論文の内容の要旨

Transport and NMR studies of charge glass in organic conductors with quasi-triangular lattices

（擬似三角格子有機伝導体における電荷ガラスの輸送及び NMR 研究）

佐藤 拓朗

1. Introduction

My thesis is on the experimental studies on quasi-two-dimensional organic conductors θ-(BEDT-TTF)$_2$X with anisotropic triangular lattices (Fig. 1a,b). So far, this family has been considered as a typical platform of strongly correlated electron system, which exhibits metal-charge ordered (CO) insulating transition triggered by long-ranged Coulomb repulsion [1]. In the conducting layers, however, geometrical frustration originating from triangular lattice potentially works against the long-ranged CO formation, leading to the possibly emergence of unconventional electronic states without long-range order, namely, charge glass (CG) states. Indeed, previous studies on θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (hereafter θ-RbZn) reported that the first-ordered CO transition at 200 K was easily suppressed by thermal quenching [2], strongly indicating the emergence of supercooled states as in classical glass-forming systems (Fig. 1c). NMR measurements for θ-RbZn also supported this glass picture by detecting the inhomogeneous charge density in the supercooled regime [3]. Furthermore, a more frustrated material, θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ (hereafter θ-CsZn), which shows no signature of CO transition even when slowly cooled, was found to be in almost the same electronic state as in the rapid cooled θ-RbZn in terms of NMR spectra [4], suggesting that the strong frustration may be a key to the emergence of the CG state. Note that glassy electronic states have often been argued in a range of strongly correlated electron systems; e.g., high-T_c cuprate or Manganites [5]. In these systems, however, disorders are considered to be a driving force for the appearance of inhomogeneous states. In contrast, the present organic system, θ-(BEDT-TTF)$_2$X, is basically disorder-free, being distinguished from the disorder-dominant systems. Motivated by such intriguing scenario for novel glass, I started to investigate this organic family of materials in the light of “glassiness”, and aimed to establish the concept of glass in charge degrees of freedom.

In conventional structural glasses, glassy freezing in the absence of disorder is well established in several families of materials, most famously the supercooled liquids [6]. In this system, glass states emerge when solidification from liquid is kinetically bypassed by cooling the system more rapidly than the characteristic time to the ordered state. In the quenching regime, the dynamics of structural relaxation becomes extremely slow at lower temperatures, and eventually exceeds the time scale of our experimental observation. This is the glass

transition. Therefore, the information on the dynamics is crucially important to know the nature of the glass.

This thesis is organized as follows. In Sec. 2, I briefly describe the experimental methods employed to explore the dynamical properties in supercooled CG candidates. Results and discussions section is divided into two parts; Section 3.1 presents the experimental evidences for the existence of the CG state. In the following section (Sec. 3.2), I report the observation of transient process from CG into CO, that is, electronic crystal growth. Finally, I conclude the present works in Sec. 4.

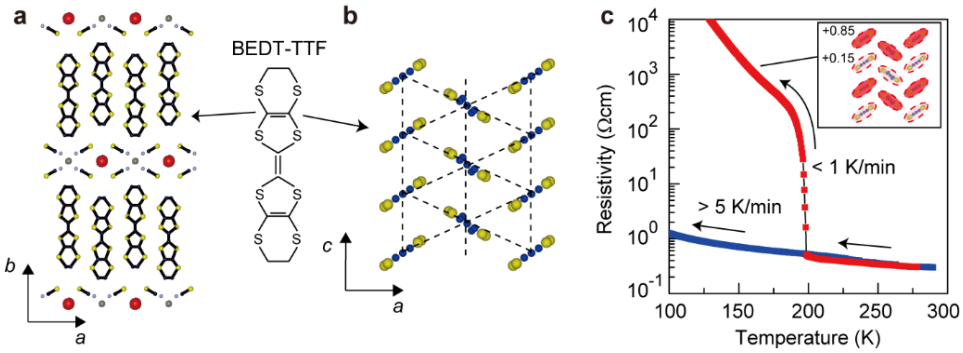

Fig. 1 (a)(b) Crystal structure of θ-(BEDT-TTF)$_2$X. (c) *T*-ρ profile for θ-RbZn.

2. Experimental

CO or CG states are characterized by charge configuration on lattices, offering the opportunity to probe their dynamics by charge-sensitive measurements. It is an experimental advantage for studying glassiness in charge, distinctively from the case of the atomic or molecular systems. Sec. 3.1 describes three different experiments; (i) dc resistivity measurements, (ii) resistance fluctuation spectroscopy (so-called noise measurements), and (iii) X-ray diffuse scattering measurements. The noise measurements were conducted by the conventional four-terminal method. The X-ray diffuse scattering measurements were performed at the BL-8A,B beamline of the Photon Factory (PF) at KEK. The following Section 3.2 describes ^{13}C-NMR and resistivity measurements to probe the process of the electronic crystal growth microscopically and macroscopically, respectively. For NMR measurements, two central carbon atoms of BEDT-TTF molecules are selectively enriched by ^{13}C atoms. NMR spectra are obtained by the Fourier transformation of spin-echo signals.

3. Results and Discussions

3.1. Evidences for the Charge Glass

In the present work, three materials with different frustration parameters were studied; θ -CsZn (highest frustrated), θ-RbZn (intermediately frustrated), and θ-TlCo (less frustrated). This section focuses on the highest frustrated system, θ-CsZn, possibly the most stable CG former,

and describes demonstrated the hallmarks of glass; non-equilibrium, slow dynamics, and short-range correlation.

I first measured cooling-rate and time dependence in resistivity. Especially, time-dependent resistivity growth while keeping temperature, namely, physical aging, can be found only below 100 K (Fig. 2a). Physical aging is the process of slowly relaxation into more stable configuration, confirming that the system falls into non-equilibrium state at T_g=100 K. Above T_g, in contrast, such slow relaxation process is detectable as a dispersion in resistivity, hence, noise measurements serve as a powerful probe to capture it. In the present case, as well as so-caled 1/*f*-type of power spectrum, an appreciable deviation from background 1/*f* noise is also detected. By focusing this deviation, the characteristic frequency, f_c, in charge fluctuations can be successfully deduced. Figure 3 displays f_c versus 1/*T* as well as relaxation time of physical aging below T_g. Remarkably, both plot can be fitted by the same Arrhenius function with the gap of approximately 2600 K, indicating that the present CG system is categorized into "strong glass" within the classical glassiness scheme (Fig. 2b). Finally, I tested whether short-range correlation evolves towards glass transition or not by measuring X-ray diffuse scattering. As a result, I observed two different diffuse characterized by the wave vector of $\boldsymbol{q_1}$~(2/3, *k*, 1/3) and $\boldsymbol{q_2}$~(0, *k*, 1/2), and found that only $\boldsymbol{q_1}$ domains stop growing its size at around T_g (Fig. 2c). Only $\boldsymbol{q_1}$ domains seem to couple with glassy freezing. All these results show that a CG state is realized in organic conductor, θ-CsZn. It should be emphasized that the medium frustrated θ -RbZn and the least frustrated θ -TlCo are also revealed to be a CG former, but the only difference lies in the critical cooling speed required for glass formation; a stronger frustration gives a higher-CG former. This is the main result of the section. My work also proposes that the cooling speed is potentially key control parameter to give rise to new electronic state.

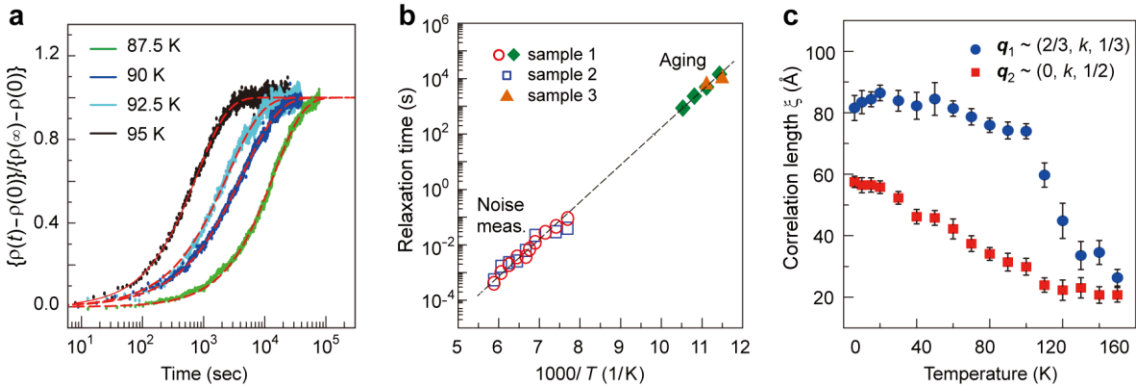

Fig. 2 (a) Physical aging below T_g. (b) 1/*T*-relaxation time profile. (c) *T*-dependence of CO domains.

3.2. Electronic Crystal Growth

Next, I focus not on the CG state itself but on the transforming process from CG into CO, that is, electronic crystal growth. First, time dependence of resistivity during the process is measured. I found that obtained crystallization time can be well described by dome-like structure called Time-Temperature-Transformation (T-T-T) curve (Fig. 3). It provides a strong evidence for the existence of two distinct processes in electronic crystal growth; nucleation and growth. Furthermore, NMR measurements, which serve as a probe of local charge density profile, gives us the remarkable data that the intermediate states different from both initial CG and final CO states are formed before the formation of true CO near T_g. It is reminiscent of two-step nucleation discussed intensively in classical colloidal system, indicating the universality of such novel nucleation process.

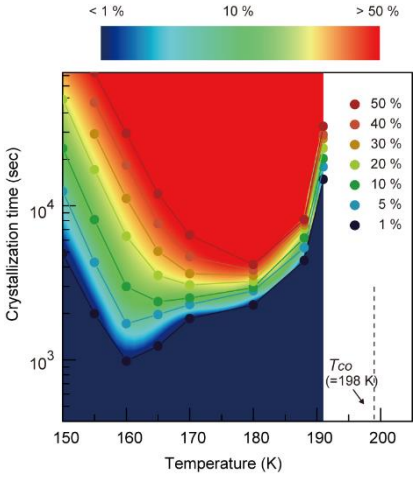

Fig. 3 T-T-T curve in electronic crystal

4. Conclusion

This thesis demonstrates the concept of the new class of glass in electrons in organic conductor. In Sec. 3.1, typical hallmarks of glass are clearly confirmed, giving strong evidences for the presence of CG. Material dependence also provides an insight for the origin of CG state; geometrical frustration not disorder plays a significant role in forming CG, distinctively from previous inhomogeneous electronic state in strongly correlated electron systems. In Sec. 3.2, I reported T-T-T curve during electronic crystal growth, strongly indicating the existence of nucleation and growth process in line with classical crystal growth. Moreover, near T_g, the novel two-step nucleation is revealed by NMR measurements. This is the first macro- and micro-scopic observation of electronic crystal growth. All these results provide the important statement that glassy behavior is no longer limited in classical soft materials but is extended quantum hard materials. Series of my study uncovers organic conductor θ-(BEDT-TTF)$_2$X serve as a novel interdisciplinary platform uniting the strongly correlated electron system and soft matter, and opens up new possibilities in the field of glassiness.

5. Reference

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