Crystallization and vitrification of strongly correlated electrons on a geometrically frustrated triangular lattice

Glassy materials are ubiquitous in nature [1]. The history of glassmaking traces back thousands of years and sophisticated glass-forming technology has been utilized by humans for centuries. Yet, the 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 have been observed, ranging from structural to spin, electric-dipole, and superconducting vortex glasses. The dynamics and mechanisms by which the materials acquire the glassy state, however, have been a long-standing issue in both theoretical and experimental physics. Here, we focus 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 θ_m-(BEDT-TTF)$_2$TlZn(SCN)$_4$ studied here (henceforth θ_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(c)) [2]. 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(b)). In θ_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 [3,4].

To clarify the origin of charge-glass formation in θ_m-TlZn, we utilized various complementary experimental techniques. Among them, infrared optical spectroscopy has provided important information on the local charge distribution on the BEDT-TTF molecules at a microscopic level. The brilliance of synchrotron radiation light at **BL43IR** in SPring-8 is more than two orders of magnitude higher than that of a laboratory light source, which enables accurate optical measurements for tiny single crystals such as organic compounds.

Figure 2(a) shows the charge-sensitive vibrational mode ν_{27} of the BEDT-TTF molecule. The ν_{27} mode is known as a local probe of the molecular charge and splits into two modes in the presence of a difference in charge between the A and B sites in the unit cell (Figs. 1(b) and 1(c)). A clear peak around 1420 cm^{-1} is assigned to the charge-rich mode of ν_{27} (Fig. 2(b)). A sizable intensity was observed above T_m (Fig. 2(c)), indicating the presence of charge disproportionation. Because the A and B sites are crystallographically equivalent above T_m, the time-averaged charge distribution above T_m should be +0.5 per BEDT-TTF molecule (Fig. 1(b)). Therefore, the splitting of ν_{27} above T_m implies that charge disproportionation is not static but dynamically fluctuates on a time scale slower than that of the molecular vibrational ν_{27} motion. Because the intensity of the charge-rich mode reflects the volume of dynamically fluctuating charge clusters, its increase with decreasing temperature suggests that the heterogeneous slow dynamics grows towards the charge-glass transition.

The present results, combined with the X-ray structural analysis, revealed that the charge-glass state of θ_m-TlZn is described by the superposition of various chain-striped states as shown in Fig. 3(a). This situation can be understood by an energy landscape with multiple local minima, as illustrated in Fig. 3(b) — that is, a metastable state with an amorphous stripe-glass structure as proposed on the basis of recent theoretical calculations [4].

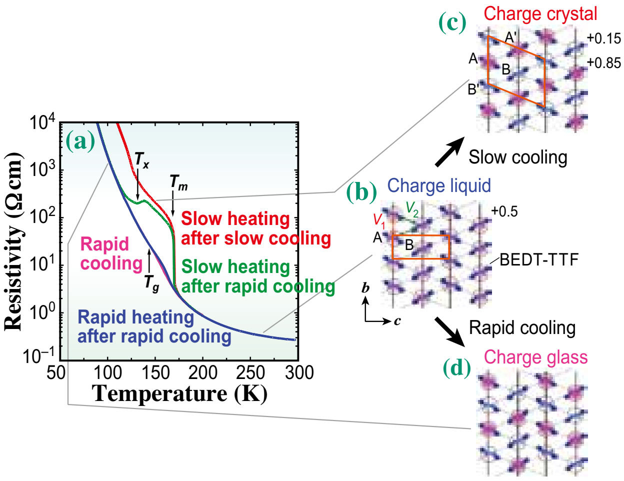

Fig. 1. **(a)** Temperature dependence of the resistivity for θ_m-TlZn measured in various cooling/heating processes. **(b)–(d)** Illustrations of **(b)** the charge-liquid state, **(c)** the charge-crystal state, and **(d)** the charge-glass state in θ_m-TlZn. V_1 and V_2 are the nearest-neighbor Coulomb interactions, where V_2/V_1 ~0.8.

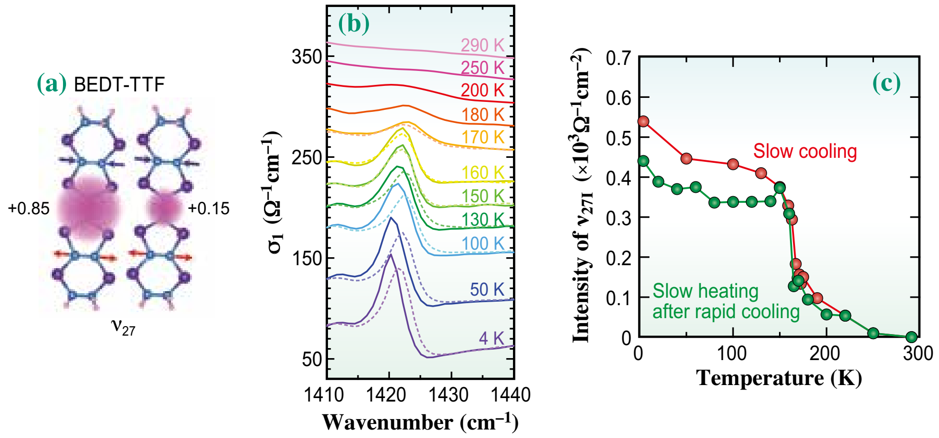

Fig. 2. **(a)** Sketch of the infrared active vibrational mode ν_{27} of the BEDT-TTF molecule. The charge-rich and charge-poor modes are observed at 1420 cm^{-1} and 1515 cm^{-1}, respectively. **(b)** Temperature dependence of the ν_{27} mode of the charge-rich site measured during slow cooling (solid line) and slow heating after rapid cooling (dashed line). **(c)** Temperature dependence of the intensity of ν_{27} of the charge-rich site.

Next we compared our organic molecular material containing 'frustrated' electrons with the atomic/molecular dynamics of glass formation in conventional glass-forming liquids. We quantitatively evaluated the CO volume fraction from the time evolution of the resistivity during the charge crystallization process from the supercooled charge-liquid or charge-glass state. Figure 3(c) displays the contour map of the CO fraction plotted in the time-temperature plane [a so-called time-temperature-transformation (TTT) diagram]. The relaxation time becomes faster with decreasing temperature, and then slower below ~160 K, which is referred to as the "nose temperature"; this characteristic temperature dependence of the relaxation time can be explained by the theory of nucleation and growth at a first-order liquid-crystal phase transition. Our observation demonstrates that the crystallization process of electrons in solids can be described by the nucleation and growth process of a liquid, as observed in conventional glass-forming liquids. The surprising similarities between our system and conventional glass formers highlight the universal nature of the liquid-glass transition.

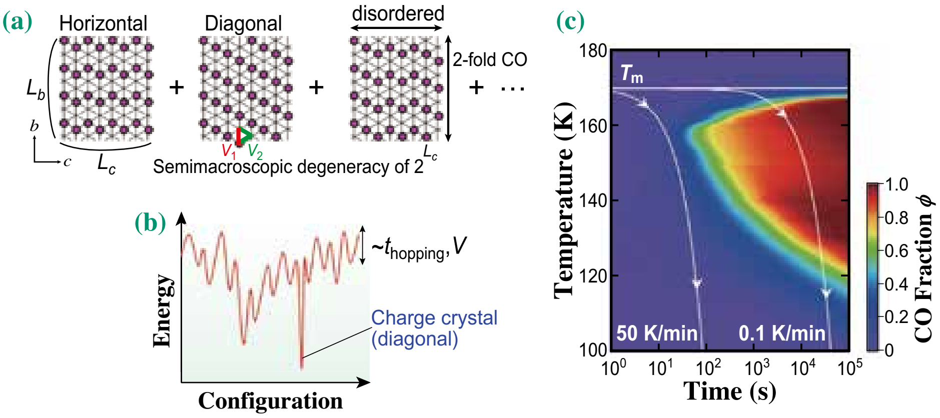

Fig. 3. **(a)** Schematics of various chain-striped CO patterns. The magenta circles represent the charge-rich sites. **(b)** Illustration of an energy landscape with multiple local minima separated by barriers having an energy scale of the hopping integral t_{hopping} and/or the long-range Coulomb interaction V. The horizontal axis represents the various spatial configurations of charge patterns as illustrated in (a). **(c)** TTT diagram derived from the time evolution of the resistivity.

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