Nonequivalence of the anisotropy in the normal state to that in the superconducting state of $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M = Mn, Fe, Co, and Ni)

X. F. Sun,[1] X. Zhao,[1] L. Wang,[1] Q. F. Zhou,[1] W. B. Wu,[2] and X.-G. Li[1,2]
[1]*Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China*
[2]*Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China*
(Received 26 October 1999)

The anisotropic resistivity and second peak of magnetization curves were studied for $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M = Mn, Fe, Co, and Ni) single crystals. The c-axis resistivity $\rho_c(T)$ and the anisotropy in the normal state $\gamma_n[=(\rho_c/\rho_{ab})^{1/2}]$, decrease rapidly with increasing doping concentration x, while the anisotropy factor in the superconducting state, γ_s, obtained from the second peak field by the relation $B_{\rm sp}=\Phi_0/(s\gamma_s)^2$, increases systematically with x. This indicates that the anisotropy in the normal state is different from that in the superconducting state, inconsistent with the conventional concept. The present results show that γ_n and γ_s should be determined by different mechanisms in highly layered cuprates.

One of the peculiar characteristics of high-T_c superconductors is the large electromagnetic anisotropy manifested in the transport and magnetic properties for both the normal and superconducting states. It mainly results from the layered crystal structure, which consists of alternate stacking of superconducting CuO_2 layers and poorly conducting block layers, and has great influence on the physical properties. There are two ways to define the anisotropy. One is the anisotropy in the normal state, usually characterized by the ratio of c-axis resistivity to ab-plane resistivity, i.e., $\gamma_n=(\rho_c/\rho_{ab})^{1/2}$. Another is the anisotropy factor in the superconducting state defined as $\gamma_s=\lambda_c/\lambda_{ab}=(m_c^*/m_{ab}^*)^{1/2}$; here, λ_c and λ_{ab} are the London penetration depths due to currents flowing perpendicular and parallel to the CuO_2 planes, and m_c^* and m_{ab}^* are the effective masses of the electrons for motion perpendicular and parallel to the CuO_2 planes, respectively. Under the nearly free electron approximation, the resistivity is proportional to the effective mass and the resistivity anisotropy can be expressed as $\gamma_n=(\rho_c/\rho_{ab})^{1/2}=(m_c^*/m_{ab}^*)^{1/2}=\gamma_s$. So it is usually taken for granted that the anisotropy is a unique parameter in both the normal and superconducting states. However, it is well known that the normal-state resistivity of high-T_c cuprates is too complex to be described by the nearly free electron approximation.[1] In this case the conventional three-dimensional (3D) Bloch transport breaks down and the c-axis transport proceeds through an incoherent mechanism due to charge confinement coming from the highly two-dimensional nature of the electronic states. On the other hand, λ_c and λ_{ab} strongly depend on the superconducting properties, such as the paring symmetry of order parameter.[2] Thus one may expect that the anisotropy in the normal state in fact has a different physical meaning than that in the superconducting state. With respect to the experimental results, a lot of works have been focused on the substitution effect on the anisotropy. As for the most highly anisotropic system $Bi_2Sr_2CaCu_2O_y$(Bi2212), it was found that both γ_n and γ_s decrease monotonously with an increase of the carrier concentration by changing the oxygen content,[3–6] doping Pb on the Bi site,[7] or substituting Ca with rare-earth elements.[8,9] But for the substitution of Cu by other $3d$ transition elements, which hardly changes the carrier concentration, but greatly affects the properties of the CuO_2 plane, the doping effect on the anisotropy is far from consensus.[10–13] In particular, for Ni-doped Bi2212, Yoshizaki *et al.*[12] found a γ_n decrease with Ni concentration, which is just contrary to the variation trend of the anisotropy factor γ_s reported by Ha *et al.*[13] from measurements of the dimensional crossover field in magnetization curves. This opposite doping dependence of the anisotropy obtained by different means cannot be solely attributed to the sample discrepancy: instead, it may indicate that the anisotropies in the normal and superconducting states are different from each other and this difference should be detected by certain means. So detailed studies of the substitution effect on the anisotropy of Bi2212 are still needed. In this paper, we systematically study both the anisotropic resistivity and magnetic second peak, from which the anisotropies in the normal and superconducting states can be obtained for $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M = Mn, Fe, Co, and Ni) single crystals. It is observed that the γ_n and γ_s change with opposite trends with substitution on the Cu site.

High-quality $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M = Mn, Fe, Co, and Ni) single crystals were grown by a self-flux method as reported previously.[14] The crystals used for the present study have sizes around $1.5\times1\times0.02\,\mathrm{mm}^3$ with the smallest dimension along the c axis. The thickness of the crystal was measured by a scanning electron microscope. The structural characterizations of single crystals have been done by x-ray diffraction using a rotating-anode diffractometer (Rigaku, D/Max-γA) with Cu$K\alpha$ radiation. The cation stoichiometry of single crystals was determined by energy-dispersive x-ray (EDX) analysis using a scanning electron microscopy (Stereoscan 440, Leica). The anisotropic resistivity was measured using the Montgomery method.[15] Electrical contacts of less than 2 Ω resistance were established by soldering the copper leads onto the crystal surface on which pure gold was evaporated. The dc magnetization measurements were carried out with a Quantum Design $MPMS_2$ superconducting quantum interference device (SQUID) magnetometer. Before the transport and magnetic measurements, all the crystals

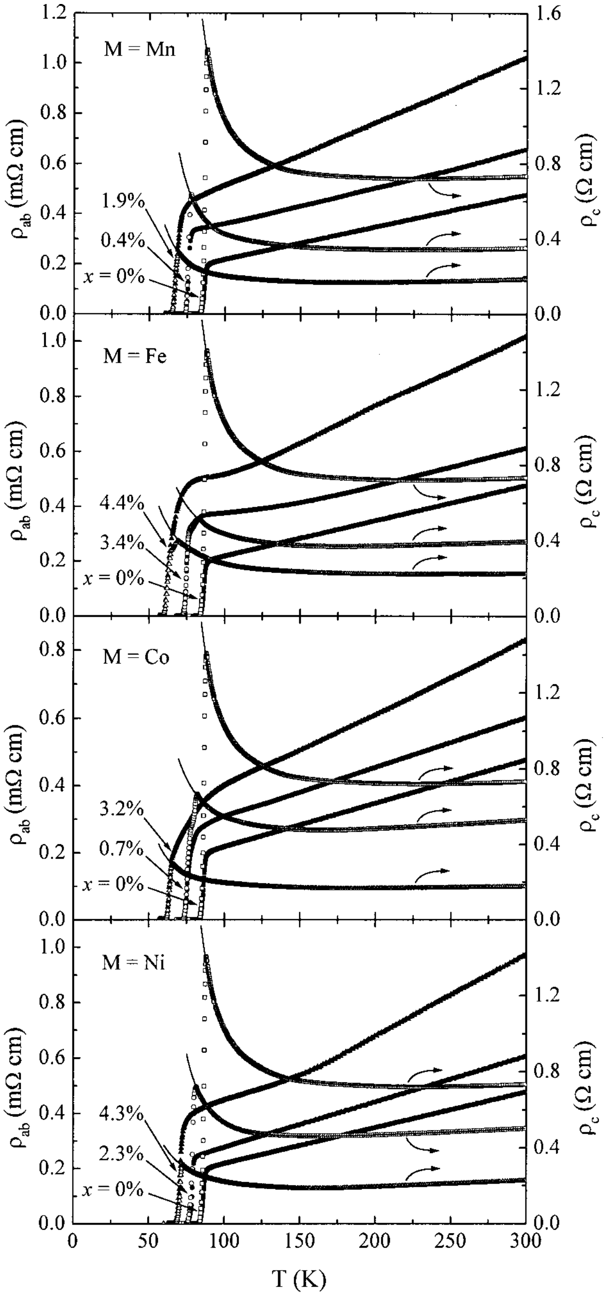

FIG. 1. Temperature dependence of the *ab*-plane resistivity $\rho_{ab}(T)$ and the *c*-axis resistivity $\rho_c(T)$ for $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M=Mn, Fe, Co, and Ni) single crystals. The doping concentrations measured by EDX are indicated in the panels. The solid and open symbols represent the experimental data of $\rho_{ab}(T)$ and $\rho_c(T)$, respectively. The solid lines are fits of ρ_c data to Eq. (1).

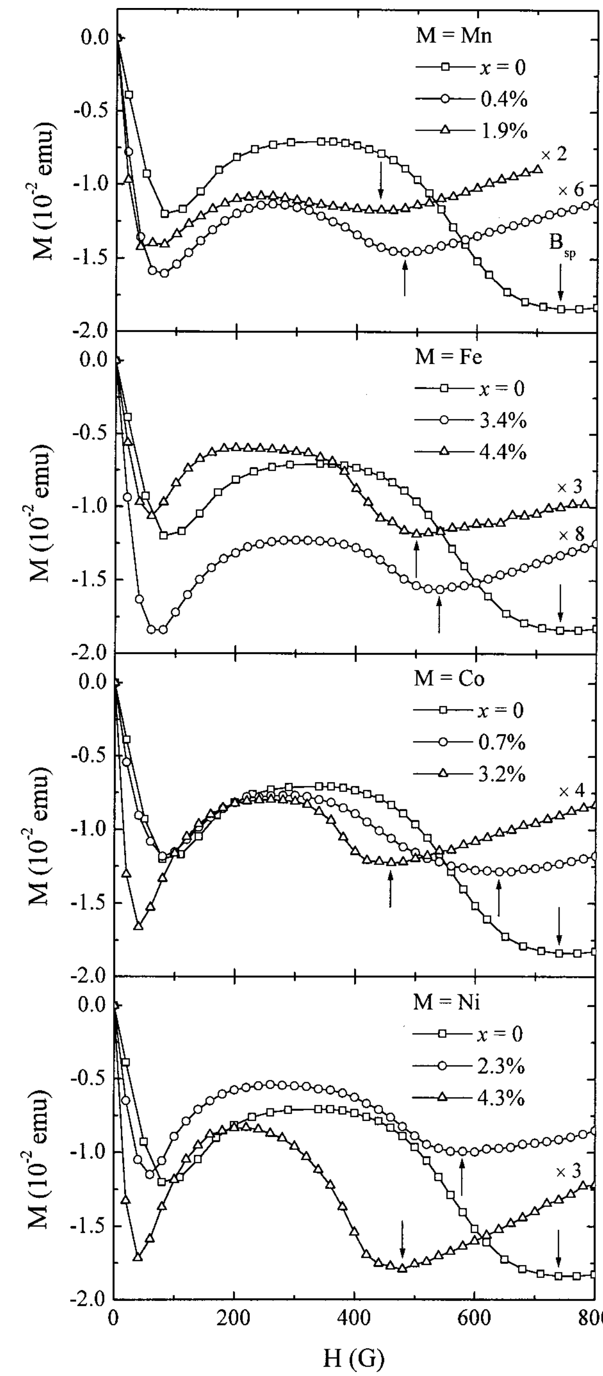

FIG. 2. Magnetization curves $M(H)$ at 25 K of $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M=Mn, Fe, Co, and Ni) single crystals with applied field $\mathbf{H}\|c$ axis. The second peak B_{sp} for each curve is indicated by an arrow.

were annealed in air at 400 °C for 48 h to improve the homogeneity. Although annealing under so low temperature results in a slightly overdoped instead of optimal oxygen content for Bi2212 single crystals, it can avoid the well-known surface phase decomposition.[16] It should be pointed out that the magnetic and transport measurements had been done on the same crystal for each doping concentration.

Figure 1 shows the temperature dependence of the *ab*-plane resistivity $\rho_{ab}(T)$ and the *c*-axis resistivity $\rho_c(T)$ for a group of $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M=Mn, Fe, Co, and Ni) single crystals. The superconducting transition temperature T_c, defined as the zero-resistance temperature, decreases quickly with the substitution for Cu, especially in case of Mn doping. For all dopants, the ρ_{ab} increases with an increase of the doping level, while the ρ_c decreases monotonously. This results in the systematic suppression of the resistivity anisotropy ρ_c/ρ_{ab} with increasing x. The variations of the anisotropic resistivity are qualitatively consistent with previous results on Zn- and Ni-doped Bi2212 crystals.[10,12] Most of the in-plane resistivity shows a nearly linear function of temperature with both the residual resistivity $\rho_{ab}(0\,\mathrm{K})$ and the temperature coefficient $d\rho_{ab}/dT$ increase upon doping. Ac-

TABLE I. The fitting parameters *a*, *b*, *d*, and Δ of Eq. (1) to the $\rho_c(T)$ data. T_c is given in the first column.

Samples	T_c (K)	a (Ω cm K)	b (mΩ cm/K)	d (Ω cm)	Δ (K)
$x=0$	83.5	0.410	0.106	0.687	439
Mn 0.4%	73	0.359	0.009	0.336	320
Mn 1.9%	63	0.745	0.152	0.128	198
Fe 3.4%	71.5	3.103	0.390	0.261	147
Fe 4.4%	59	3.229	0.147	0.162	111
Co 0.7%	72	2.719	0.607	0.330	175
Co 3.2%	60.5	0.879	0.096	0.138	159
Ni 2.3%	75.5	0.387	0.411	0.374	341
Ni 4.3%	67.5	5.275	0.522	0.048	80

cording to a gauge field theory based on the t-J model,[17] the T-linear resistivity of high-T_c cuprates may originate from spin scattering and the coefficient $d\rho_{ab}/dT$ increases with decreasing the antiferromagnetic spin correlation. It can be expected that the antiferromagnetic spin correlation in CuO_2 plane weakens when the Mn, Fe, Co, or Ni ions substitute some Cu ions.[18] The increase of residual resistivity is due to the disorder in the CuO_2 plane introduced by the substitutional elements. For all the samples, the temperature dependence of the *c*-axis resistivity shows a slightly metallic behavior at high temperature and a semiconductive behavior at low temperature. The mechanism of the anomalous semiconductive behavior of ρ_c in high-T_c superconductors has attracted a lot of interest and many models have been proposed; however, a clear picture still has not been established.[1] Recently, more and more theories and experimental evidence[19–22] showed that the semiconducting T dependence of ρ_c is associated with the normal-state pseudogap, which presents a barrier to the *c*-axis charge transport. In fact, our ρ_c data were found to be well fitted by the formula introduced by Yan *et al.*[19] assuming the presence of a pseudogap Δ:

$$\rho_c(T)=(a/T)\exp(\Delta/T)+bT+d, \tag{1}$$

where *a*, *b*, and *d* are constants. The fitted curves are also shown in Fig. 1 with the fitting parameters listed in Table I. It should be noted that the most effective parameter responsible for the reduction of ρ_c with doping level is the decrease in the size of the pseudogap Δ. If one assumes that the origin of the pseudogap is related to the antiferromagnetic spin correlation of Cu spins,[23] the ion substitution for Cu will disturb the correlation and result in the reduction of the pseudogap.

Figure 2 shows the magnetization curves of $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ ($M=$Mn, Fe, Co, and Ni) single crystals measured at 25 K with applied field parallel to the *c* axis. After the crystal was zero-field cooled to the experimental temperature, the magnetization was measured with increasing field. The well-known second peak B_{sp} appears in each curve and shifts gradually to lower field with an increase of the doping concentration. As for the Bi2212 system, the origin of the second peak has attracted a lot of interest and many explanations have been put forward.[24–30] Although it may relate to the vortex motion and pinning, the second peak intrinsically depends on the anisotropy in the superconducting state. A reasonable understanding is that the

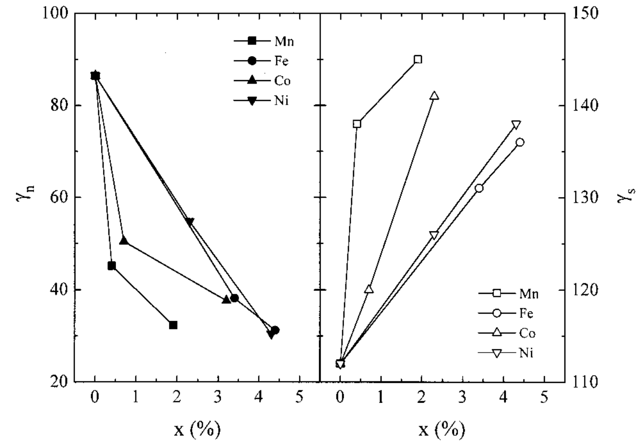

FIG. 3. Variations of γ_n at the superconducting onset transition temperature and γ_s with the doping concentration for $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ ($M=$Mn, Fe, Co, and Ni) single crystals.

occurrence of the second peak is due to the dimensional crossover from 3D vortex lines to 2D pancake vortices[28,29] and the crossover filed B_{2D} was predicated by Vinokur *et al.*[30] as $B_{2D}=\Phi_0/(s\gamma_s)^2$; here, Φ_0 is the flux quantum and *s* is the space between two CuO_2 blocks. This picture was strongly supported by the observations of the flux-line lattice by neutron diffraction,[31] muon spin rotation,[32,33] and local magnetization measurements.[34] Moreover, it provides a useful and convenient means to obtain the anisotropy factor in the superconducting state.[7,8,27] So the anisotropy factor in the superconducting state, γ_s, of $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ single crystals can be easily obtained from the second peak by the relation

$$B_{sp}=\Phi_0/(s\gamma_s)^2. \tag{2}$$

The doping dependence of γ_s is shown in Fig. 3. In contrast, the resistivity anisotropy γ_n at the superconducting onset transition temperature is also given in Fig. 3. It is clear that γ_s increases with *x*, which is just contrary to the variation of γ_n. This discrepancy indicates the different mechanisms that determine the anisotropy in the normal state and that in the superconducting state.

The anisotropy in the superconducting state is mainly determined by the interlayer Josephson coupling between CuO_2 layers, in frame of the Lawrence-Doniach model,[35] especially for the highly anisotropic Bi2212 system. The weaker the coupling strength is, the larger γ_s is. While the resistivity anisotropy in the normal state is mainly determined by the *c*-axis charge transport behavior, which depends on both the carrier density and the potential barrier for the incoherent transport. So the γ_n and γ_s characterizes different physical properties and they do not necessarily change with doping in the same behavior. One may notice that the rare-earth ion substitution on the Ca site always increases the γ_s of Bi2212 single crystals in spite of T_c increases or decreases,[8] while the increase of the oxygen content or Pb substitution for Bi decreases the anisotropy γ_s.[6,7] And these changes of γ_s are qualitatively consistent with the variations of γ_n. The reason may be due to the fact that,[7–9] on the one hand, the rare-earth substitution for Ca will effectively destroy the interlayer Josephson coupling between CuO_2 layers in the superconducting state, while excess oxygen or Pb substitution has the opposite effect on the interlayer coupling; on the other hand, the rare-earth substitution for Ca decreases the carrier concentration, while excess oxygen or Pb substitution increases the carrier concentration. In contrast, for the substitution on the Cu site in the present study, an inconsistency between γ_s and γ_n appears. Since the carrier concentration changes little due to the very low doping concentration for Cu, the rapid reduction of ρ_c and γ_n is mainly caused by the decrease of the barrier potential Δ. And the dopant will destroy the local superconductivity in CuO_2 layers, which will weaken the interlayer coupling and result in an increase of γ_s.[8] We would like to point out that similar studies are still lacking for substituting a Cu ion by a Zn ion, which is a nonmagnetic impurity, different from Mn, Fe, Co, and Ni ions. Jeon *et al.*[10] have found that Zn doping leads to a rapid decrease of the ρ_c and ρ_c/ρ_{ab} of Bi2212 single crystals. However, a systematic study on the Zn-substitution effect on the second peak has not been reported up until now. Further studies are needed in this field.

In conclusion, the anisotropies in both the normal and superconducting states were systematically studied for $Bi_2Sr_2Ca(Cu_{1-x}M_x)_2O_y$ (M=Mn, Fe, Co, and Ni) single crystals. The γ_n decreases with x, while the γ_s increases with x. It means that the anisotropy in the normal state is different from that in the superconducting state, inconsistent with the conventional concept.

We are grateful to Y. P. Sun for the magnetization measurements. This work was supported by the National Natural Science Foundation of China and the National Center for Research & Development on Superconductivity.

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