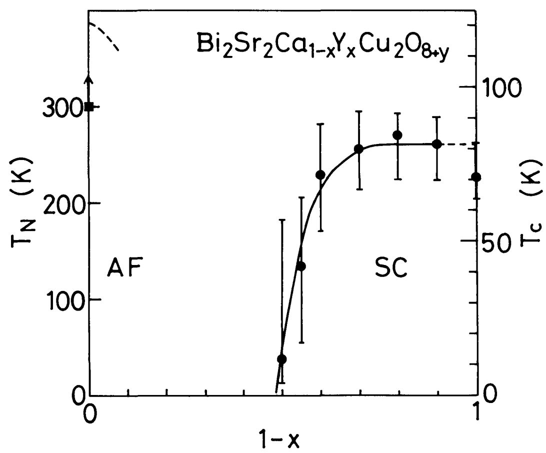

Fig. 6. Electronic phase diagram for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. SC and AF denote superconducting and antiferromagnetic phases, respectively. Neel temperature (T_N) for $x=1$ and T_c for $x \leqq 0.5$ are determined as described in the text.

valency is estimated as $+2.29$ for $Bi_2Sr_2CaCu_2O_{8+y}$ by the iodometry method if we neglect the presence of the secondary phase. This seems to be slightly larger than the value from which we can expect the highest T_c with analogy of $YBa_2Cu_3O_{7-y}$. Experiments on $Bi_2Sr_2CaCu_2O_{8+y}$ with different oxygen contents may resolve this question.

Acknowledgments

One of the authors (T. T.) thanks S. Sato for his valuable comments. This work is partly supported by Grant-in-Aid for Scientific Research on Priority Areas, ''Mechanism of Superconductivity'' from the Ministry of Education, Science and Culture.

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