Charge-Cluster Glass in an Organic Conductor with Triangular Lattice

Spin interactions can lead to unconventional states, such as quantum spin liquids and spin glasses, in which long-range ordering is prohibited by geometric frustration. Here, we report observations of unconventional electronic states resulting from charge frustration. Using a combination of frequency-resolved transport measurements and X-ray diffraction, we have demonstrated that a charge cluster glass is formed in a high-quality organic system with a triangular lattice. Surprisingly, these observations correspond to recent ideas regarding the structural glass formation of supercooled liquids, potentially opening up a new area of interdisciplinary physics.

Interacting many-body systems comprised of molecules, electrons, or spins can spontaneously exhibit long-range order when thermal agitations are suppressed. This tendency may be avoided in several ways and, as a result, the systems freeze in inhomogeneous or glassy states [1]. Though not well-established, correlated electrons confined in a triangular lattice may be good candidates for charge-glass formers. A new paradigm might be a Wigner-type charge ordering (CO), in which an equal number of charge-rich and charge-poor sites tile the entire lattice to avoid neighboring rich-rich (or poor-poor) pairs as much as possible. However, in a triangular lattice, this constraint is insufficiently stringent to determine a specific CO from the various charge configurations, thereby potentially undermining the tendency toward long-range ordering, analogous to a situation in geometrically frustrated spin systems [Fig. 1(a)] [2]. As a result, glassy electronic states may be realized; however, such a charge-glass-forming nature has not been identified thus far. Research groups at the University of Tokyo, RIKEN CEMS and KEK revealed that the charge-glass state is formed in an organic conductor with a triangular lattice [3].

The material investigated is the organic conductor θ-(ET)$_2$RbZn(SCN)$_4$ (denoted θ-RbZn), where ET denotes bis(ethylenedithio)tetrathiafulvalene [4]. The crystal structure has an alternate stacking of conducting ET layers and insulating anion layers, and the ET molecules form a two-dimensional triangular lattice [Fig. 1(b)]. The ET conduction band is hole-1/4-filled and exhibits CO instability [5], and the charge frustration caused by the underlying triangular lattice may prevent long-range ordering. In reality, a structural transition occurs at ~200 K and relaxes the charge frustration; as a result, horizontal CO that is compatible with the structural modulation is formed with a charge disproportionation ratio of ~0.15:0.85 accompanied by a steep increase in resistivity [Fig. 1(c)] [6, 7]. The structural transition can be avoided by rapid cooling at >5 K/min [8], and the “charge-liquid” phase above 200 K can be thus maintained below 200 K [Fig. 1(c)]. Therefore, to observe the possible charge-glass state, the electronic properties below 200 K in a rapidly cooled condition should be examined. To demonstrate the charge-glass, several key concepts need to be tested, for example, the temperature evolution of the slow charge dynamics, the absence of long-range ordering, and the electronic-glass transition. The slow dynamics in the charge-liquid phase were detected using resistance fluctuation spectroscopy [3]. The typical dynamics are found to be 10–10^4 Hz (strongly temperature dependent) and it slows down at low temperatures. These slow dynamics appear to be understood by considering that the charge-liquid state above 200 K is transforming into a classically disordered state, that is, a charge glass.

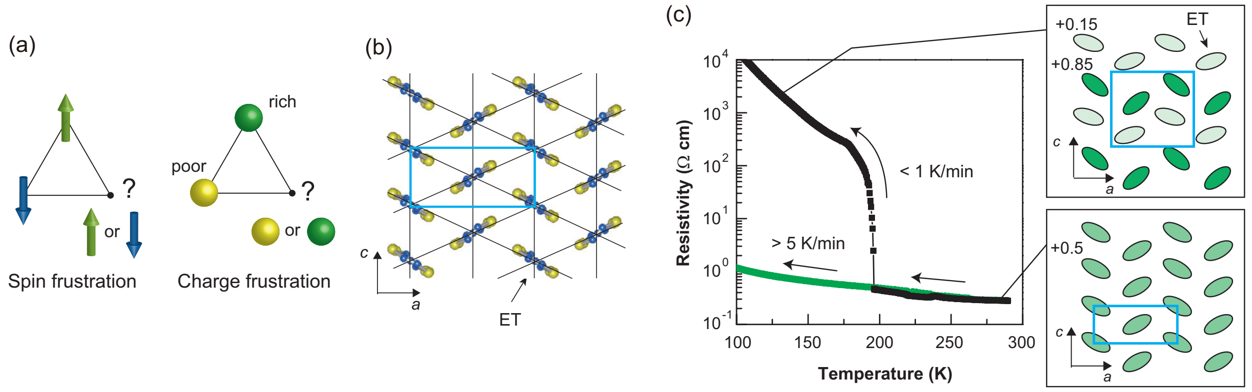

Figure 1: Charge frustration and crystal structure of θ-(ET)$_2$RbZn(SCN)$_4$. (a) An illustration of the analogy between spin frustration and charge frustration. (b) The structure of the ET layer. (c) The temperature dependence of the resistivity during cooling for different temperature-sweeping rates. The insets indicate the crystal structures of the high-temperature phase (lower inset) and the low-temperature phase (upper inset). In the upper inset, the charge-ordering pattern is also shown.

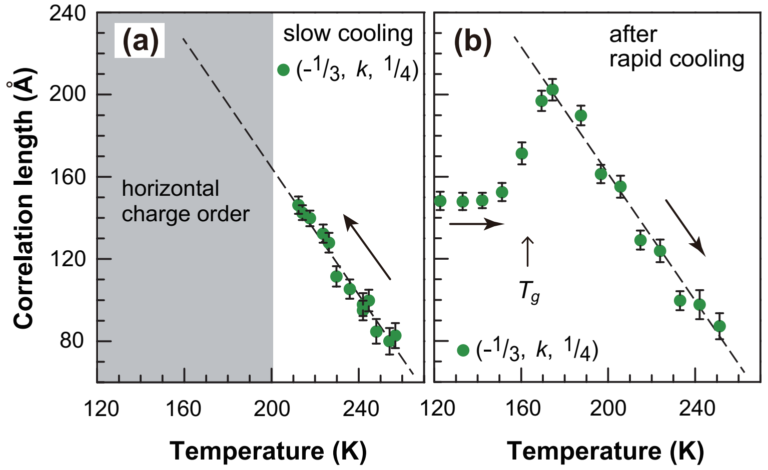

Figure 2: Spatial correlation of the charge clusters investigated using X-ray diffuse scattering. (a) Temperature dependence of the charge-cluster correlation length ξ during slow cooling. (b) Temperature dependence of ξ during heating after rapid cooling to 120 K. The value of ξ is estimated along the −2a*+c* direction on the (11/3 *k* 1/4) diffuse rod. The broken lines in (a, b) are drawn as guides for the eye.

To obtain further insight into the observed glassy dynamics, it is necessary to determine whether some type of metastable “crystalline” islands evolve with the slow dynamics [9-12]. To this end, X-ray diffuse scattering measurements were conducted. It was revealed that diffuse spots characterized by $\boldsymbol{q}_d$ ~ (±1/3 *k* ±1/4) exist around the Bragg spots, where *k* denotes negligible coherence between the ET layers. In Fig. 2(a), the evolution of the correlation length ξ as a function of temperature can be clearly seen. ξ is not short-ranged but is ~140 Å at 210 K, which corresponds to ~25 triangular spacings. This behavior is essentially distinct from conventional critical phenomena, where ξ diverges for a continuous transition; here, ξ goes to a medium-range length in a non-divergent (i.e., non-critical) manner. The growth of the slow dynamics and of ξ seems well correlated, indicating that the charge clusters cause the slow dynamics.

The charge-glass transition is clearly observed in the correlation length ξ-temperature profile when measured during a warming process after rapid cooling (~90 K/min) [Fig. 2(b)]. From 120 to 150 K, ξ is temperature insensitive with an appreciably shorter length than expected. Such a “frozen” metastable state with no long-range order is characteristic of glassy states, demonstrating that a charge-glass is formed in the quenched state. Upon further warming, ξ increases abruptly to the expected value at T_g ~160–165 K and becomes temperature-dependent above this temperature. This behavior demonstrates that the charge-liquid nature is recovered above T_g, and T_g can therefore be regarded as the charge-glass transition temperature.

Generally, correlated electrons are neither well itinerant nor well localized at high temperatures, so they are considered a “bad metal” [13]. The present results suggest that the bad metallic regime in charge-frustrated systems can be better described as a glass-forming charge-liquid, although the actual charge-glass transition may be avoided by a preceding frustration-relaxing structural transition.

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