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Anomalous Effect in $La_{2-x}Sr_xCuO_4$ on Doping Level $x=1/4^n$

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The Hall measurement on the bulk sintered material and epitaxially grown film of $La_{2-x}Sr_xCuO_4$ shows clear increase of carrier mobility on the special doping level $x \approx 4^{-1}$, $4^{-2}$and 4^{-3}. When the crystal orientation of specimen film of the special doping level is such that current penetrates CuO_2 layers, the appearance of intrinsic negative resistance is observed almost reproducibly in 4-terminal current-voltage measurement at low temperature and small current.

1. INTRODUCTION

It is said that the the normal state characteristic of the high temperature superconductor (HTS) is very anomalous in comparison with ordinary metals. As one of the anomalous characteristics, we pointed [1-3], using at first the experimental data of Uchida *et al*.[4] and next our own data [2,3], that the sharp drop of the resistivity ρ in bulk $La_{2-x}Sr_xCuO_4$ materials is observed on Sr doping levels $x=4^{-n}$ (n ; integer) from low temperature up to room temperature with some appurtenant anomaly on $x=2\times4^{-n}$, and attributed the origin of the resistivity drop to the formation of a spatially ordered state of the stabilized hole pairs in each CuO_2 conduction layer. It was supposed [2] that the appurtenant anomaly may be connected with the well known reduction of threshold temperature T_c at $x \approx 1/8$ found in La-system HTS [5,6].

2. HALL MEASUREMENT

In order to make detailed study of the x dependent conduction anomalies of $La_{2-x}Sr_xCuO_4$, we conduct Hall measurement on both bulk sintered material and thin film. The bulk samples of doping range $0 \leq x \leq 0.1$ has $2.5\times5\times0.45$ [mm^3] size to which 4 leads of 0.03[mm] thick gold wire are bonded at the $\sim$400[°C] with small contact area $\sim$ 0.07 [mm^2] and low resistance. The van der Pauw method is used at 273[K] in magnetic field 1[T]. The Hall voltage V_H is measured on 6 current levels I in the range $1 \leq I \leq 10$ [mA]. Reliable V_H measurement is difficult for $x>0.1$ because $V_H<10$ [nV] there. The observed Hall coefficient R_H almost agrees with the one determined by x value within the discrepancy <10 %. On the other hand, the Hall mobility μ_H is found to be nearly constant $\mu_H \approx 10^{-4}$ [m^2/Vs], except anomalous increase at $x \approx 4^{-2}$and 4^{-3} up to twice of the basic value.

Hall measurement on the film specimens is made in the doping range $0.01 \leq x \leq 0.26$. Films are epitaxially grown on single crystal substrate of (100) $SrTiO_3$ kept at 650 [°C] by RF-magnetron- sputtering method. The films of $\approx$500 [nm] thickness are formed by Ar ion etching into Hall-bridge-shaped specimens (see the inset of Fig. 1). X-ray pattern shows that most films are c-axis oriented. The V_H is measured in 1[T] field and 1$\sim$10 [mA] current. Just as in the bulk specimens, R_H of the specimen of $x \leq 0.23$ almost agrees with the nominal value within the discrepancy of 10 % in the temperature range 100 $\sim$ 273 [K]. When $x \geq 0.25$, R_H diverts from the nominal value. On the other hand, the μ_H shows clear increase at $x \approx 1/4$ and $1/4^2$ with some hump around 1/8 (see Fig. 1). The fabrication of the film specimens of the definite Sr doping level is difficult when $x \leq 0.02$ in our sputtering method because of the poor controllability of the Sr doping level there.

3. ANOMALOUS CONDUCTION

In the measurement of film specimens of the doping $x \approx 4^{-1}$, 4^{-2}, we occasionally find "unusual" specimens with exceptionally large μ_H value. The large peak values of μ_H shown in Fig. 1 are the data obtained from those "unusual" specimens. In order to obtain reliable data of Hall voltage, the Hall measurement must be conducted on relatively large current level 1$\sim$10 [mA]. On the other hand reliable measurement of current-voltage relation can be made on much smaller current level. When R-T relation by the 4-terminal method is made on the "unusual" specimens on much reduced current level, they reveal anomalous resistivity transition, an example for a specimen of $x \approx 1/4$ is shown in the inset of Fig. 1. The transition is seemingly similar to ordinary superconducting transition with sharp resistance decrease below certain "transition temperature" T_s. It has, however, the following properties clearly different from the ordinary superconductivity transition of $La_{2-x}Sr_xCuO_4$ material. (i) The x value of the "unusual" specimens is limited only to $x \approx 4^{-1}$, 4^{-2} in the measured doping range. (ii) T_s is strongly current dependent and increases up to 200 $\sim$300[K] on current level less than 1 [μA]. (ii) Although the specimen voltage V(AB) (see the inset of Fig.1) always shows positive resistivity at finite current I(AB), the specimen voltage V(CD) under the small current I(AB) reveals negative resistivity at $T<T_s$ with "negative voltage" whose sign is opposite to the sign of ohmic voltage. (iii) Being

different from simple thermo-electric voltage, the "negative voltage" vanishes when the current vanishes, and changes its sign according to I(AB) sign change. (iv) The appearance of "negative voltage" does not depends on the terminal-contact condition. (v) This unusual characteristic very easily disappears after 1$\sim$3 heat cycles between room temperature and low temperature. Deteriorated specimen shows simple ohmic relation with resistance much higher than original state. (vi) The reproducibility in fabrication of the "unusual" specimens is extremely bad.

Although we found the unusual effect nearly at the same time as the report of Lagues *et al.* who described the unusual zero-resistivity transition at $T_c \sim 260$ [K] in an artificial cuprate material belonging to BiSrCaCuO [7], we hesitated about its publication because of the lack of reproducibility and the appearance of seemingly unreasonable "negative voltage". After experimental efforts, we recently find out several necessary conditions prerequisite to observe the anomalous effect reproducibly. The conditions are as follows. (1) Thin film specimens should be made of $La_{2-x}Sr_xCuO_4$ of $x=4^{-n}$. (2) The crystal orientation of the specimen films should be such that the current *penetrates* CuO_2 layers. (3) In ordinary films composed of the aggregation of small single crystals, strong electrostatic shielding using Al foil *etc.* and the elimination of external noise are necessary to observe with stability the appearance of the anomalous effect especially at low temperature.

One method to obtain the "unusual" films relatively easily ($\sim$50% yield) is to make $La_{2-x}Sr_xCuO_4$ films on (110) $SrTiO_3$ substrate. In this case the c axis of the crystal of the film tends to tilt $\sim45°$ toward the substrate surface, and current in the film may flow penetrating the CuO_2 layers. In Fig. 2 are shown an example of current dependence of the voltages V_1 and V_2 (see the sample form in the inset) observed in the films of $x \approx 4^{-2}$ with thichness $\approx$ 130 [nm] fabricated in this method. The 4 terminals are made by direct evaporation of Pd film strips on the $La_{2-x}Sr_xCuO_4$ film strip. Although "2 terminal voltage" V_1 gives always positive resistivity, "4 terminal voltage" V_2 reveals negative resistivity when current is small and $T<T_S$. The current range for the appearance of "negative voltage" increases with the decrease of temperature. As seen in the inset, the characteristic at 4.2 [K] reveals the appearance of the "negative voltage" with high stability on vanishing current level. However, the voltage appears unstable on finite current level. Sometimes we observe the sudden "collapse" or disappearance of the "negative voltage" probably due to the influence of external noise. It must be noted that this example is represented to emphasize that the anomalous effect is independent of the terminal condition. We can also easily observe the appearance of the "negative voltage" using the film of this type of crystal orientation in the sample shape as shown in Fig. 1.

Besides the conduction anomaly described above, we have observed when $x \approx 4^{-n}$ the "capacitive anomaly" which may have the same ground as the "negative voltage". The capacitance C_t of Pd/$La_{2-x}Sr_xCuO_4$/$SrTiO_3$/Pd multi-layer structure is found to be larger than the capacitance C_{STO} of Pd/$SrTiO_3$/Pd structure with the same area and insulator thickness. Ordinary theory teaches us $C_t \leq C_{STO}$ relation whether $La_{2-x}Sr_xCuO_4$ is conductive or insulative.

4. DISCUSSION AND CONCLUSION

In normal conduction model the "negative voltage" is completely unreasonable effect to be excluded due to some experimental error. We have checked possible parasitic origins of the "negative voltage" such as possibilities of thermo-electric effect, the incompleteness of terminal contact, the appearance of anomalous 1D conduction property, etc. Finding the method to observe the "unusual" effect almost reproducibly, we have been able to exclude the parasitic causes. Considering the above denoted prerequisite conditions (1)$\sim$(3) necessary to observe the anomaly, we are now

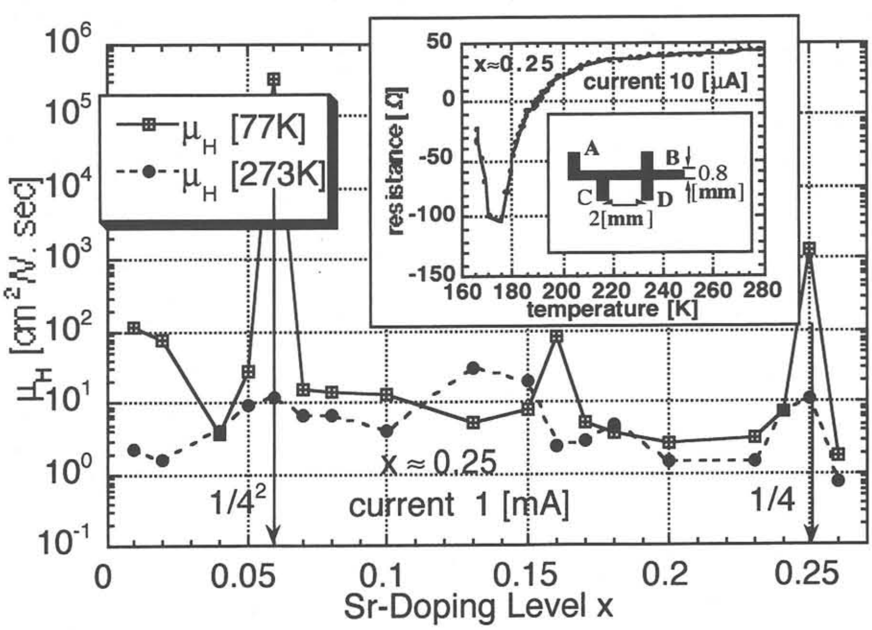

Fig. 1. The dependence of Hall mobility μ_H on the Sr-doping level x found in a $La_{2-x}Sr_xCuO_4$ films made on (100) $SrTiO_3$ substrate. Insets show the form of sample and the "negative voltage" observed in an "unusual" specimen at a small current.

studying the following tentative model to give explanation for the "negative voltage". The fact that the carriers in $La_{2-x}Sr_xCuO_4$ exist in 2D CuO_2 layers and that the unusual effect occurs on special carrier level $x = 4^{-n}$ remind us the quantum Hall effect [8] where the anomalous quantization of Hall resistance appears in the 2D electron system satisfying the following condition. (a) In magnetic field each electron takes *localized steady state* in one of the Landau levels. (b) The quantization occurs when the 2D electron density σ satisfies $\sigma = (eB/2\pi\hbar)n$ (n; integer), where the 2D conduction layer is considered to be replete with carriers of one *localized steady state* of a Landau level n. (c) The *spatial repletion* state in one quantum state means the macroscopically ordered state. (d) The quantum Hall effect occurs as a macroscopic quantum effect of the spatially ordered carrier system only when the gate-voltage-induced carrier density coincides with σ .

After the quantum Hall effect, we may suppose the following mechanism of the appearance of the "negative voltage" in the 2D hole carrier system in CuO_2 layers.
(i) It is assumed that the 2D hole carriers are originally in pairing state. (ii) Each hole pair at $x \approx 4^{-n}$ takes one of the quantized *localized steady state* (n'th order hole pair ; nHP) with quantized area $2\times4^n S_{CuO_2}$, where S_{CuO_2} is the area of a CuO_2 unit [1] , and where each CuO_2 layer is spatially replete with nHP with the repulsive coulomb interaction between hole pairs. (iv) This *spatially ordered state* is a macroscopic quantum state with properties dual to superconductivity where carrier-pairs system makes *ordering in the momentum space*.
(v) Similar to the fluxons is superconductor, the external charge Q_e introduced into the spatially ordered system occupies a CuO_2 layer with charge quantity of 2e per area $2\times4^n S_{CuO_2}$, around which distributes shielding charge of compensating charge quantity. The shielding charge is made by the displacement (or "polarization") of the ordered hole pair system. We call the quantized planar charge structure "chargeon", which is composed of one externally introduced charge plane and two shielding planes of polarization charge. (vi) Just as fluxons moves inside the superconductor from the surface accelerated by the mutual repulsive interaction among fluxons, the chargeons intrude into the material from the interface (with electrode) being accelerated by the mutual repulsive force among chargeons. (vii) Since Q_e and the polarization charge $Q_P(=-Q_e)$ moves simultaneously, one may observe "negative voltage" when the voltage terminals make charge exchange with the hole pair system in the small current limit. (viii) In equilibrium this situation is a "complete dielectricity" where the polarization $\vec{D}_e$ made by Q_e is compensated by the polarization $\vec{P}_p$ made by Q_P or $(\vec{D}_e + \vec{P}_p) = 0$. (xi) This model also gives explanation for the capacitive anomaly.

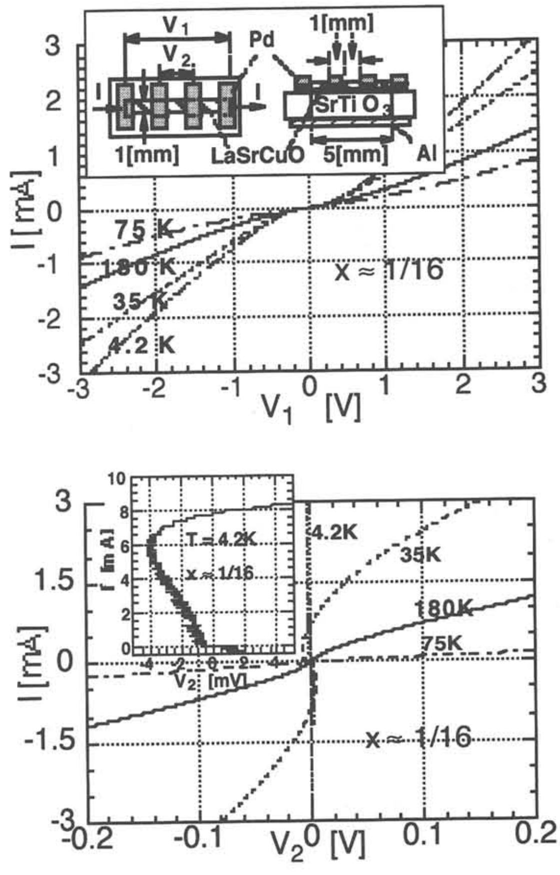

Fig. 2. The current dependence of the voltage V_1 in the 2-terminal regime and the voltage V_2 in the 4-terminal regime found in a film sample made on (110) $SrTiO_3$ substrate. Insets show the sample shape and the "negative voltage" at 4.2 [K].

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