

## Superconductivity of $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$ (M=Fe, Co, Ni, Zn)

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Electrical resistivity and magnetic susceptibility of superconducting  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  (M=Fe, Co, Ni, Zn) system have been measured in the temperature range from 4.2 to 300 K. The substitution of 3d transition elements for Cu element shows that the superconducting transition temperature  $T_c$  decreases smoothly with increasing the concentration  $x$  of 3d transition elements, and that the decreasing rate of  $T_c$  vs  $x$  decreases with increasing the atomic number of 3d transition elements. The effects of magnetic moments of Fe, Co and Ni elements on the superconductivity are not notable.

### §1. Introduction

Since the observation of the high- $T_c$  superconductivity by Bednorz and Müller<sup>1)</sup>, many works have been done on related materials. Recently, new high- $T_c$  oxide superconductors have been discovered in the Bi-Sr-Ca-Cu-O system by Maeda *et al*<sup>2)</sup>. The sample exhibited the superconducting transition in two steps at 80 K and 105 K, which correspond to the formula of  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3\text{Cu}_2\text{O}_{8+y}$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y}$ , respectively<sup>3),4)</sup>. It had been identified that the high- $T_c$  phase ( $T_c=105$  K) had triple Cu-O layers with two Cu(2)-O<sub>5</sub> pyramids and one Cu(1)-O chain sandwiched by two Bi<sub>2</sub>O<sub>2</sub> layers and the low  $T_c$  phase ( $T_c=80$  K) had double Cu(2)-O<sub>5</sub> pyramids. These results show that the Cu(1)-O linear chains in the basal plane are not essential to the superconductivity of the oxide compounds. Therefore, Cu(2)-O planes seem to play a significant role in the electronic conduction in this oxide.

It is interesting to study systematically the substitution of 3d magnetic (Fe, Co, Ni) and nonmagnetic (Zn) elements for Cu(2) site ions in the low  $T_c$  phase. All the samples observed by X-ray powder diffraction showed the single phase of low  $T_c$  superconductor. In this paper we report the results of electrical resistivity and magnetic ac susceptibility of superconducting  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  (M=Fe, Co, Ni, Zn) with  $0 \leq x \leq 0.06$  in the temperature range from 4.2 to 300 K.

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## §2. Experimental Procedure

The low  $T_c$  phase Bi-Sr-Ca-Cu-M-O samples were prepared by solid-state reaction using  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CuO}$  as starting reagents. Appropriate amounts of reagents powders were thoroughly mixed and placed in an alumina crucible in an atmosphere of air. The powder was heated at  $780^\circ\text{C}$  for 10 hrs and followed at  $820^\circ\text{C}$  for 5 hrs and then cooled to  $400^\circ\text{C}$  at a rate of  $80^\circ\text{C/hr}$ . After the first reaction, the pellet was ground to powder using a moter and pestle. The powder mixture was pressed at the applied pressure of 0.4 kbar. Subsequently, the pellets were sintered at  $840^\circ\text{C}$  for 5 hrs in air and cooled to room temperature out of the furnace.

The crystal structure of the synthesized oxides was examined by X-ray powder diffraction analysis at room temperature with monochromated  $\text{Cu K}_\alpha$  radiation. The lattice parameters of  $a$ - and  $c$ -axes are obtained from the  $(2\ 10\ 0)$  and  $(0\ 0\ 10)$  peaks, respectively.

The resistivity measurements were made by the four probe method over the temperature range of 4.2 to 300 K. Electrical contact was made to the sample by using the ultrasonic vibration soldering system. The temperature was measured using a calibrated Lake-Shore Cryotronics-Inc. platinum resistance thermometer with an accuracy better than 0.1 K. The Meissner effect was measured in the temperature range from 4.2 to 300 K using an ac Harts-horn-type bridge. The sample temperature was monitored by a  $\text{Au(Fe)-Ag}$  thermocouple. The diamagnetic susceptibility was calibrated by use of a standard Nb powder.

## §3. Experimental Results and Discussion

Figures 1 (a), (b), (c) and (d) show the temperature dependence of the electrical resistivity for some typical composition  $x$  ( $0 \leq x \leq 0.06$ ) of  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  samples with  $\text{M}=\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$ , respectively. The resistivities decrease monotonously with decreasing temperature in the normal state region, and then starts to drop around 80 K. The onset and offset of superconducting transition temperatures decrease with increasing the composition of 3d transition elements M. The values of the resistivity at 300 K in the metallic conduction state decrease with increasing the atomic number from Fe to Zn atoms. The superconducting offset transition temperatures  $T_c$  vs the concentration  $x$  of 3d transition metals are shown in Fig. 2. The values of  $T_c$  decrease with increasing the concentration  $x$ . The decreasing rate of  $T_c$  vs  $x$  decreases with increasing the atomic number of 3d transition elements from Fe to Zn atoms.

Figures 3 (A), (B), (C) and (D) show the temperature dependence of ac susceptibility  $X_g$  for  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  samples with  $\text{M}=\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$ , respectively. The  $T_c$  and magnitude of diamagnetic susceptibility decrease with increas-

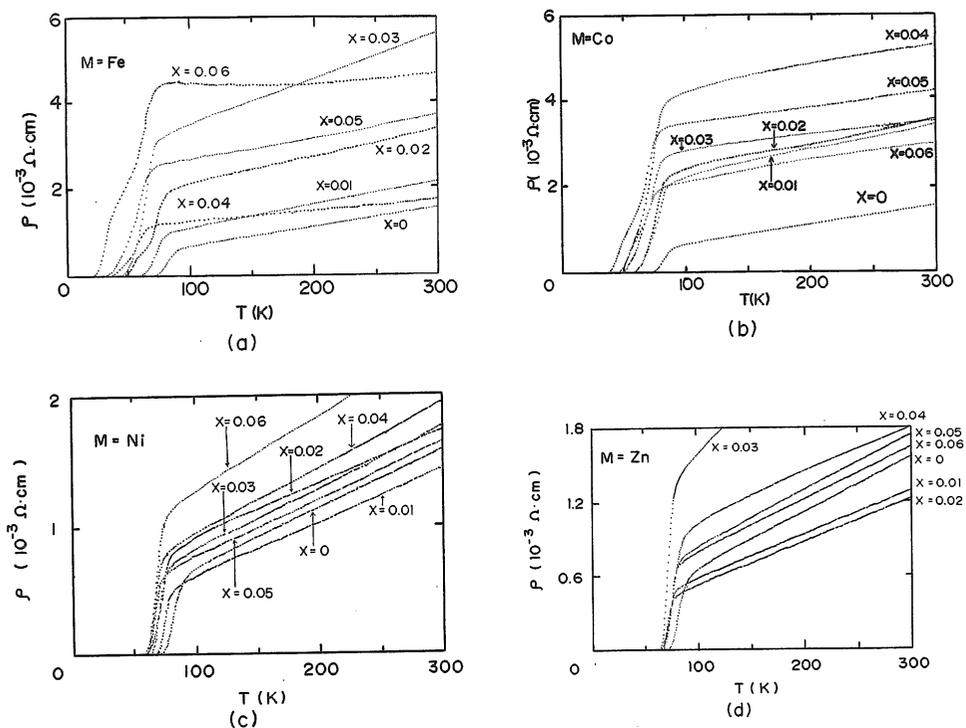


Fig. 1. (a), (b), (c) and (d) Temperature dependence of electrical resistivity for  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  samples with M=Fe, Co, Ni and Zn, respectively.

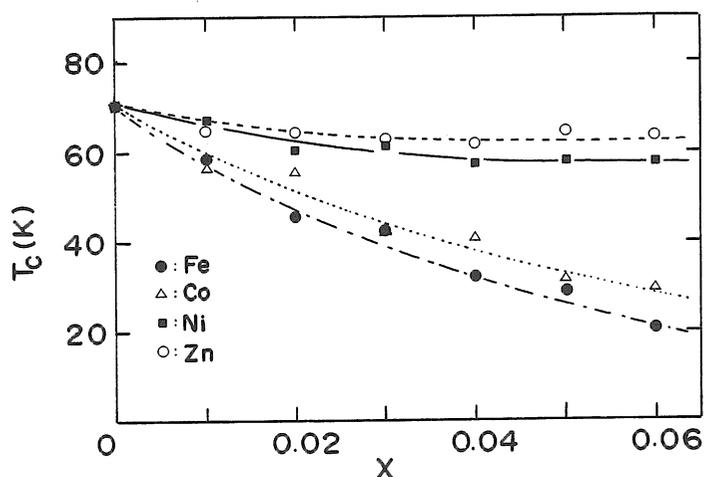


Fig. 2. Superconducting offset transition temperature  $T_c$  for  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  (M=Fe, Co, Ni, Zn) vs the concentration  $x$  of 3d transition elements.

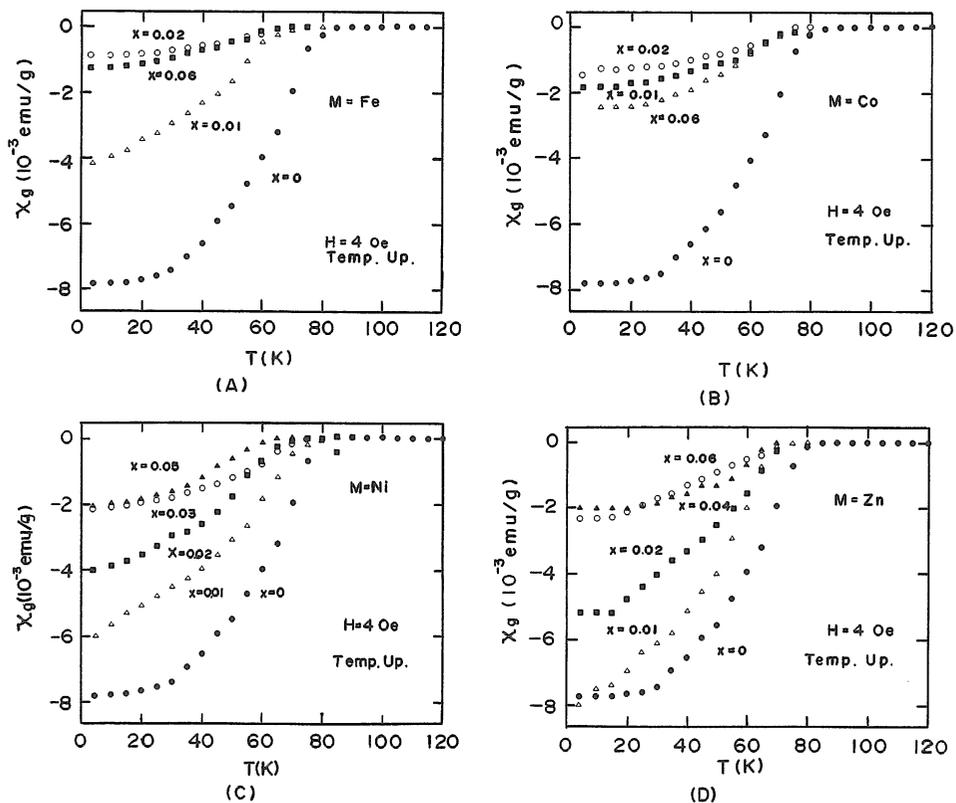


Fig. 3. (A), (B), (C) and (D) Temperature dependence of ac susceptibility  $X_g$  for  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  samples with  $M = \text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$  and  $\text{Zn}$ , respectively.

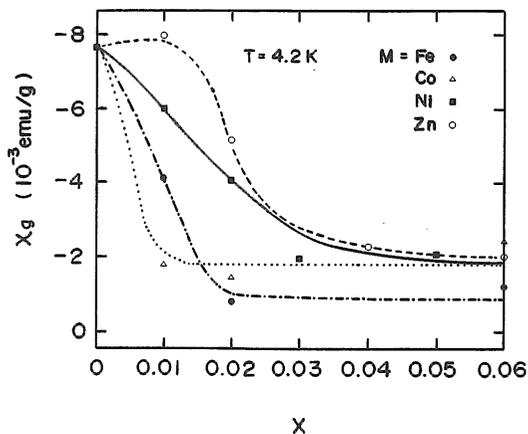


Fig. 4. Diamagnetic susceptibility at 4.2 K for  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  ( $M = \text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Zn}$ ).

ing the concentration  $x$  of 3d transition metals. This means that the volume fraction of superconductivity decrease with increasing the concentration  $x$ . The values of diamagnetic susceptibility at 4.2 K vs the concentration  $x$  of 3d transition elements are shown in Fig. 4. The decreasing rate of volume fraction of superconductivity vs  $x$  decreases with increasing the atomic number of 3d transition metals.

The substitutions of 3d transition elements Fe, Co, Ni and Zn for Cu element in  $\text{Bi}_2(\text{Sr}_{0.6}\text{Ca}_{0.4})_3(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+y}$  show that the superconducting transition temperatures  $T_c$  decreases smoothly with increasing the concentration  $x$  of 3d transition elements, and that the decreasing rate of  $T_c$  vs  $x$  decrease with increasing the atomic number of 3d transition elements. The elements of Fe, Co and Ni have magnetic moments and the element of Zn is nonmagnetic. The effects of magnetic moments on the superconductivity are not notable. The existence of impurity which break the translational symmetry of lattice in real space affect the anisotropic gap-parameter of superconductivity in  $k$ -space. The shift of anisotropic gap-parameter suppresses the superconductivity.

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