Journal of Superconductivity and Novel Magnetism manuscript No.
(will be inserted by the editor)

Pump- and probe-polarization analyses of ultrafast carrier dynamics in organic superconductors

K. Nakagawa · S. Tsuchiya · J. Yamada · Y. Toda

Received: date / Accepted: date

Abstract We investigated photo-excited carrier relaxation dynamics in the strongly correlated organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, using different polarizations of pump and probe pulses. Below the glasslike transition temperature (T_g) anisotropic responses for probe polarization were observed in both compounds. Decomposing the data into anisotropic and isotropic components, we found the anisotropic component shows no pump polarization dependence, meaning that dissipative excitation process was dominant for the anisotropic carrier relaxation. This behavior indicates that the appearance of anisotropic responses can be associated with spatial symmetry breaking due to structural change of BEDT-TTF molecules.

Keywords Time-resolved spectroscopy · Organic superconductor ET salts · Polarization dependence

PACS 74.70.Kn · 74.72.Kf · 78.47.jg

1 Introduction

Ultrafast pump-probe spectroscopy has been widely used to measure carrier relaxation resolved in the time domain. Especially in a strongly correlated electron system such as cuprates, photo-induced carrier dynamics of pseudogap and superconductivity have been detected individually by differences in relaxation time, magnitude of transmission reflectivity changes, and the temperature dependences between them [1–6]. Recently, in the cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ the detailed research on the probe-polarization dependence of the carrier dynamics has revealed that the observed polarization anisotropy arises from spontaneous symmetry breaking (SB) in the superconducting and pseudogap phases [7]. Since broken symmetry is essential for characterization of electronic state, symmetry analysis in the pump-probe measurement can provide critical insights into fundamental physics in other strongly correlated electron systems.

Superconducting charge transfer salts κ-(BEDT-TTF)$_2$X (X: inorganic anion molecules) family have attracted much attention in terms of similarity on cuprates [8]. The electronic phase diagram is similar to that of cuprates if electron correlation or pressure is replaced with carrier doping. Thus in this system electron correlation effect on their electronic properties can be investigated regardless of carrier doping effect. However, although unusual metallic properties have been suggested by various measurements [9], it remains unclear whether SB occurs above T_c or not. This is because a few systematic pump-probe measurements have been performed in the organics so far.

In this study to investigate SB in the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$(κ-NCS, $T_c = 10$ K) and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br(κ-Br, $T_c = 12$ K) we performed pump-probe spectroscopy using two-color pulses with different pump and probe polarizations. As a result, anisotropic carrier dynamics for probe polarization appeared below 70 K and 80 K for κ-NCS and κ-Br, respectively. With varying pump polarization, amplitude and direction of the anisotropy were not changed. This behavior means that the anisotropic responses can be originated from spatial SB.

K. Nakagawa · S. Tsuchiya · Y. Toda
Department of Applied Physics, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan
Tel.: +81-11-706-6115
E-mail: k.nakagawa@eng.hokudai.ac.jp

J. Yamada
Graduate School of Material Science, University of Hyogo, Ako-gun, Hyogo 678-1297, Japan
Tel.: +81-78-794-6580

2 Experimental

The single crystals of κ-NCS and κ-Br were grown electrochemically [10]. These compounds consist of alternate stacking of the BEDT-TTF conducting layers and the insulating anion X layers, forming highly two-dimensional electron system. In order to avoid structural disorder of BEDT-TTF molecules [11] the samples were slowly cooled at rates of 0.1-1 K/min. The electronic state is dominated by effective electron correlation t/U, where t and U are the transfer integral between dimers of BEDT-TTF molecules and the on-site Coulomb repulsion, respectively. It has been pointed out that the t/U value of κ-Br is smaller than that of κ-NCS, corresponding to the fact that κ-Br has stronger effective electron correlation than κ-NCS [12].

In optical pump-probe measurement the pump and probe beams were generated from a cavity-dumped Ti: sapphire oscillator with a repetition rate 54 kHz (to suppress the heating effect) whose pulse durations were about 120 fs centered at 400 nm and 800 nm. The two pulses were coaxially overlapped by a dichroic mirror and focused perpendicular to the conducting plane by an objective lens. The diameters of the pulses were roughly estimated $\sim$ 13 μm for the pump and $\sim$ 3 μm for the probe. The relative angle between optical pulse polarization and a crystal axis was measured from the direction tilted by 45 $^\circ$ from b (c) axis for κ-NCS (κ-Br, which was inferred from the previous report [13]) using a half-wave plate.

3 Results and Discussion

Figs. 1 (a) and (b) show transient changes of reflectivity $\Delta R/R$ for pump and probe polarization angle $\theta_{\rm pu}$, $\theta_{\rm pr}$ = 0° and intensity plots as a function of $\theta_{\rm pr}$ in κ-NCS at 36 and 75 K, respectively. The polar plots of the amplitudes of $\Delta R/R$ are shown in Figs. 1 (e) and (f). At 75 K the $\Delta R/R$ is almost independent of $\theta_{\rm pr}$, corresponding to the electron energy relaxation in the metallic state. On the other hand, the signals are enhanced along the $\theta_{\rm pr} = 45^\circ$ and 225° directions at 36 K. Similar trends were observed in κ-Br as shown in Figs. 1 (c),(d) and (g),(h). $\Delta R/R$ shows no probe polarization dependence at 83 K while it becomes anisotropic at 36 K.

To investigate relationship between the anisotropic response and pump polarization we measured $\Delta R/R$ for various pump polarizations, where the pump fluence was fixed to be constant. Figs. 2(a)-(c) show $\theta_{\rm pr}$ dependence of $\Delta R/R$ for $\theta_{\rm pu} = 0^\circ$, 45°, and 90°, respectively at 30 K in κ-NCS. $\Delta R/R$ for $\theta_{\rm pu} = 45^\circ$ and 90° are quite similar to that for $\theta_{\rm pu} = 0^\circ$. Moreover, in κ-Br no $\theta_{\rm pu}$ dependence of the anisotropic $\Delta R/R$ for the probe was observed at 40 K as shown in Figs. 2(a)-(c).

Figs. 3 (a) and (b) show polar plots of amplitude of $\Delta R/R$ as a function of $\theta_{\rm pr}$ for $\theta_{\rm pu} = 0^\circ$, 45°, and 90° in κ-NCS and κ-Br, respectively. The signals are found to be enhanced along the same directions for all $\theta_{\rm pu}$ and the amplitudes become slightly larger with rotating $\theta_{\rm pu}$ from 0° to 90° in both compounds.

To perform quantitative discussion we decomposed the angular dependence data by fitting with the following form:

$$\frac{\Delta R}{R} = \Delta R_{\rm ani}\cos(2(\theta_{\rm pr} - \phi_{\rm c})) + \Delta R_{\rm iso}, \quad (1)$$

where $\Delta R_{\rm ani}$, $\Delta R_{\rm iso}$ and $\phi_{\rm c}$ present anisotropic and isotropic components of $\Delta R/R$ and a phase, respectively. The solid lines in Fig. 3 are fitting results, which agree well with our data for all $\theta_{\rm pu}$ values in both compounds. The fitting yields $\Delta R_{\rm ani}$, $\Delta R_{\rm iso}$ and $\phi_{\rm c}$ values, which are plotted as a function of $\theta_{\rm pu}$ in Figs. 4(a) and (b) for κ-NCS and κ-Br, respectively. The error bars of $\phi_{\rm c}$ indicate the 95 % confidence intervals which arise from the fitting. For $\Delta R_{\rm ani}$ and $\Delta R_{\rm iso}$ the standard errors are smaller than $\sim 0.1 \times 10^{-4}$, which are not visible in the scale. In the amplitudes, the isotropic components are slightly increased with rotating $\theta_{\rm pu}$ while the anisotropic components are almost constant. Moreover, $\phi_{\rm c}$ seems to be constant for any $\theta_{\rm pu}$ values within the errors. These results indicate that the anisotropic carrier dynamics is independent of pump polarization in amplitude and direction.

We now discuss the origin of the anisotropic responses below 70 and 80 K for κ-NCS and κ-Br, respectively, from the perspective of the excitation process induced by pump pulse. Two types of the pump excitation process which yield probe polarization-dependent relaxation dynamics have been suggested: one is stimulated Raman excitation (SRE) and another is dissipative excitation (DE)[7]. The former is coherent process indicating that the polarization anisotropy for the probe should depend on pump polarization. On the other hand in the latter, the probe polarization dependence of $\Delta R/R$ shows no pump polarization dependence because information of pump pulse is lost during relaxation due to inelastic scattering. Our results exhibit clearly that the anisotropic responses are independent of the pump polarizations, indicating the DE process is dominant.

In the case of DE process the polarization anisotropy can be provided by spontaneous SB [7, 14]. However, any electronic ordered states accompanied by SB such as CDW have not been suggested for κ-NCS and κ-Br, respectively. Instead, the recent thermal expansion measurements suggest that the glasslike structural transition occurs at $T_{\rm g} \sim$ 80 K for κ-Br salt and 70 K for κ-NCS [11], where the $T_{\rm g}$s agree well with our results. In this report the glasslike transition may correspond to order-disorder transition of end terminal ethylene group of BEDT-TTF molecules. Ethylene group of the molecules has two types of conformation, eclipsed and staggered type. In κ-NCS (κ-Br) the ethylene groups of the molecule are thermally fluctuated at high temperatures. When temperature decreases and lowers below $T_{\rm g}$, the ethy-

lene groups are ordered forming staggered (eclipsed) type conformation. Such structural changes can lead to the spatial SB responsible for our observations.

We mention the origin of the isotropic components. As shown in Figs. 4 (a) and (b), the amplitudes of the isotropic components slightly change with varying the pump polarization whereas the anisotropic response shows no changes. Generally, $\Delta R/R$ is proportional to a transient nonequilibrium carrier occupation Δf. Thus the difference of optical penetration depth for each crystal axis can attribute to that of $\Delta R/R$ in amplitude. In this case, however, the amplitudes of both isotropic and anisotropic components should be changed with changing pump polarization, which is contradict to our results. Another possibility is that some components due to the SRE are included in the isotropic responses. In the SRE process, as various degrees of freedom are excited by pump pulse, totally symmetric (isotropic) modes may be induced by the coupling between different degrees of freedom. This can lead to a slight variation in amplitude of the ΔR_{iso}.

The appearance of the anisotropic components in $\Delta R/R$ suggests that two different electronic states exist below T_{g}. Such coexistence of the different states can be explained by phase separation, which has been observed in other superconductors [15]. In κ-Br the phase separation induced by photon irradiation [13] has been suggested. In this case irradiation of a pump pulse modulates the t/U, acting the electronic state as negative pressure. As a result, parts of the sample in real space change from metallic to insulating states and/or an energy gap opens on a part of the Fermi surface, leading to two kinds of photo-excited carriers originated from metallic and insulating states. Although t/U in κ-NCS is larger and located far from the quantum critical point as compared to that in κ-Br, the instantaneous photoexcitation can induce similar phase separation.

4 Conclusions

Using different polarizations of pump and probe pulses, we investigated carrier dynamics in the organic superconductors κ-NCS and κ-Br. When temperature lowered below T_{g}, the anisotropic responses for the probe were found to appear in both compounds. Moreover, the amplitudes and directions of the responses were independent of the pump polarization, indicating that the incoherent DE process was dominant in the anisotropic carrier dynamics. In this case the anisotropy can be attributed to spatial symmetry breaking accompanied by the order of ethylene groups of BEDT-TTF molecules.

Acknowledgements This work was partially supported by a Grant-in-Aid for Young Scientists B (No. 15K17685) from the Japan Society for the Promotion of Science (JSPS).

References

1. J. Demsar, B. Podobnik, V. V. Kabanov, Th. Wolf, and D. Mihailovic, Phys. Rev. Lett. **82**, 4918 (1999).
2. D. Dvorsek, V. V. Kabanov, J. Demsar, S. M. Kazakov, J. Karpinski, and D. Mihailovic, Phys. Rev. B **66**, 020510 (2002).
3. C. W. Luo, C. C. Hsieh, Y.-J. Chen, P. T. Shih, M. H. Chen, K. H. Wu, J. Y. Juang, J.-Y. Lin, T. M. Uen, and Y. S. Gou, Phys. Rev. B **74**, 184525 (2006).
4. Y. H. Liu, Y. Toda, K. Shimatake, N. Momono, M. Oda, and M. Ido, Phys. Rev. Lett. **101**, 137003 (2008).
5. L. Stojchevska, P. Kusar, T. Mertelj, V. V. Kabanov, Y. Toda, X. Yao, and D. Mihailovic, Phys. Rev. B **84**, 180507 (2011).
6. G. Coslovich, C. Giannetti, F. Cilento, S. Dal Conte, T. Abebaw, D. Bossini, G. Ferrini, H. Eisaki, M. Greven, A. Damascelli, and F. Parmigiani, Phys. Rev. Lett. **110**, 107003 (2013).
7. Y. Toda, F. Kawanokami, T. Kurosawa, M. Oda, I. Madan, T. Mertelj, V. V. Kabanov, and D. Mihailovic, Phys. Rev. B **90**, 094513 (2014).
8. R. H. McKenzie, Science **278**, 820 (1997).
9. T. Arai, K. Ichimura, K. Nomura, S. Takasaki, J. Yamada, S. Nakatsuji, H. Anzai, Solid State Commun. **116**, 679 (2000).
10. H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakajima, and J. Yamada, J. Cryst. Growth **154**, 145 (1995).
11. J. Müller, M. Lang, F. Steglich, J. A. Schlueter, A. M. Kini, and T. Sasaki, Phys. Rev. B **65**, 144521 (2002).
12. B. J. Powell and R. H. McKenzie, J. Phys.: Condens. Matter **18**, R827 (2006).
13. Y. Toda, T. Mertelj, T. Naito and D. Mihailovic, Phys. Rev. Lett. **107**, 227002 (2011).
14. S. Tsuchiya, Y. Sugawara, S. Tanda and Y. Toda, J. Opt. **17**, 085501 (2015).
15. A. Ricci, N. Poccia, B. Joseph, G. Arrighetti, L. Barba, J. Plaisier, G. Campi, Y. Mizuguchi, H. Takeya, Y. Takano N. L. Saini and A. Bianconi, Supercond. Sci. Technol. **24**, 082002 (2011).

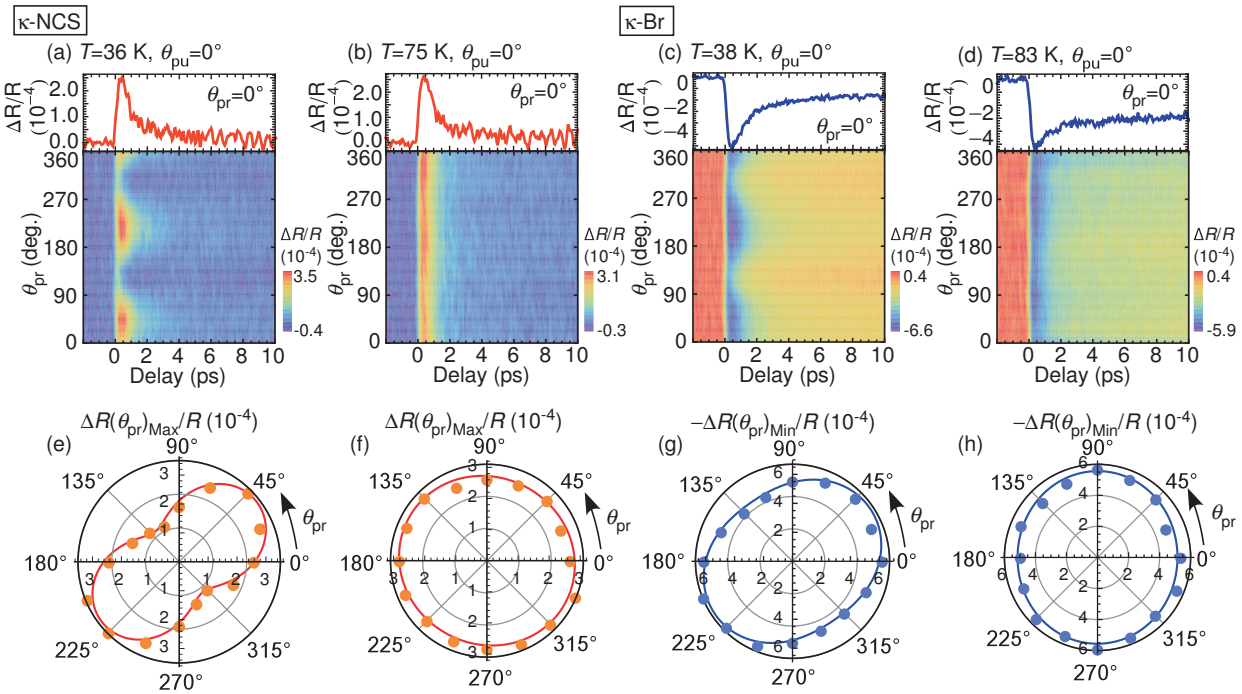

Fig. 1 (Color online) (a)-(b) and (c)-(d): Probe polarization angular dependence of $\Delta R/R$ transients for $\theta_{pu} = 0°$ at typical temperatures in κ-NCS and κ-Br, respectively. (e)-(h): Polar plots of amplitudes of $\Delta R/R$. The solid lines indicate the fitting results using Eq. (1).

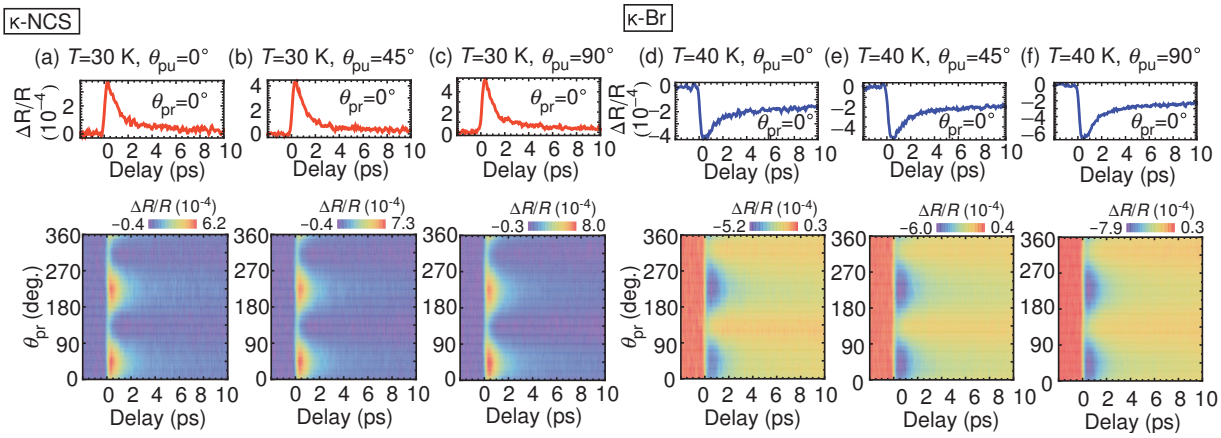

Fig. 2 (Color online) (a)-(c) and (d)-(f): Probe polarization angular dependence of $\Delta R/R$ transients for $\theta_{pu} = 0°$, 45° and 90° in κ-NCS at T =30 K and κ-Br at T =40 K, respectively.

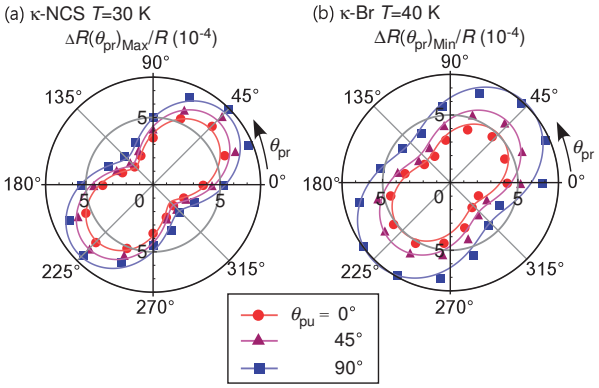

Fig. 3 (Color online) (a),(b): Polar plots of amplitudes of $\Delta R/R$ as a function of $\theta_{\rm pr}$ for $\theta_{\rm pu} = 0^\circ$ (circles), 45° (triangles) and 90° (squares) in κ-NCS at 30 K and κ-Br at 40 K, respectively.

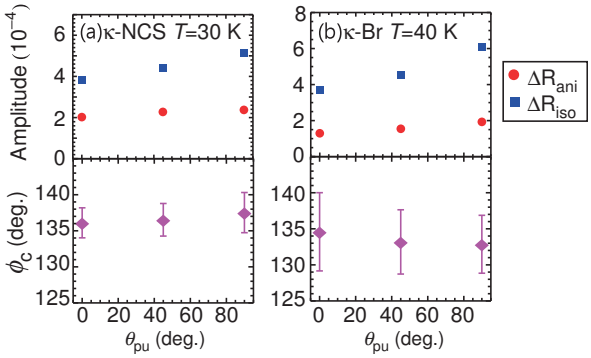

Fig. 4 (Color online) (a),(b): Pump polarization angular dependence of $\Delta R_{\rm ani}$, $\Delta R_{\rm iso}$ and ϕ for κ-NCS at 30 K and κ-Br at 40 K, respectively.