

## Molecular Displacement Directing Antiparallel to Macroscopic Polarization in TTF-CA

Kensuke Kobayashi,<sup>1\*</sup> Sachio Horiuchi,<sup>2,3</sup> Reiji Kumai,<sup>1,2,3</sup> Fumitaka Kagawa,<sup>3,4</sup>  
Youichi Murakami,<sup>1</sup> and Yoshinori Tokura<sup>2,4,5</sup>

<sup>1</sup>Condensed Matter Research Center (CMRC) and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, 305-0801, Japan.

<sup>2</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8562, Japan.

<sup>3</sup>CREST, Japan Science and Technology Agency (JST), Tokyo 102-0076, Japan.

<sup>4</sup>Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan.

<sup>5</sup>Correlated Electron Research Group (CERG) and Cross-correlated Materials Research Group (CMRG), ASI-RIKEN, Wako 351-0198, Japan

### Introduction

The organic charge-transfer complex TTF-CA comprised of an electron donor, tetrathiafulvalene (TTF) and an acceptor, *p*-chloranil (CA) have been attracting much attention because of novel ferroelectric neutral-to-ionic phase transition [1]. Recently, in contrast to conventional point-charge picture, the first-principles calculations invoked a much larger spontaneous polarization (3~10  $\mu\text{Ccm}^{-2}$  along the *a*-direction) with two contrasting candidates of electronic states [2]. The total polarization is predicted to direct either parallel or antiparallel to the ionic polarization, depending on the antiferromagnetic or nonmagnetic state. Such predictions strongly motivated us to experimentally determine both the magnitude and the direction of spontaneous polarization.

### Experimental Results and Discussions

The symmetry-breaking of TTF-CA crystal structure under electric field was probed by the intensity difference between Bijvoet pair (*hkl* versus  $\bar{h}\bar{k}\bar{l}$ ) reflections, which arises from the anomalous x-ray scattering effect. The simulation based on the crystal structures at  $T = 15$  and 40 K [3] predicts that the Bijvoet pair reflections 101 and  $\bar{1}0\bar{1}$  have sufficient intensities and are the most susceptible to the anomalous x-ray scattering for x-ray wavelength  $\lambda = 1.55 \text{ \AA}$  used. Figure 1 depicts the temperature dependence of their normalized integrated intensity  $I_+ \equiv I(101)/\{I(101) + I(\bar{1}0\bar{1})\}$  and  $I_- \equiv I(\bar{1}0\bar{1})/\{I(101) + I(\bar{1}0\bar{1})\}$ . Just below  $T_c$ , the observed  $I_+$  and  $I_-$  readily approach 0.705 or 0.295 (horizontal broken lines in Fig. 1), which corresponds to the full polarization into either polarity according to the simulation. Therefore, the poling field of 4  $\text{kVcm}^{-1}$  is regarded as sufficient for developing a single-domain state. By comparing the observed intensity of Bijvoet pair ( $I_+$  and  $I_-$ ) with the simulation, we found that the positively charged TTF molecules shift toward the positive electrode and the negatively charged CA toward the negative electrode. These experimental observations

confirm recent first-principles calculations predicting an extreme contribution of the electronic polarization, which directs antiparallel to the ionic displacement and governs the magnitude of polarization. The electronic ferroelectricity itself is currently one of the key issues for multiferroelectrics. The electronic response with less energetic cost of lattice deformations will promise both high-performance and high-frequency operations as well as new functionalities.

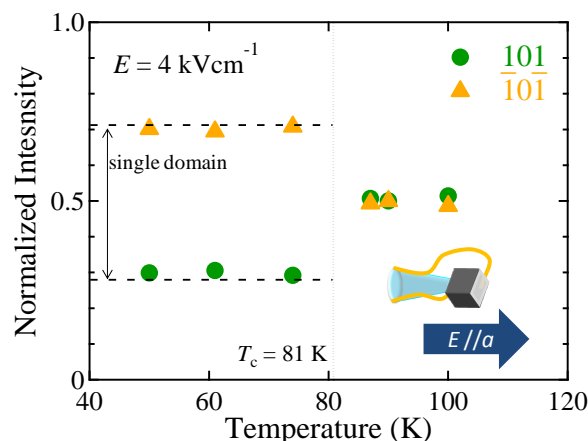


Fig. 1: Temperature dependence of normalized integrated intensities of Bijvoet pair reflections 101 and  $\bar{1}0\bar{1}$  at constant  $E = +4 \text{ kVcm}^{-1}$ . Inset shows a schematic drawing of diffraction experiment. Broken lines indicate calculated values of single domain model.

### References

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\* kensuke.kobayashi@kek.jp