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Acceleration of domain wall movement by photoirradiation in perovskite-type cobaltite

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Femtosecond reflection spectroscopy was performed on a perovskite-type cobalt oxide, namely, $Pr_{0.5}Ca_{0.5}CoO_3$, that undergoes a photoinduced spin-state transition. After photoirradiation at 30 K, the time profile of the reflectance change shows a broad peak reflecting the propagation of the photodomain (about 60 Co sites per one photon). Analysis of the peak position indicates the sudden increase of the velocity of the propagation with increasing the excitation intensity. Such acceleration with increase in fluence originates from an abrupt sound velocity change driven by a cooperative photoinduced structural transition.

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Strongly correlated electron materials exhibit various interesting electronic phases, which are achieved by a subtle energy balance between spin, charge, and lattice degrees of freedom. Perovskite-type transition-metal oxide, as exemplified by high-T_c cuprates, magnetoresistive manganites, and so on, is a typical example. Researches on the photoexcited state in strongly correlated electron systems, aiming at photonically controlling such energy valance woven by the degrees of freedom and finding the resultant novel phase hidden in materials,[1] have recently drawn considerable attention.

In the study of the photoinduced phase transition (PIPT), femtosecond laser light with strong intensity and ultrashort duration has played an important role in triggering the photoexcitation process. The ultrafast excitation, which can be viewed as an external stimulus, perturbs the delicate energy balance and makes it possible to access the photoinduced phase on the femtosecond time scale. Vanadium or manganese oxides are interesting examples of materials that exhibit PIPT, and many experimental[2–6] and theoretical[7] studies on them have been reported over the past few decades.

As another candidate that exhibits PIPT, perovskite-type cobalt oxide is noteworthy. One of the most important physics in the cobaltite system is the unconventional spin-state transition in the trivalent cobalt ion surrounded by a CoO_6 octahedron. By the subtle balance between the crystal field energy and Hund's rule coupling, the spin configuration in Co^{3+} shows a thermal change from the low-spin state (LS: $S = 0$, $t_{2g}^6 e_g^0$) to the high-spin state (HS: $S = 2$, $t_{2g}^4 e_g^2$) or intermediate-spin (IS: $S = 1$, $t_{2g}^5 e_g^1$) state with an increase in temperature. One example system is $Pr_{0.5}Ca_{0.5}CoO_3$ (PCCO).[8] This material contains the same number of Co^{4+} and Co^{3+} ions; the former Co^{4+} site is always in a low-spin state with a configuration of $t_{2g}^5 e_g^0$, while the latter shows a magnetic transition between the LS and IS spin states at $T_C = 89$ K.[8] Importantly, excited e_g electrons above T_C play a role as carriers; thus, the spin-state transition is inevitably accompanied with an insulator metal transition.[9]

The authors recently reported an ultrafast time-resolved study on the perovskite-type cobaltite PCCO (Ref. 10) and revealed a PIPT from LS insulator state to IS metallic state as well as a successive propagation of a photonic domain at the velocity of an ultrasonic wave, which is a different example of the real-space variation after photoirradiation.[11] It was concluded that propagation of the photodomain occurs according to the following model[10]: The photoirradiation instantly forms an IS metallic domain at the surface of PCCO, which propagates in the direction of z, where z is the distance from the surface in the depth direction. It is assumed that the total dielectric function (ε) can be described as

$$\begin{aligned}\varepsilon(z) &= \gamma\varepsilon^{\mathrm{M}}\ (0 < z < d^{\mathrm{PI}}) \\ &= \gamma \exp[-(z - d^{\mathrm{PI}})/d]\varepsilon^{\mathrm{M}} \\ &\quad + \{1 - \gamma \exp[-(z - d^{\mathrm{PI}})/d]\}\varepsilon^{\mathrm{I}}\ (d^{\mathrm{PI}} < z), \end{aligned} \quad (1)$$

where d is the penetration depth of the pump light (about 60 nm), ε^{M} and ε^{I} are the dielectric functions at the IS metallic phase and the initial insulating state, respectively, γ is the efficiency of the photoinduced phase transition ($0 < \gamma < 1$), and d^{PI} denotes the thickness of the propagated domain. Once $\varepsilon(z)$ is established, $\Delta R/R$ can be numerically calculated as a function of d^{PI}. As a result, the time profile of $\Delta R/R$ for a wide photon-energy region (i.e., 0.5–2.1 eV) can be reproduced with a constant value of $\gamma \sim 0.7$. The comparison between d^{PI} and t_{d} indicates an ultrasonic motion of the photodomain (i.e., $d^{\mathrm{PI}} = v_s t_{\mathrm{d}}$, where v_{s} and t_{d} are sound velocity and delay time, respectively) and overdamping of the propagation around $d^{\mathrm{PI}} \sim$130 nm. The ultrafast formation as well as the mechanically driven dynamics strongly indicates that simple heating by laser irradiation can not explain the observed results. The microscopic origin of the domain wall motion is still unknown, although the fact that the IS metallic state is subject to external pressure may be an important key to understanding it.[12]

In this paper, we further investigated PCCO, in terms of the fluence dependence, by femtosecond reflection spectroscopy and revealed sudden acceleration of the movement of the photoinduced domain wall with increasing excitation intensity. This acceleration is due to a thresholdlike structural transition with fluence, indicating not only ultrasonic expansion of

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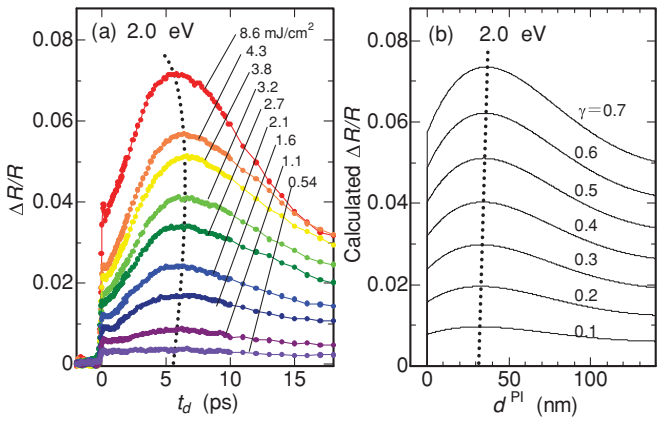

FIG. 1. (Color online) (a) The time profiles of the relative change of reflectivity ($\Delta R/R$) for various fluence at 2.0 eV (t_d denotes a delay time). The dashed line is a guide to the eyes to show the peak position in $\Delta R/R$. (b) The γ dependence of numerically calculated $\Delta R/R$ as a function of d^{PI} at 2.0 eV in terms of Eq. (1). γ and d^{PI} denote ratio of ε^{IS} at surface and thickness of the propagated metallic region, respectively. The dashed line shows the peak position in the calculated $\Delta R/R$.

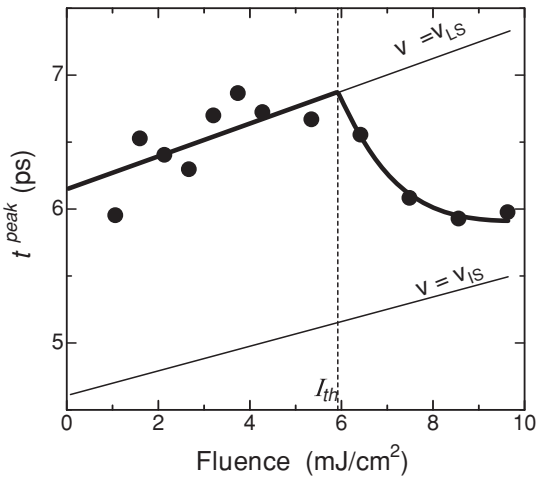

FIG. 2. The peak time (t^{peak}) obtained from the experimental $\Delta R/R$ as a function of fluence (black circles). The solid curve is a fitted result in terms of Eqs. (2)–(4). The solid lines denote the calculated peak time d^{PI}_{peak}/v in the IS metallic state ($v = v_{IS}$) and the LS insulating state ($v = v_{LS}$).

the photodomain but also active control of the domain wall dynamics on a picosecond time scale.

In a previous study,[8] we grew polycrystalline samples of PCCO. The relative change of reflectivity ($\Delta R/R$) driven by irradiation of femtosecond laser light was obtained by using a conventional pump-probe technique. We used a mode-locked Ti:sapphire regenerative amplified laser (pulse width: 120 fs; repetition rate: 1 kHz; photon energy: 1.58 eV) as a light source. The amplified light was divided by a beam splitter into two pulses. One pulse (1.58 eV) was used as a pump light for the excitation. The photon energy corresponds to an electronic transition from the Co t_{2g} states hybridized with the O $2p$ band to the empty Co e_g band[13] and can trigger the spin-state transition. The other split pulse was introduced into an optical parametric amplifier, and the photon energy was converted to 2.0 eV to monitor $\Delta R/R$ after the pumping.

Figure 1(a) shows the time profile of $\Delta R/R$ and its fluence dependence by irradiating the pump light of 2.0 eV. When fluence is about 9 mJ cm^2, $\Delta R/R$ instantly increases after the photoirradiation and shows successive change, forming a broad peak at around about 5 ps. As mentioned before, this peak in $\Delta R/R$ originates from the interference of the probe light in the moving photonic area.[10] As fluence decreases, the total magnitude of $\Delta R/R$ is suppressed while the broad peak structure is kept. Figure 1(b) shows the calculated $\Delta R/R$ profiles with several values of γ as a function of d^{PI} in terms of Eq. (1). If we simply identify t_d with d^{PI}, the numerical results qualitatively reproduce two features, namely, the gradual suppression of $\Delta R/R$ and the peak formation in the $\Delta R/R$ profiles, indicating that the excitation intensity can be viewed as γ. The formation of the interference peak indicates that the photoinduced domains have a typical size smaller than the wavelength of the probe beam even at lower fluence. Such formation of the photoinduced state is in contrast to the case of vanadium oxide,[3] namely, the percolative and two-dimensional generation of photodomains.

It should be noted that the peak position in the time profiles depends on the fluence. In our experiment [Fig. 1(a)], the peak time (t_{peak}) gradually increases with weak excitation but decreases at higher fluence as denoted by the dashed line. In Fig. 2, the value of t_{peak} is plotted as a function of fluence by closed circles, and t_{peak} shows a broad peak at 5 mJ/cm^2. In contrast, as shown in Fig. 1(b), the peak position in the calculated $\Delta R/R$ (d^{PI}_{peak}) profile linearly moves to the right-hand side with an increase in γ, or fluence. When uniform motion of the photonic domain is assumed, the theoretically predicted t_{peak} corresponds to d^{PI}_{peak}/v, where v is domain velocity. The decrease of t_{peak} can not be accounted for by the uniform motion of the photonic domain.

Naito *et al.*[14] recently investigated v_s in a similar cobalt perovskite undergoing the same phase transition at about 110 K. According to their results, v_s in the IS metallic state (v_{IS}) is about 33% larger than that in LS insulating state (v_{LS}). This difference in v_s results from the softening of the lattice in the LS state in PCCO. It is noteworthy that $LaCoO_3$, undergoing a similar spin change with lattice contraction, shows hardening in the LS state.[13] The difference of the elastic property has not been resolved yet, but instabilities of the charge ordering of cobalt ions (Co^{4+} and Co^{3+}) or praseodymium ions in PCCO (Ref. 15) may be important.

For comparison, the calculated peak time d^{PI}_{peak}/v in the IS state ($v = v_{IS}$) and the LS state ($v = v_{LS}$) is plotted with solid lines as a function of fluence in Fig. 2. In both the IS and LS states, the calculated d^{PI}_{peak}/v increases linearly. The comparison of t_{peak} with d^{PI}_{peak}/v implies that v suddenly changes with an increase in the yield of PIPT.

On the basis of the above discussions, to understand the anomalous change of t_{peak}, the following model is proposed. In the case of weak excitation, where the fluence of the pump light (I^{pump}) is less than a threshold value (I_{th}), it is reasonable to consider that the uniform motion of the photonic domain at the speed of v_{LS}, which is expressed by

$$t_{peak} = d^{PI}_{peak}/v_{LS} (I^{pump} < I_{th}). \quad (2)$$

TABLE I. Evaluated parameters by the fitting analysis in terms of Eqs. (2)–(4). a and b are parameters defined by $d_{\rm peak}^{\rm PI} = aI^{\rm pump} + b$ (see text).

	a	b	$I_{\rm th}$ (mJ/cm^2)	β (cm^2/mJ)
Fitting parameters	7.5	31	5.9	7.1

As shown in Fig. 1(b), $d_{\rm peak}^{\rm PI}$ is proportional to γ, or $I^{\rm pump}$, and hence $d_{\rm peak}^{\rm PI} = aI^{\rm pump} + b$, where a and b are fitting parameters. As $I^{\rm pump}$ surpasses $I_{\rm th}$, to reproduce the sudden change of the velocity from $v_{\rm LS}$ to $v_{\rm IS}$, it is assumed that a thresholdlike increase of v (v') is described as

$$v' = v_{\rm LS} + \Delta v \frac{2}{\pi} \tan^{-1}[\beta(I - I_{\rm th})] \quad (I^{\rm pump} > I_{\rm th}), \qquad (3)$$

where $\Delta v = v_{\rm IS}$-$v_{\rm LS}$ ($\Delta v/v_{\rm LS} = 1.33$),[13] and we used a function of arctangent as a simple step function. Under these conditions, $t_{\rm peak}$ in the strong excitation region can be expressed as

$$t_{\rm peak} = d_{\rm peak}^{\rm PI}/v'(I^{\rm pump} < I_{\rm th}). \qquad (4)$$

In terms of Eqs. (2) and (4), the experimentally measured $t_{\rm peak}$ is fitted by means of the least-squares analysis. The bald line in Fig. 2 shows the result of the fitting, which reproduces the observed sudden decrease of the $t_{\rm peak}$ well. (The obtained values of the parameters are listed in Table I) This agreement strongly supports the above-described idea of the thresholdlike acceleration of the photonic domain in accordance with PIPT.

It is reasonable to consider that the change of the domain speed is mechanically driven by the structural change. In spin crossover (SC) material, the size of the crystal in the IS or HS state is larger than that in the LS state because of electron-lattice interaction. It can thus be expected that the increase of v indicates macroscopic lattice expansion. Such a thresholdlike expansion with increase in fluence is also observed in SC Fe complexes[16] owing to the cooperative effect by the interaction between a FeO_6 octahedron through a local volume change.

However, it is interesting to compare the domain velocity with the transient reflectance change. Figure 3 shows pump fluence dependence of v (solid line) and $\Delta R/R$ (closed circles) just after the photoirradiation at 2.0 eV. With an increase in fluence, v suddenly increases around $I_{\rm th}$ (as mentioned above), whereas $\Delta R/R$ almost linearly increases regardless of the threshold. This result indicates that the irradiated photons locally create IS metallic sites by increasing γ in Eq. (1), resulting in the linear increase of $\Delta R/R$. Such a gradual change of the optical property is in contrast to the sudden structural variation seen in the fluence dependence of v. This signals that, when $I^{\rm pump} < I_{\rm th}$, the electronic state of the charge and spin gradually approaches the IS metallic state, with holding the small lattice constant (i.e., without expansion of $Co^{3+}O_6$ octahedron) even in the LS insulating state. This fluence dependence is quite characteristic of the PCCO system and is different from the photoinduced phenomena in the case of the Fe SC complexes.[16]

As discussed above, the photonically excited IS metallic region propagates, and we calculate a total conversion efficiency

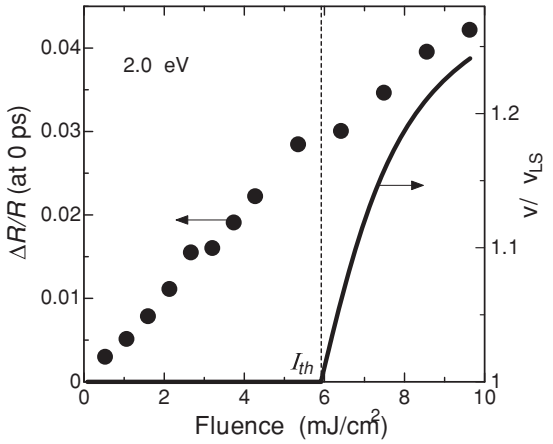

FIG. 3. The excitation intensity dependence of $\Delta R/R$ just after the photoexcitation (about 0 ps) at 2.0 eV (black circles) and the relative change of the velocity of the propagation (a solid line).

of the PIPT in the PCCO system. The number of photoexcited cobalt sites per photon (η) was calculated from the relation

$$\eta = \gamma v t_{\rm d} \frac{\hbar\omega}{V_0 I^{\rm pump}}, \qquad (5)$$

where V_0 is the volume per cobalt atom.[8] In the case of weak excitation ($I^{\rm pump} < I_{\rm th}$), η is proportional to $t_{\rm d}$. As $I^{\rm pump}$ increases further above $I_{\rm th}$, η is proportional to $v't_{\rm d}$ [v' is expressed in Eq. (3)]. and suddenly increases above the threshold. Figure 4 shows the contour plot of η in the plane of $I^{\rm pump}$ and $t_{\rm d}$. (The propagation is overdamped at around $t_{\rm d} = 30$ ps according to the previous report,[10] so the contour image is plotted up to the time.) The value of η reaches about 60 sites per photon. Such high efficiency is caused by the propagation assisted by the acoustic phonon.

In summary, cobalt perovskite oxide (PCCO) was studied by femtosecond reflection spectroscopy from the viewpoint of fluence dependence of the photoexcitation. The suppression of the magnitude as well as the peak shift observed in the fluence dependence of $\Delta R/R$ could be reproduced in terms

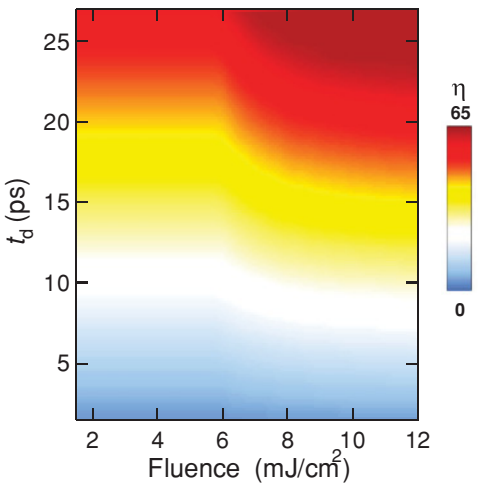

FIG. 4. (Color online) Contour plot of the number of photoexcited Co sites per one photon (η) in the plane of fluence and delay time.

of a model of the real-space propagation of a photodomain. The model calculation also revealed a thresholdlike change of the velocity of a photoinduced domain driven by a cooperative structural transition. Such domain movement assisted by the phonon in PCCO can be classified as a unique example of photocontrol of the ultrafast nonequilibrium phenomenon.

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[1]For a comprehensive review, see *Relaxations of Excited States and Photoinduced Structual Phase Transitions*, edited by K. Nasu (World Scientific, Singapore, 2004).

[2]A. Cavalleri, Cs. Toth, C. W. Siders, J. A. Squier, F. Raksi, P. Forget, and J. C. Kieffer, Phys. Rev. Lett. **87**, 237401 (2001).

[3]D. J. Hilton, R. P. Prasankumar, S. Fourmaux, A. Cavalleri, D. Brassard, M. A. El Khakani, J. C. Kieffer, A. J. Taylor, and R. D. Averitt, Phys. Rev. Lett. **99**, 226401 (2007).

[4]K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **78**, 4257 (1997); K. Miyasaka, M. Nakamura, Y. Ogimoto, H. Tamaru, and K. Miyano, Phys. Rev. B **74**, 012401 (2006).

[5]Y. Okimoto, H. Matsuzaki, Y. Tomioka, I. Kezsmarki, T. Ogasawara, M. Matsubara, H. Okamoto, and Y. Tokura, J. Phys. Soc. Jpn. **76**, 043702 (2007).

[6]M. Rini, R. Tobey, N. Dean, J. Itatani, Y. Tomioka, Y. Tokura, R. W. Shoenlein, and A. Cavalleri, Nature (London) **449**, 72 (2007); D. Polli, M. Rini, S. Wall, R. W. Shoenlein, Y. Tomioka, Y. Tokura, G. Cerullo, and A. Cavalleri, Nat. Mater. **6**, 643 (2007).

[7]H. Matsueda and S. Ishihara, J. Phys. Soc. Jpn. **76**, 083703 (2007); Y. Kanamori, H. Matsueda, and S. Ishihara, Phys. Rev. B **82**, 115101 (2010).

[8]S. Tsubouchi, T. Kyomen, M. Itoh, P. Ganguly, M. Oguni, Y. Shimojo, Y. Morii, and Y. Ishii, Phys. Rev. B **66**, 052418 (2002); S. Tsubouchi, T. Kyomen, M. Itoh, and M. Oguni, *ibid.* **69**, 144406 (2004).

[9]T. Saitoh, Y. Yamashita, N. Todoroki, T. Kyomen, M. Itoh, M. Higashiguchi, M. Nakatake, and K. Shimada, J. Electron. Spectrosc. Relat. Phenom. **144**, 893 (2005).

[10]Y. Okimoto, X. Peng, M. Tamura, T. Morita, K. Onda, T. Ishikawa, S. Koshihara, N. Todoroki, T. Kyomen, and M. Itoh, Phys. Rev. Lett. **103**, 027402 (2009).

[11]For example, C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, Phys. Rev. B **34**, 4129 (1986); K. Sokolowski-Tinten, J. Bialkowski, M. Boing, A. Cavalleri, and D. vonder Linde, *ibid.* **58**, R11805 (1998).

[12]T. Fujita, T. Miyashita, Y. Yasui, Y. Kobayashi, M. Sato, E. Nishibori, M. Sakata, Y. Shimojo, N. Igawa, Y. Ishii, K. Kakurai, T. Adachi, Y. Ohishi, and M. Takata, J. Phys. Soc. Jpn. **73**, 1987 (2004).

[13]J. Zhou, P. Zheng, and N. L. Wang, J. Phys. Condens. Matter **20**, 055222 (2007).

[14]T. Naito, H. Sasaki, H. Fujishiro, and M. Yoshizawa, J. Phys. Conference Series **200**, 012137 (2010).

[15]J. Hejtmanek, E. Santava, K. Knizek, M. Marysko, Z. Jirak, T. Naito, H. Sasaki, and H. Fujishiro, Phys. Rev. B **82**, 165107 (2010).

[16]Y. Ogawa, A. Mino, S. Koshihara, K. Koshino, T. Ogawa, C. Urano, and H. Takagi, Phys. Rev. Lett. **84**, 3181 (2000); Y. Ogawa, T. Ishikawa, S. Koshihara, K. Boukheddaden, and F. Varret, Phys. Rev. B **66**, 073104 (2002).