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We demonstrate the ultrafast photoinduced Mott transition from a charge transfer insulator to a metal in a halogen-bridged Ni-chain compound by pump-probe reflection spectroscopy. Upon the irradiation of a 130-femtosecond laser pulse, the spectral weight of the gap transition is transferred to the inner-gap region. When the photoexcitation density exceeds 0.1/Ni site, the Drude-like high-reflection band appears in the infrared region, signaling the formation of a metallic state. The photogeneration of the metallic state and the subsequent recovery to the original gapped state occur within a few picoseconds.

Since the discovery of high-T_c superconductivity, doping-induced insulator (I)–metal (M) transitions or filling-control Mott transitions in $3d$ transition-metal compounds have been attracting much attention. In most undoped $3d$ transition-metal oxides, electrons are localized on atomic sites due to the strong Coulomb repulsion energy U, forming antiferromagnetic insulators [Mott insulators or charge transfer (CT) insulators]. Their electronic and magnetic properties can, however, be modified to a large extent by chemical doping [1–3]. The transition from an antiferromagnetic insulator to a ferromagnetic metal [1] induced by doping and the related colossal magnetoresistance phenomena in the perovskite manganites [2,3] are a very dramatic example as well as the high-T_c superconductivity that emerges in the hole- or electron-doped layer-structured cuprates [1]. Photoirradiation is another effective method of producing carriers in materials [4]. In this context, the photocarrier doping will also give rise to a large response in the Mott insulators and CT insulators. By using a femtosecond-pulse laser as a light source for the photocarrier doping, control of the conducting properties may be achieved in an ultrafast time domain. This is an important strategy for the realization of the ultrafast devices with Tb/s class operation [5–8].

Here, we report the photoinduced *I-M* switching of the halogen-bridged Ni-chain compound, which is a prototypical 1D CT insulator. Photocarrier doping by using a 130-femtosecond laser pulse on the Ni-chain compound induces a marked change of the electronic structure. When the photoexcitation density exceeds 0.1 per Ni site, a Drude-like high-reflection band appears in the infrared (IR) region, signaling the formation of a metallic state. Ultrafast dynamics of the photoinduced metallic state will be discussed on the basis of the results of temporal and doping-density dependence of the reflectivity spectra.

Figure 1(a) shows the crystal structure of $[\text{Ni(chxn)}_2\text{Br}]\text{Br}_2$ [9]. The Ni^{3+} and Br^- ions line up alternately along the **b** axis. Four N atoms of the two ligand units (chxn:cyclohexanediamine) coordinating a Ni ion produce such a strong ligand field that the Ni^{3+} ion is in a low spin state ($d^7:S = 1/2$) with an unpaired electron in the d_{z^2} orbital. The 1D electronic state is formed via the hybridization between Ni d_{z^2} and Br p_z orbitals. The large U of Ni $3d$ electrons opens a gap between the Ni $3d$ upper Hubbard (UH) band and the lower Hubbard (LH) one [Fig. 1(b)]. The occupied Br $4p$ band positions itself within the Mott-Hubbard gap, and hence the lowest-energy electronic excitation is a CT transition from the Br $4p$ valence band to the Ni $3d$ UH
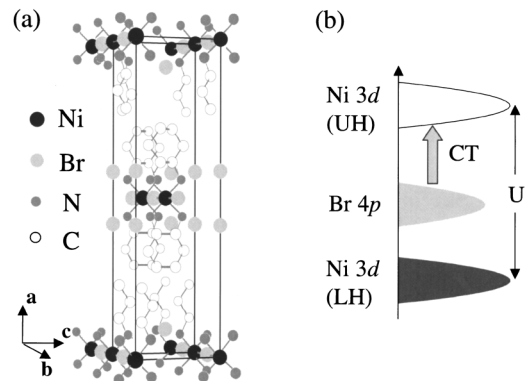

FIG. 1. (a) Crystal structure and (b) electronic structure of $[\text{Ni(chxn)}_2\text{Br}]\text{Br}_2$.

band [10]. Thus, the electronic structure of this system is similar to that of the 1D cuprates such as M_2CuO_3 ($M =$ Sr or Ca) [1]. Strong one-dimensional antiferromagnetic interaction $J \sim 3000$ K [11] works between the spins on the neighboring Ni site, similarly to the case of Sr_2CuO_3 ($J \sim 2200$ K) [12].

It has recently been reported [13] that this Ni compound has a gigantic third-order nonlinear susceptibility $\chi^{(3)}$. The enhancement of $\chi^{(3)}$ is due to the large dipole moment (≈ 20 Å) between the odd- and even-parity CT excited states, which are nearly degenerate with each other. Such a large dipole moment and large J are consequences of strong p-d hybridization. In addition, the ultrafast decay of the photoexcited states within a few ps has been reported in another 1D CT insulator, Sr_2CuO_3 [14]. The strong p-d hybridization and the ultrafast relaxation of the photoexcited states expected for the Ni-chain compound will provide a good arena for testing an ultrafast optical switching from I to M.

To probe the photodoping-induced change of the electronic structure, we adopted pump-probe reflection spectroscopy. In the measurement, a Ti:Al₂O₃ regenerative amplifier system (Spectra Physics Hurricane) operating at 1 kHz was employed as a light source. Output from the laser (800 nm:1.55 eV) with the pulse width of 130 fs was

divided into two beams. One beam was used for a pump light, and the other for the excitation of an optical parametric amplifier system (Spectra Physics OPA-800), from which the probe light pulses ranging from 0.1 to 2.5 eV were obtained. The time resolution of the apparatus is 200 fs. Single crystals of [Ni(chxn)₂Br]Br₂ were synthesized electrochemically according to the procedure described in the literature [15].

In Fig. 2(a), the polarized reflectivity spectrum is presented by a broken line. A sharp peak at 1.3 eV is due to the CT gap transition. The transient reflectivity (TR) spectra observed at the delay time t_d after the photoirradiation are shown by colored dots and lines in the same figure. The intensity of the irradiated light was 3.6 mJ/cm². Under this condition, the average excitation density x_{ph} of the absorbed photon is 0.5 per Ni site within the absorption depth (460 Å), as evaluated by taking account of the reflection loss (30%) and the unit cell volume (8.68×10^{-21} cm³). Immediately after the photoirradiation ($t_d = 0.1$ ps), the reflectivity in the mid-IR region remarkably increases, being reminiscent of the Drude-like response, while the reflectivity around the CT band decreases due to photoinduced bleaching. The magnitude of the reflectivity R' at $t_d = 0.1$ ps reaches about 70% at the lowest photon energy of the probe light (0.12 eV), where the change of reflectivity [$\Delta R/R = (R' - R)/R$] is as large as 260% of the original reflectivity R. The imaginary part of the dielectric constant ε_2 was obtained by performing the Kramers-Kronig transformation (KKT) of the reflectivity spectrum. (The validity of the KKT procedure is discussed later with respect to Fig. 3. See also the note described in Ref. [16]). The ε_2 at $t_d = 0.1$ ps monotonically increases with lowering the probe photon energy to 0.12 eV, suggesting the closing of the optical gap. Such a remarkable photoinduced feature is observed only for the probe light polarization parallel along the Ni-Br chain ($\mathbf{E} \parallel \mathbf{b}$) and not for $\mathbf{E} \perp \mathbf{b}$ at all, suggesting the photogeneration of a quasi-one-dimensional metallic state.

To clarify the photoinduced change of the electronic state in greater detail, we have investigated the excitation density x_{ph} dependence. Spectra of the TR and ε_2 at $t_d = 0.1$ ps for various x_{ph} are presented in Figs. 3(a) and 3(b). For the weak excitation of $x_{ph} = 6.2 \times 10^{-4}$, a midgap absorption with a peak around 0.4 eV is observed in the ε_2 spectrum as shown in Fig. 3(b). A similar photoinduced midgap absorption has also been reported in 2D cuprates such as Nd_2CuO_4 and La_2CuO_4 [17]. As x_{ph} increases, the low-energy part of ε_2 below 0.2 eV significantly grows, and for $x_{ph} > 0.1$, the optical gap seems to disappear.

To investigate the evolution of the photoinduced Mott transition as well as to ascertain the validity of the overall analysis of the TR spectra using KKT, it is useful to examine the transfer of the spectral weight from the CT gap region to the innergap one. The spectral weight can be quantitatively analyzed in terms of the effective number of electrons $N_{eff}(\omega)$ defined as
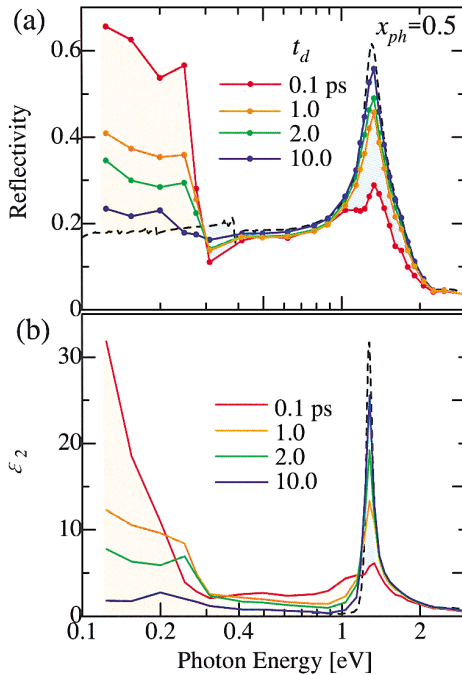

FIG. 2 (color). (a) Reflectivity spectra observed prior to the photoexcitation (a broken line) and at delay time t_d after the photoexcitation (colored dots and solid lines) at room temperature. The excitation density x_{ph} is 0.5 photon/Ni site. Polarizations of the pump and probe lights are both parallel to the chain axis $\mathbf{b}$. (b) Spectra of the imaginary part of the dielectric constant ε_2 before (a broken line) and after (colored solid lines) photoexcitation, obtained by Kramers-Kronig analysis of the reflectivity data shown in (a).
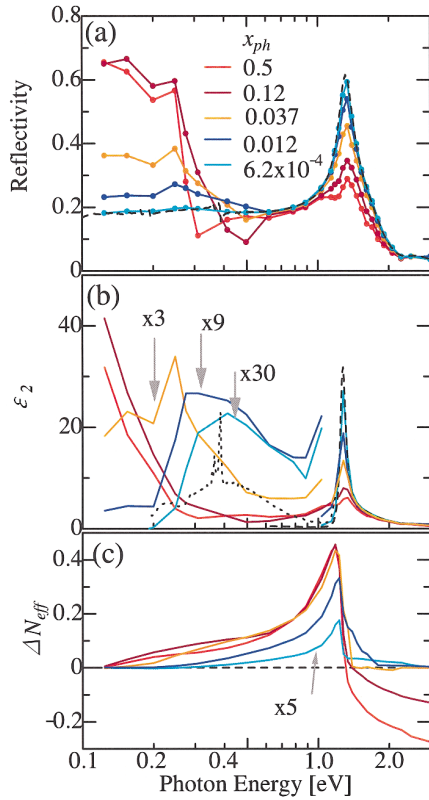
FIG. 3 (color). (a) Reflectivity spectra before (a broken line) and immediately after the photoexcitation ($t_d = 0.1$) (colored dots and solid lines) at room temperature. The excitation densities x_{ph} are shown in the figure. (b) ε_2 spectra before (broken line) and immediately after the photoexcitation ($t_d = 0.1$) (colored solid lines). A dotted line shows the spectrum before the photoexcitation, which is obtained by the direct measurement of the polarized absorption. (c) Photoinduced change in the effective number of electrons N_{eff} (ω) [$\Delta N_{eff}(\omega)$] at $t_d = 0.1$ ps for various x_{ph}.

$$N_{eff}(\omega) = \frac{2m_0}{\pi e^2 N} \int_0^\omega \frac{\omega' \varepsilon_2(\omega')}{4\pi} d\omega'.$$

Here, m_0 is the free electron mass and N the number of Ni atoms per unit volume [18]. N_{eff} (ω) is the measure for the kinetic energy of electrons on an energy scale of $\hbar\omega$. Since the lower energy bound of the measured photoinduced signals is 0.12 eV, the photoinduced change in N_{eff} (ΔN_{eff}) was calculated using ε_2 from 0.12 eV to $\hbar\omega$. The results for various x_{ph} at $t_d = 0.1$ ps are presented in Fig. 3(c). $\Delta N_{eff}(\omega)$ monotonically increases with $\hbar\omega$ up to 1 eV, reflecting the accumulation of the spectral weight below 1 eV. Then, it abruptly drops almost to zero at 1.3 eV due to the bleaching around the CT band, indicating that the spectral weight of the CT gap transition is transferred to the innergap region by the photodoping. The negative values of ΔN_{eff} above 1.5 eV for $x_{ph} = 0.12$ and $x_{ph} = 0.5$ as seen in Fig. 3(c) might be attributed to some flaws in the analysis [16] originating in the difference in absorption depths of the pump and probe lights or the

inhomogeneity of the generated carrier concentration [19–21]. Nevertheless, the observed systematic changes of ΔN_{eff} (ω) and the approximate holding of the sum rule over the wide range of x_{ph} ensure that the analysis using KKT presented here reflects well the photoinduced changes of the electronic state.

In Fig. 4(a), we plot $\Delta N_{eff}(1 \text{ eV})$ and $\Delta N_{eff}(0.2 \text{ eV})$ at $t_d = 0.1$ ps as a function of x_{ph}. $\Delta N_{eff}(1 \text{ eV})$, which represents the total spectral weight transferred from the CT band to the innergap region, saturates for $x_{ph} > 0.04$. On the other hand, $\Delta N_{eff}(0.2 \text{ eV})$, i.e., the spectral weight accumulated in the lower energy region between 0.12 and 0.2 eV, increases almost linearly with x_{ph} up to $x_{ph} = 0.1$. The steady increase of $\Delta N_{eff}(0.2 \text{ eV})$ for $x_{ph} > 0.04$ is attributable to the growth of the Drude weight. Such x_{ph} dependence of ΔN_{eff} is analogous to the chemical doping dependence of N_{eff} in the 2D cuprates and other Mott transition systems [1]. Thus, the Mott transition is driven by the photodoping in this Ni-chain compound.

A noteworthy aspect of the photoinduced Mott transition is the influence of the electron-hole asymmetry on the transient optical spectra. Being distinct from the chemical doping case, the photoirradiation creates both electrons and holes. In the Ni-chain compound, it has been clarified from the measurement of the dc conductivity [22] and the Seebeck coefficient [23] that a small number of electron carriers exist in an as-grown sample. A weak midgap absorption due to such carriers or small polarons is indeed observed in the ε_2 spectrum ($E \parallel b$) as shown by the dotted curve in Fig. 3(b). The photoinduced absorption observed for small x_{ph} ($= 6.2 \times 10^{-4}$) resembles this midgap absorption in spectral shape and energy position. This resemblance suggests that electron-type carriers are responsible for the photoinduced midgap absorption. The hole-type carriers with the Br p
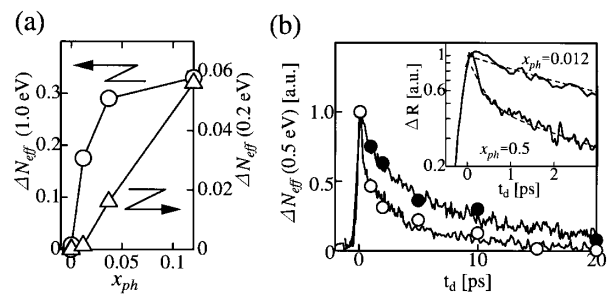

FIG. 4. (a) $\Delta N_{eff}(1.0 \text{ eV})$ and $\Delta N_{eff}(0.2 \text{ eV})$ at $t_d = 0.1$ ps as a function of the photodoping concentration x_{ph}. (b) Time evolutions of $\Delta N_{eff}(0.5 \text{ eV})$ for $x_{ph} = 0.5$ (open circles) and 0.012 (closed circles). Time evolutions of the photoinduced reflectivity change (ΔR) observed at 0.12 eV are also shown by solid lines. The inset shows the semilogarithmic plot of the time profiles of ΔR. The broken curves show the calculated decay profiles [$\Delta R(t_d) = 0.4 \exp[-(t_d/3)] + 0.5 \exp[-(t_d/8)] + 0.1$ for $x_{ph} = 0.012$ and $\Delta R(t_d) = 0.5 \exp[-(t_d/0.4)] + 0.25 \exp[-(t_d/3)] + 0.25 \exp[-(t_d/8)]$ for $x_{ph} = 0.5$, respectively].

character and resultant strong electron-lattice interaction may be strongly localized and hence make the least contribution to the spectral weight of the midgap absorption. When the metallic state is formed for $x_{ph} > 0.1$, however, there should be no distinction between electrons and holes for the strongly d-p hybridized state near the Fermi level.

The ultrashort lifetime of the metallic state is another important aspect of the present photoinduced Mott transition. Figure 4(b) shows the temporal characteristics of $\Delta N_{eff}(0.5 \text{ eV})$ for $x_{ph} = 0.012$ and $x_{ph} = 0.5$. In the same figure, we also present the time evolutions of ΔR (0.12 eV), which are in agreement with those of $\Delta N_{eff}(0.5 \text{ eV})$. The decay profiles of $\Delta N_{eff}(0.5 \text{ eV})$ and ΔR (0.12 eV) for $x_{ph} = 0.012$ are reproduced by the sum of the small constant term with the weight of 10% and the two exponential functions whose time constants τ_d (weights) are 3 ps (40%) and 8 ps (50%). On the other hand, those for $x_{ph} = 0.5$ can be reproduced by the sum of the three exponential function with τ_d (weights) of 0.4 ps (50%), 3 ps (25%), and 8 ps (25%). The experimental and calculated decay profiles of ΔR (0.12 eV) are presented in the inset of Fig. 4(b). The fast decay component with $\tau_d = 0.4$ ps is dominant for $x_{ph} = 0.5$, while such a fast decay was not discerned for $x_{ph} = 0.012$. Therefore, it is likely that the fast decay is characteristic of the photo-induced metallic states.

The decay dynamics of the photoexcited state in CT insulators has also been studied on the 2D cuprates (Nd_2CuO_4 and $Sr_2CuO_2Cl_2$) [24,25] and 1D cuprate (Sr_2CuO_3) [14]. The lifetime τ_d of the photoproducts has been revealed to be 1 ps ~ several tenth ps which is significantly faster than that in conventional semiconductors. The electron-electron scattering with emission of spin excitations or spinons is considered as a possible mechanism for the ultrafast relaxation in the CT insulators [14]. In the present halogen-bridged Ni-chain compound, enhancement of similar electron-electron scattering in the quasi-one-dimensional metallic state may play a major role in the increase of the recombination rate of photocarriers. In summary, a photoswitching from an insulator to a metal has been successfully demonstrated in a 1D CT insulator of the halogen-bridged Ni-chain compound. The increase of the excitation density changes the photoproduct from the midgap state to the metallic state. This is the first observation of the photoinduced Mott transition in the strongly correlated electron systems.

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[16] When applying KKT on TR spectra, there are two important effects to be considered: (1) carrier concentration changes depending on the distance from the surface, and (2) absorption depths of the probe light l_r and the pump light l_p are different. The spectral shape of the TR due to the midgap absorption observed for $x_{ph} < 0.012$ is almost unchanged and, therefore, will not be so affected by those two effects. It is, however, reasonable to consider that the absolute values of the TR and ε_2 are somewhat underevaluated, since $l_r > l_p (= 460 \text{ Å})$. To evaluate the two effects on the Drude-like reflection band observed for $x_{ph} > 0.1$, we postulated a metallic state expressed by a simple Drude model with thickness l_t (200–2000 Å) on the surface of the Ni-chain compound and simulated the R and ε_2 spectra. The result of the simulation shows that for $l_t > 1000$ Å, spectral shape and absolute value of R and ε_2 are independent of l_t. In the Ni-chain compound, thickness of photoinduced metallic state (region with carrier concentration > 0.1) exceeds 1000 Å for $x_{ph} > 0.2$. So we can consider that the Drude-like reflection band observed for $x_{ph} > 0.2$ will not be so influenced by the two effects. For the intermediate excitation density ($0.2 > x_{ph} > 0.02$), it might be necessary to take account of some errors in the analysis. In addition, the obtained N_{eff} values missed the far-infrared contribution of the Drude term, which will give the large contribution.

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