Experimental report

15/04/2019

Proposal:	**DIR-156**	**Council:**	4/2017
Title:	Special Neutron Polarimety analysis under high-pressure for investigation of pressure-induced ferroelectric phases of multiferroic CuFeO2		
Research area:	Physics		

This proposal is a continuation of 5-51-514

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Samples: CuFeO2

Instrument	Requested days	Allocated days	From	To
D3	4	8	12/04/2018	18/04/2018
			22/05/2018	25/05/2018

Abstract:

Experimental report for “Investigation of high-pressure phases of Multiferroic Delafossite $CuFeO_2$ by using CryoPAD and Hybrid-Anvil-Cell”

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Abstract: In these experiments, we extended the first experiment in 2016, and measured the pressure and temperature dependence of polarization matrix elements to determine the magnetic phase boundary between pressure induced phases in multiferroic $CuFeO_2$, by using the CryoPAD apparatus on D3 beamline and our developed Hybrid-Anvil-Cell (HAC). From these experiments, we have succeeded in determining the phase boundary in the pressure versus temperature phase diagram of $CuFeO_2$.

Experiment: The neutron polarimetry experiments were carried out using a CRYOPAD apparatus[1, 2] on the D3 beam line. Single crystal samples of $CuFeO_2$, grown by the floating zone technique, were cut into rectangular shapes with dimensions of 1.1 × 1.1 × 0.2 mm^3 and 0.4 × 0.5 × 0.2 mm^3 for experiments at P = 0.2 and 2.0 GPa, and P = 4.0 GPa, respectively. The former and latter crystals have mosaic widths, 0.40 ± 0.02 and 0.50±0.05, respectively. The crystal qualities were kept even under pressure up to 4.0 GPa, by using glycerin as the pressure transmission medium. The cut samples were mounted in the HAC with the monoclinic *a*-axis (hexagonal [1 -10]) vertical, in order to provide access to the monoclinic (0, *K*, *L*) (hexagonal (*H, H, L*)) reflections. The incident neutrons are polarized and monochromatized at the Heusler monochrometer. The incident wavelength 0.85 Å was employed. The final neutron spin was analyzed with ^3He filter cells. The data has been corrected for the exponential decay of the ^3He polarization. A sapphire anvil with a 4.2 mm diameter culet, supported by CuBe, and a nonmagnetic diamond composite (with a SiC binder) were used up to 2.0 GPa, while the supported sapphire anvil of 2.7 mm diameter culet and WC with a nonmagnetic Ni binder were employed during the 4.0 GPa experiments. These materials were confirmed to be nonmagnetic by magnetization measurements. Aluminum gaskets (Al2017) with 2.0 or 1.0 mm diameter hole were used for the P = 0.2 and 2.0 GPa, and P = 4.0 GPa experiments, respectively. The HAC was inserted into a Orange cryostat.

The first experiment in December 2016, we succeeded in measuring the full polarization matrix without any depolarization of neutrons, and determined the all magnetic structures of pressure induced ferroelectric phases of $CuFeO_2$.

Results: In the extended experiments, we measured temperature dependence of polarization matrix elements, sensitive to the magnetic structure such as P_{yy} and $P_{yz,}$ for the pressure region 0.7 GPa < P < 3.7 GPa. The observed matrix elements obtained in 4.0 GPa and 10 K were completely different from those obtained for the ICM1 phase: the P_{yz}, P_{zy}, P_{yy} and P_{zz} values at 4.0 GPa were much smaller than the values calculated using the SDW model for the ICM1 phase. The difference in the matrix elements was also seen in lower pressure region. The temperature dependence of P_{yy} (-P_{zz}) and P_{yz} (P_{yz}), sensitive to magnetic structure model, for 0.7 GPa ≤ P ≤ 3.7 GPa is summarized in Fig. 1. The P_{yy} and P_{yz} observed at 0.7 GPa and 1.4 GPa can be explained by the SDW model for the data measured at T ≥ 11 K. These results are consistent with the absent macroscopic electric polarization above 10 K up to 2.0 GPa. (the inset of Fig. 3a) In contrast, for the data at 2.2 GPa and 3.7 GPa, the P_{yy} (-P_{zz}) and P_{yz} (P_{zy}) values deviate from those of SDW model below $T \sim$12 K and $T \sim$13.5 K, respectively. These results indicate that a phase transition occurs from the ICM1 phase in low pressure region to another phase in high pressure region, which is defined as ICM4 phase. However, in the present experiment, we cannot distinguish the two possibilities, either phase mixing with the ICM1 phase inside the ICM4 phase, or that a single ICM4 phase exists, due to the same peak position at **Q** = (0, q, 1/2) (or **Q** = (0, -q, -1/2)). The gradual change in the matrix elements with varying temperature at 2.2 GPa and 3.7 GPa in ICM4 phase (Fig. 1) can be caused by either change in the volume fraction between ICM1 and ICM4 phases or a continuous changing of the spin noncollinearity toward the collinear SDW (with warming).

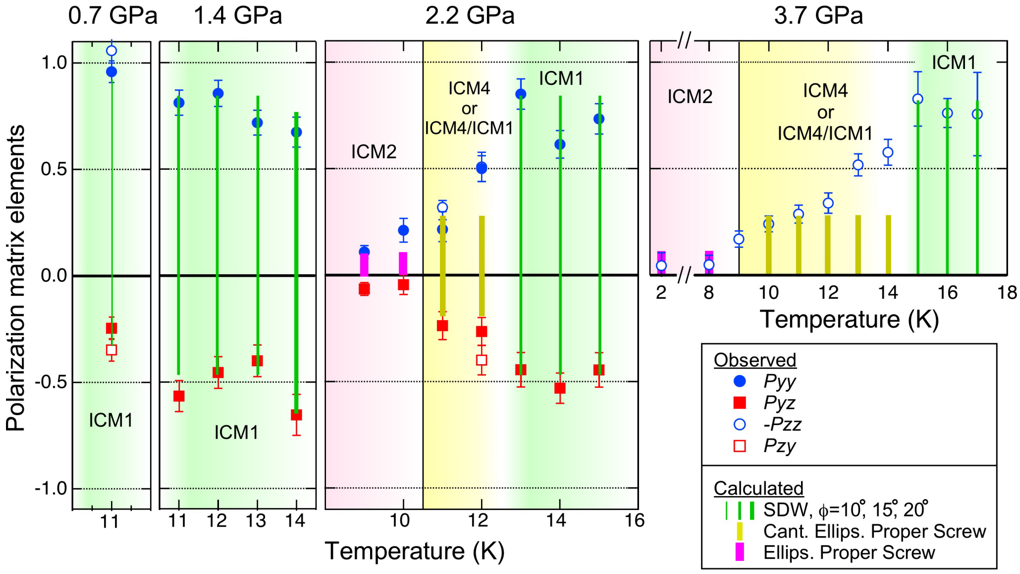

Fig. 1 Polarization matrix elements data at several pressures. Temperature dependence of the polarization matrix elements for 0,-q,-1/2 reflection, P_{yy} (filled circles), P_{yz} (filled squires), -P_{zz} (open circles) and P_{zy} (open squires) at P = 0.7, 1.4, 2.2 and 3.7 GPa. The vertical bars represent the calculated values: the spin-density-wave structure with φ = 10°, 15°, 20°, the canted ellipsoidal proper screw with 0.60 ellipsoidal ratio and 5 degrees canting angle and ellipsoidal proper screw with 0.92 ellipsoidal ratio. Note that we cannot distinguish a single ICM4 phase from coexistence of ICM4 and ICM1 phases for the intermediate temperature regions at 2.2 GPa and 3.7 GPa in the present experiment, as indicated by ICM4 or ICM4/ICM1. The solid lines denote the phase transition temperatures between ICM2 and ICM4.

Conclusion: As mentioned above, we determined the magnetic structure in the pressure-induced ferroelectric phases in the first experiment in 2016, and investigated the full phase boundary in the pressure versus temperature phase diagram in the second experiments in multiferroic $CuFeO_2$, by using the nonmagnetic HAC and CRYOPAD combination. In conclusion, we have succeeded in showing that it is feasible to measure the full neutron polarization matrix even under high pressure for the first time, and determined the magnetic structures in the pressure induced ferroelectric phases and the phase diagram of multiferroic $CuFeO_2$. These results have been published in Nature Communications **9** 4367 (2018).