

# Ultrafast Dynamics of Photoinduced Electronic Phase Modulation in Ladder Cuprate of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$

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Ultrafast carrier dynamics caused by photoexcitation in quasi-one-dimensional two-leg ladder cuprate  $\text{Sr}_4\text{Ca}_{10}\text{Cu}_{24}\text{O}_{41}$  was investigated by the femtosecond reflection spectroscopy. After the photoexcitation along the leg direction, the transient reflectivity changes ( $\Delta R/R$ ) in the mid-infrared region showed instant decrease within 150 fs. The suppressed  $\Delta R/R$  increased so rapidly on the picosecond time scale that the reflectivity value finally became larger than that in the initial state. Such a successive response in  $\Delta R/R$ , which was also observed in other photon energy regions, is discussed in terms of ultrafast variation of the Drude weight in the ladder system by the photoirradiation.

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## 1. Introduction

Photoinduced phase control in the strongly correlated electron system by using a femtosecond (fs) laser pulse has been attracting much attention because of ultrafast changes of physical properties. As is known for doping-induced insulator-to-metal transitions or high- $T_c$  superconductivity, the electronic state in 3d transition metal oxides are changed markedly by hole- or electron-doping. From the viewpoint, cuprates are suitable system for investigating the ultrafast control of the electronic state by photoirradiation. The dynamics in the photoexcited state has been studied on one-dimensional (1D)-chain- and two-dimensional (2D)-layer-structured cuprates [1, 2]. In addition to those, ladder cuprates with an intermediate structure between 1D and 2D systems are an intriguing candidate, because of the unique physical nature [3].

Two-leg ladder compound,  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  has been known as the unique quasi-1D cuprate exhibiting superconductivity [4]. The crystal structure is mainly composed of 1D edge-sharing  $\text{CuO}_2$  chains and two-leg corner-sharing  $\text{Cu}_2\text{O}_3$  ladders as shown in Fig. 1a [5, 6]. The chain and ladder planes are stacked alternately along  $b$ -axis, as shown in Fig. 1b, and those are separated by Sr/Ca layers. The superconductivity is realized under high pressure of 3–8 GPa in the highly doped region ( $x \geq 10$ ) [7]. The  $\text{Ca}^{2+}$  substitution for  $\text{Sr}^{2+}$  plays a role

in not only controlling the average valence of the chain- and ladder-Cu ions but applying the chemical pressure by the difference of the ionic volume. As the nominal valence of Cu ion is +2.25, the system is self-doped with holes from the chain to ladder sites. While the resistivity ( $\rho$ ) at small  $x$  is insulating, the ladder plane obtains a metallic behavior (i.e.,  $d\rho/dT > 0$ ) and the resistivity largely decreases with the hole doping especially in the direction of the  $c$ -axis (leg) [8, 9]. Under the high pressure, it shows a metallic behavior even along the direction of the  $a$ -axis (rung) [7]. The optical spectroscopy revealed that Ca substitution led to the redistribution of the hole carriers from the chains to ladder plane and gave us a clue to estimating the hole densities of Cu in the chain and ladder [10].

The electronic structure in  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  can be controlled by the physical and chemical pressures. In addition to them, the photoexcitation can be an important method to control the electronic state. In this study, we investigate the ultrafast dynamics in  $\text{Sr}_4\text{Ca}_{10}\text{Cu}_{24}\text{O}_{41}$ , which is metallic and shows superconductivity at low temperature with external pressure, and clarify the variation of the electronic structure by the photoexcitation.

## 2. Experimental

Single crystals of  $\text{Sr}_4\text{Ca}_{10}\text{Cu}_{24}\text{O}_{41}$  were grown by the travelling-solvent-floating-zone method. The reflectivity spectrum was measured using polarized light in the energy range 0.01–0.7 eV with a Fourier transform-type interferometer and 0.6–5 eV with a grating monochromator. The time-resolved reflectivity change ( $\Delta R/R$ ) was

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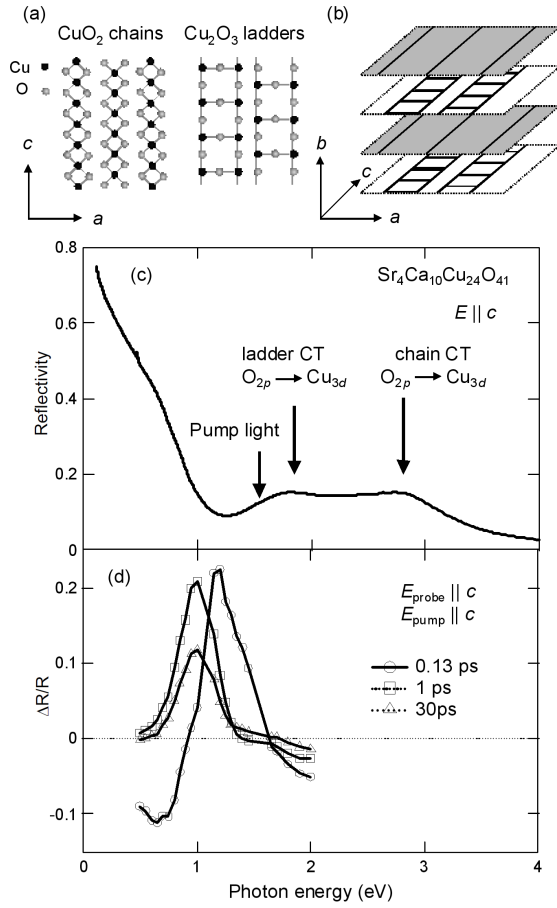


Fig. 1. (a) Schematic structures of an edge-sharing CuO<sub>2</sub> chain layer and two-leg Cu<sub>2</sub>O<sub>3</sub> ladder layer contained in Sr<sub>14-x</sub>Ca<sub>x</sub>Cu<sub>24</sub>O<sub>41</sub>. (b) Schematic three-dimensional illustration of Sr<sub>14-x</sub>Ca<sub>x</sub>Cu<sub>24</sub>O<sub>41</sub> structure. The chain layer (gray square) and ladder layer (white square) are stacked alternately along *b*-axis. The Sr/Ca layers are located between the chain and ladder layers. (c) Reflectivity spectrum measured with polarization of *E* || *c* in Sr<sub>4</sub>Ca<sub>10</sub>Cu<sub>24</sub>O<sub>41</sub>. (d)  $\Delta R/R$  spectra at 0.13, 1, and 30 ps.

measured by means of a pump-probe (P-P) technique. A Ti:sapphire regenerative amplifier system (photon energy: 1.53 eV, pulse duration: 120 fs, and repetition rate: 1 kHz) was used as a light source. The output pulse from the amplifier system was divided into pump and probe beams. The frequency of probe pulse was converted from 0.5 to 2.0 eV with an optical parametric amplifier. The polarizations of pump and probe pulses were parallel to the *c*-axis of the samples. The reflectivity and the P-P measurements were performed at room temperature.

### 3. Results and discussions

The reflectivity spectrum in Sr<sub>4</sub>Ca<sub>10</sub>Cu<sub>24</sub>O<sub>41</sub> with the polarization parallel to *c*-axis is shown in Fig. 1c. Reflecting the metallic behavior in this compound, the spectral shape is a Drude-type metallic feature in the low-energy

region and a clear plasma edge is discerned at around 1.2 eV. In contrast to 2D cuprates, the spectral weight below the plasma edge is dominated by a single Drude component [10]. The peaks observed at 1.8 and 2.7 eV are assigned to the charge-transfer (CT) transitions from O 2*p* band to the Cu 3*d* upper Hubbard band in the ladder plane and the chains, respectively [10, 11]. The photon energy of pump pulse (1.53 eV) is closer to the CT band in the ladder than the chain.

The transient reflectivity change  $\Delta R/R$  spectra at 0.13, 1 and 30 ps are shown in Fig. 1d. The excitation density of pump pulse is 8.6 mJ/cm<sup>2</sup>, which corresponds to 0.15 photons/(Cu in ladders and chains). Immediately after the photoexcitation at 0.13 ps, the characteristic  $\Delta R/R$  responses are observed in three regions of the photon energy; the mid-infrared region (0.5–0.9 eV), the near-infrared region (1.0–1.4 eV), and the visible region (1.7–2.0 eV). The time evolutions of  $\Delta R/R$  by dividing them into the three energy regions are shown in Fig. 2a–c. At 0.5 eV as shown in Fig. 2a, the  $\Delta R/R$  signal shows a negative response just after excitation and decays within 150 fs. After that, the signal is changed to positive on the time scale of *ca.* 1 ps. The time profile consists of two components; the fast decay component observed just after excitation and the slow decay component. With increasing the probe energy, the two components are still observed, changing the amplitude as well as the sign of each component.

Around the near-infrared energy region in Fig. 2b, the  $\Delta R/R$  signals are positive for the whole time domain. The fast decay component is hardly observed at 1.0 eV, indicating that the fast component changes its sign from negative to positive at 1.0 eV. The rising time just after excitation at 1.2 eV is even faster than that at 1.0 eV, which implies the reappearance of the fast component. At 1.4 eV, the slow component seems to be suppressed. In the visible region as shown in Fig. 2c, the sign of  $\Delta R/R$  signals becomes negative again. The  $\Delta R/R$  still has the fast component changing within 150 fs and the slow component with a relatively large decay time.

From the results of the time evolution of  $\Delta R/R$ , we discuss the photoinduced carrier dynamics. Immediately after the excitation, the electron-hole pairs are generated by the CT transition in the ladder. As a result, the photogenerated-hole carriers are injected in the ladder plane. In the case of a usual semiconductor, the injected carriers bring about the increase of the Drude weight, and it can be expected that the  $\Delta R/R$  signal shows a resultant positive increase in the mid-infrared region and a negative in the near-infrared energy region. In fact, the Drude weight increases with increasing hole density in Sr<sub>14-x</sub>Ca<sub>x</sub>Cu<sub>24</sub>O<sub>41</sub> system [10]. However, the observed  $\Delta R/R$  values of the fast component just after excitation show the negative change in the mid-infrared region (see in Fig. 2a) while positive in the higher energy region, strongly indicating the reduction of the Drude weight. The ultrafast suppression of metallicity cannot be explained in terms of an electronic-band-filling

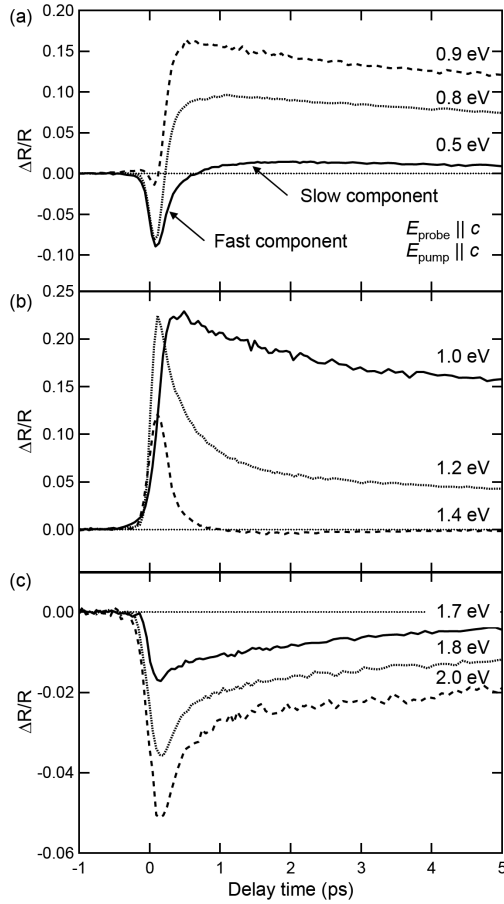


Fig. 2. Time evolutions of  $\Delta R/R$  in the probe energy of (a) the mid-infrared, (b) the near-infrared, and (c) the visible region. The polarization of pump and probe pulse are parallel to  $c$ -axis.

modulation by the photocarrier doping similar to the 1D-chain and 2D-layer cuprates [2, 3]. If the carrier mobility is disturbed more than the increase in the hole density, the Drude weight will be reduced even though the photocarriers are injected in the ladder. The carrier mobility depends on the electronic structure. As one of the possible scenarios of the suppression of metallicity, we suggest the ultrafast change of the electronic structure by photoirradiation. In contrast, as shown in the slow components in the mid-infrared region (positive) and near-infrared region (negative), the suppressed Drude weight recovers on the timescale of ps and is enhanced more than that in the initial state. The enhanced Drude weight is consistent with a usual photodoping effect observed in semiconductors and cuprates. This can be interpreted as the enhancement

of metallicity by the photogenerated-hole carriers. Therefore, we suggest that the disturbed carrier mobility recovers. This scenario can explain the observed unique phenomena. The ultrafast change of the electronic structure may be characteristic of the ladder system and can be viewed as a photoinduced *metal-to-insulator* transition.

#### 4. Conclusions

Photoinduced carrier dynamics in the metallic compound of two-leg ladder cuprate  $\text{Sr}_4\text{Ca}_{10}\text{Cu}_{24}\text{O}_{41}$  was studied by femtosecond pump-probe reflection spectroscopy. The Drude weight instantly reduces within 150 fs, after that, the suppressed Drude weight increases rapidly on the timescale of ps and more enhanced than that in the initial state. We conclude that the observed unique phenomenon is ascribed to the photoinduced electronic-structure modulation in the ladder system.

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