# Energy Landscape in the Electronic Glassy State of an Organic Conductor

Charge ordering (CO) is a phenomenon in which electrons in solids crystallize into a periodic pattern of charge-rich and charge-poor sites owing to strong electron correlations, usually resulting in long-range order. In geometrically frustrated systems, however, a glassy electronic state without long-range CO has been observed. In this comprehensive study including X-ray diffraction measurements we revealed that a charge-ordered organic material with an isosceles triangular lattice shows charge dynamics associated with crystallization and vitrification of electrons, which can be understood by an energy landscape arising from the degeneracy of various CO patterns.

Glassy materials are ubiquitous in nature. The history of glassmaking dates back thousands of years and sophisticated glass-forming technology has been utilized by humans for centuries. Yet, a fundamental understanding of glassy dynamics remains one of the most important unresolved problems in both physics and materials science. So far, from various fields of condensed-matter physics, a rich variety of glass-formation phenomena such as spin glasses have been observed. However, the mechanisms by which the materials acquire the glassy state have remained unclear in both theoretical and experimental physics.

Here, we focused on a unique glassy state of electrons in solids realized in an organic molecular conductor, where the lack of periodicity of the strongly correlated electrons on the triangular lattice is caused by geometrical frustration and strong quantum effects. The quasi-two-dimensional organic compound $\theta_m$-(BEDT-TTF)$_2$TlZn(SCN)$_4$ studied here (henceforth $\theta_m$-TlZn) undergoes a charge ordering (CO) transition at 170 K owing to strong electron correlations [Fig. 1(a)], where the charge carriers on the BEDT-TTF molecules are localized periodically with a diagonal stripe pattern [Fig. 1(b)] [1]. Such a periodic CO state can be regarded as a "charge-crystal" state. In contrast, above the CO transition temperature, the charge of +0.5 per BEDT-TTF molecule is distributed uniformly in space; therefore, such a delocalized state can be referred to as a "charge-liquid" state [Fig. 1(c)]. In $\theta_m$-TlZn, when the sample is cooled faster than a critical cooling rate (~50 K/min), charge crystallization is kinetically avoided, leading to a "charge glass" state where the charge is randomly quenched [Fig. 1(d)]. The mechanism of formation of the glassy electronic state has been investigated experimentally and theoretically in terms of the geometrically frustrated triangular lattice, but still remains rather elusive [2, 3].

To obtain insights into the structural origin of the charge-glass state, we performed X-ray diffraction measurements at BL-8A. Oscillation photographs measured at various temperatures are shown in Figs. 1(b)–(d). At room temperature, only Bragg reflections are observed [Fig. 1(c)], whereas in the charge-crystal state, clear satellite peaks appear at $q_0$ = (1/2, 1/2), compatible with the diagonal CO pattern [Fig. 1(b)]. In contrast, in the

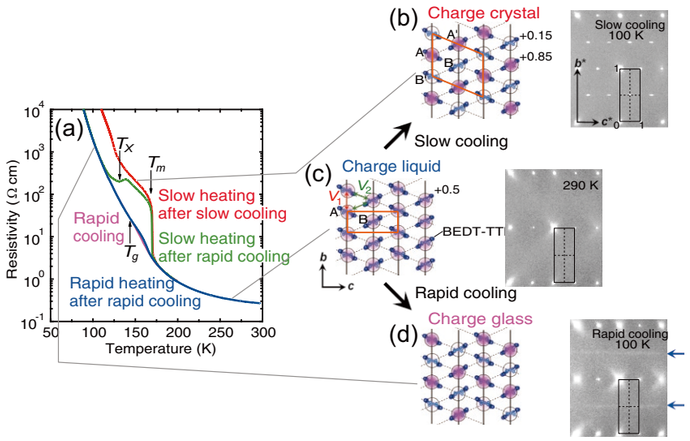


**Figure 1: (a)** Temperature dependence of resistivity for $\theta_m$-TlZn measured in various cooling/heating processes. $T_m$ is the melting temperature, $T_g$ is the glass transition temperature, and $T_X$ is the crystallization temperature. **(b)–(d)** Left panels: Illustrations of **(b)** the charge-crystal state, **(c)** the charge-liquid state, and **(d)** the charge-glass state in $\theta_m$-TlZn. $V_1$ and $V_2$ are the nearest-neighbor Coulomb interactions, where $V_2/V_1$ ~ 0.8. Right panels: Oscillation photographs of the $b^*$-$c^*$ plane measured at **(c)** 290 K and measured at 100 K after **(b)** slow cooling and **(d)** rapid cooling. The blue arrows in **(d)** indicate the diffuse lines.

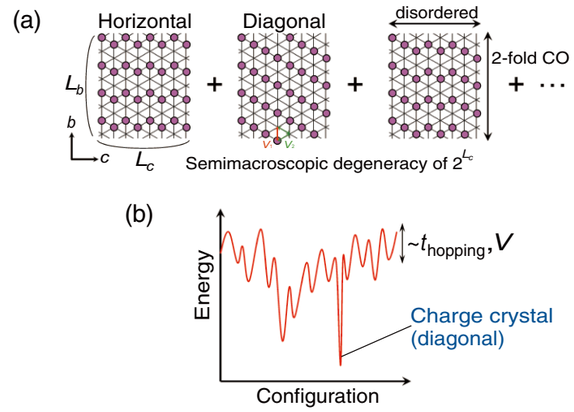


**Figure 2: (a)** Schematics of various chain-striped CO patterns. The magenta circles represent the charge-rich sites. **(b)** Illustration of an energy landscape with multiple local minima separated by barriers having an energy scale of the hopping integral $t_{hopping}$ and/or the long-range Coulomb interaction $V$. The horizontal axis represents the various spatial configurations of charge patterns as illustrated in **(a)**.

charge-glass state, diffuse lines at $q_d$ = (1/2, $l$) are observed [Fig. 1(d)]. The presence of the diffuse lines indicates that the charge-glass state of $\theta_m$-TlZn is described by the superposition of various chain-striped states as shown in Fig. 2(a). This situation can be understood by an energy landscape with multiple local minima, as illustrated in Fig. 2(b), that is, a metastable state with an amorphous stripe-glass structure as proposed on the basis of recent theoretical calculations [3]. Frustration is a key concept for understanding glass transitions in a variety of systems. For example, crystallization in metallic glasses is prevented if locally favored structures such as icosahedral order do not match the symmetry of the system [4]. Likewise, in $\theta_m$-TlZn, locally favored short-range electronic ordering with $q_d$ = (1/2, $l$) induced by geometric frustration may hinder long-range CO with $q_0$ = (1/2, 1/2), thereby causing the slow dynamics. Our results provide an experimental demonstration of recent theoretical considerations that frustration, in combination with strong quantum effects, plays an important role in the realization of quantum charge-glass states in clean systems, essentially free from impurities and defects.

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## BEAMLINE

BL-8A

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