Uniaxial-stress enhancement of spin-driven ferroelectric polarization in a multiferroic CuFe_{1-x}Ga_xO_2

S Mitsuda¹, K Yoshitomi¹, T Nakajima¹, C Kaneko¹, H Yamazaki¹, M Kosaka², N Aso³, Y Uwatoko⁴, Y Noda⁵, M Matsuura⁶, N Terada⁷, S Wakimoto⁸, M Takeda⁸, K Kakurai⁸

¹Department of Physics, Tokyo University of Science, Tokyo 162-8601, Japan
²Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan
³Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
⁴Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan
⁵Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
⁶Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
⁷National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan
⁸Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

mitsuda@nsmsmac4.ph.kagu.tus.ac.jp

Abstract. Delafossite compound CuFeO_2 is a spin-driven magneto-electric multiferroic, in which magnetic field-induced or nonmagnetic impurity-induced proper helical magnetic ordering generates a spontaneous electric polarization through the spin-orbit-interaction mediated modulation of Fe 3d-O 2p hybridization. As is expected from spin-lattice tightly coupled character of this system, we found an enhancement of spin-driven ferroelectric polarization under [1 1 0] uniaxial stress as spin-mediated piezoelectric effect. Preparing almost mono-domain state for multiferroic CuFe_{1-x}Ga_xO_2 sample with x=0.035, we have performed polarized neutron diffraction and in-situ ferroelectric polarization measurements to investigate how the helical magnetic structure is modified and how much ferroelectric polarization increases under application of [1 1 0] uniaxial stress up to 100 MPa. The uniaxial-stress variation of magnetic structural parameters characterizing helical magnetic ordering suggests decreasing of the ferroelectric polarization according to the calculation on the basis of d-p hybridization mechanism. Therefore, it is suggested that the enhancement of ferroelectric polarization originates not in variation of the magnetic structure but in the enhancement of the d-p hybridization coupling constants.

1. Introduction
Spin-driven magnetoelectric (ME) multiferroics, in which magnetic inversion symmetry breaking triggers off ferroelectricity, have been intensively investigated in recent cross-correlated materials research, since giant ME effects were discovered in TbMnO_3 [1]. The magnetic oxide CuFeO_2 to be
investigated here is a triangular lattice antiferromagnet with delafossite crystal structure, in which each Fe\textsuperscript{3+} triangular layer is well separated by one Cu\textsuperscript{2+} and two O\textsuperscript{2-} layers, and stacks along the hexagonal c axis, as is illustrated in figure 1(a). This frustrated magnet CuFeO\textsubscript{2} is a rare spin-driven magneto-electric multiferroic, in which magnetic field-induced [2] or nonmagnetic impurity-induced [3,4,5] proper helical magnetic ordering generates a spontaneous electric polarization \textit{parallel} to the helical axis through the spin-orbit-interaction mediated modulation of Fe 3d-O 2p hybridization [6]. This d-p hybridization mechanism is distinct from the spin-current (inverse Dzyaloshinskii–Moriya) mechanism [7,8] accounting for the ferroelectricity generated by cycloidal magnetic orderings [9,10], although, similarly based on spin–orbit interactions. As was revealed in recent Xray diffraction measurement [11,12], CuFeO\textsubscript{2} is also a spin-lattice coupled system; to partially lift the degeneracy in the frustrated exchange interactions, the triangular lattice spontaneously distorts so that the triangular lattice elongates in the direction of the c-plane projection of magnetic propagation vector and contracts in the perpendicular direction. Therefore, as a cross-correlated phenomena, it can be expected that uniaxial stress applied perpendicular to the c-axis, which is conjugate to the anisotropic lattice distortion, modifies the helical magnetic structure and consequently controls the emerged ferroelectric polarization, namely, spin-mediated piezoelectric effect. In this study, to demonstrate uniaxial stress control of the ferroelectric polarization via modification of the magnetic structure, we investigated, by polarized neutron diffraction and in-situ ferroelectric polarization measurements, how the helical magnetic structure is modified and how much ferroelectric polarization changes under application of uniaxial stress up to 100 MPa, using a CuFe\textsubscript{1-x}Ga\textsubscript{x}O\textsubscript{2} (x=0.035) sample which exhibits the ferroelectric phase below $T_{C}$\~8 K in zero magnetic field.

2. Preliminary Details

A single crystal of CuFe\textsubscript{1-x}Ga\textsubscript{x}O\textsubscript{2} (x=0.035) of nominal composition was prepared by floating zone method and was cut to dimensions of $\sim 1.7 \times 6 \times 1.5$ mm$^{3}$ with the [1\text{\overline{1}}0] direction parallel to the shortest dimension.

The magnetic structure of a ferroelectric phase of CuFe\textsubscript{1-x}Ga\textsubscript{x}O\textsubscript{2} (x=0.035) has been studied by experimentally and theoretically. Experimentally [13], complementary use of spherical neutron polarimetry and a four-circle neutron-diffraction measurement revealed that the proper-helical-type magnetic structure in the ferroelectric phase has a finite ellipticity of $\sim$0.9, spin phase shift of $\sim$73 $^\circ$ and the magnetic propagation wave vector $\vec{Q}=(q,q,3\lambda)$ with $q$-0.205. The helical axis of the magnetic structure is parallel to the c-plane projection of the magnetic propagation vector. Theoretically [14], on energy-considerations using the exchange parameters obtained by inelastic neutron measurements, a complex but similar distorted proper-helical-type spin configuration with a distribution of turn angles...
was proposed. In this study we employ the experimentally obtained magnetic structure [13] to characterize the spin order. Because of the trigonal symmetry of the crystal structure, this system has three magnetic domains whose wave vectors of \((q, q, \frac{3}{2})\), \((q, -2q, \frac{3}{2})\) and \((-2q, q, \frac{1}{2})\) are crystallographically equivalent to each other. We refer to the three domains as \((110)\)-, \((1\overline{2}0)\)- and \((2\overline{1}0)\)-domains, along with our previous works [13]. In each of the domains, the ferroelectric polarization emerges along the helical axes, and as shown in figure 1(b), there is a one-to-one correspondence between the direction of the ferroelectric polarization and the spin helicity of the helical magnetic structure: left-handed (LH) or right-handed (RH) helical arrangements of the spins. Therefore, the multiferroic (ferroelectric and magnetic) domains are classified into six types with volume fractions of \(V_{(110)}^{(10)}\), \(V_{(110)}^{(RH)}\), \(V_{(120)}^{(LH)}\), \(V_{(120)}^{(RH)}\), \(V_{(210)}^{(LH)}\) and \(V_{(210)}^{(RH)}\), as shown in figure 2(c). Taking the multiferroic domain structure into account, the macroscopic electric polarization \(P\) along \([110]\) axis under applied uniaxial stress \(p\) in the \([1\overline{1}0]\) direction, which is experimentally obtained by time-integration of the polarization current flowing between two Ag-electrodes on \([110]\) surfaces as shown in figure 2(c), is determined by sum of the three contribution from each multiferroic domain and can be described as

\[
P = P_{0}^{(110)}(p) D_{(110)}(p) V_{(110)}(p) + \frac{1}{2} P_{0}^{(120)}(p) D_{(120)}(p) V_{(120)}(p) + P_{0}^{(210)}(p) D_{(210)}(p) V_{(210)}(p) .
\]

Here, the asymmetry of the volume fractions having RH- and LH- helical magnetic ordering in the \((110)\)-domain, \(D_{(110)}\), is defined by \((V_{(110)}^{RH} - V_{(110)}^{LH})/(V_{(110)}^{RH} + V_{(110)}^{LH})\), and total volume fraction of the \((110)\)-domain, \(V_{(110)}\), is defined by \((V_{(110)}^{RH} + V_{(110)}^{LH})\). \(P_{0}^{(110)}\) is the value of \(P\) for mono-domain state, that is, \(V_{(110)} : V_{(120)} : V_{(210)} = 1 : 0 : 0\) and \(D_{(110)} = 1\). The symbols for other trigonal domains are also defined similarly. The factor of \(1/2\) in front of the second term in equation (1) denotes that the \([110]\) projection of the ferroelectric polarization is half the magnitude of the ferroelectric polarization emerged in the domain.

![Figure 2](image-url)

**Figure 2.** (a) Schematic drawing of the uniaxial stress device inserted in the cryostat. (b) Magnification of the sample space of the uniaxial stress device. CuBe disk springs supply uniaxial bias-stress of 5 MPA. (c) Relationships among the six possible directions of the ferroelectric polarization, applied electric field and uniaxial stress. Open and filled arrows denote the directions of the ferroelectric polarization induced by the RH- and the LH-helical magnetic domains, respectively. The sizes of the arrows qualitatively show the volume fractions of the six domains. (d) Comparison between the observed and the calculated magnetic structure factors. Red, green and blue circles denote data for the \((110)\)-, \((1\overline{2}0)\)- and \((2\overline{1}0)\)-domains, respectively.
All quantities appearing in equation (1) are generally uniaxial-stress-\( p \)-dependent and have different \( p \)-dependence for each of three trigonal domains. What we call spin-mediated piezoelectric effect here can be seen in \( p \)-dependence of the quantities of \( P_0^{(10)}(p) \), \( P_0^{(20)}(p) \) and \( P_0^{(210)}(p) \). However, the [1\( \bar{T}0 \)] uniaxial stress \( p \) enhances the anisotropic spontaneous lattice distortion for (110)-domain, whereas that may rather suppress the anisotropic spontaneous lattice distortion for (1\( \bar{2} \)0)- and (2\( \bar{1} \)0) -domains. Thus, the \( p \)-dependence of \( P_0^{(10)}(p) \) can be different from that of \( P_0^{(20)}(p) \) and \( P_0^{(210)}(p) \), and therefore different spin-mediated piezoelectric effect must be mixed up in the macroscopic electric polarization \( P \) along [110] axis under the [1\( \bar{T}0 \)] uniaxial stress \( p \). Moreover, applying the [1\( \bar{T}0 \)] uniaxial stress \( p \) causes the repopulation of three trigonal domains from (1\( \bar{2} \)0)- and (2\( \bar{1} \)0)-domains to (110)-domain so as to give rise to distinct increasing of the macroscopic electric polarization \( P \) along [110] axis, as was quite recently demonstrated in our work [15]. Therefore, to properly study the spin-mediated piezoelectric effect seen in \( P_0^{(10)}(p) \), almost mono-domain state, which satisfies the conditions of \( V_{(110)} > V_{(1\bar{2}0)} + V_{(2\bar{1}0)} \) and \( D_{(110)} \sim 1 \), is indispensable. Fortunately, in our inelastic neutron scattering experiment [16] to obtain the spin wave dispersion in 4-sublattice (4SL) ground state of CuFeO\(_2\), we have demonstrated that applying only 10 MPa of the [1\( \bar{T}0 \)] uniaxial stress at room temperature results in almost mono-domain state with \( V_{(110)} \sim 0.97 \) in the 4SL phase at low temperature. 

Taking these things into consideration, in the present study of the spin-mediated piezoelectric effect in the CuFe\(_{1-x}\)Ga\(_x\)O\(_2\) (\( x=0.035 \)) sample, we applied the [1\( \bar{T}0 \)] uniaxial stress using two different springs: CuBe disk springs and SiCr Coil spring. As shown in figure 2 (b), CuBe disk springs were set in the stress cell to keep, throughout the entire experiments, the uniaxial stress of 5 MPa applied at room temperature as a bias-stress to realize almost mono-domain state. On the other hand, as shown in figure 2 (a), the variable-uniaxial stress up to 100 MPa is additionally applied at low temperature of 20 K above \( T_c \sim 8 \) K by a SiCr coil spring and a micrometer attached on top of the cryostat, and is monitored by a load meter. In present study, we have successively performed three different neutron experiments of (i) four-circle neutron diffraction measurement, (ii) spherical neutron polarimetry and (iii) polarized neutron diffraction with in-situ pyroelectric measurement. Note that the uniaxial bias-stress of 5 MPa has been applied throughout the entire neutron experiments, including off-bench pyroelectric measurement in between successive neutron experiments.

3. Results and Discussion

3.1 Four-circle neutron diffraction measurement

In order to evaluate the volume fractions of the three magnetic domains under the uniaxial bias-stress of 5 MPa, we performed four-circle neutron diffraction measurement using FONDER installed at JRR-3 in Japan Atomic Energy Agency (JAEA). The incident neutron beam with wavelength 1.24 Å was obtained by a Ge(311) monochromator. The sample with the stress cell was mounted on a closed-cycle He-gas refrigerator, and was cooled down to 3 K. We measured intensities of 23 magnetic Bragg reflections, of which 9, 8, and 6 magnetic reflections belong to the (110)-, (1\( \bar{2} \)0)- and (2\( \bar{1} \)0)-domains, respectively. The effect of neutron absorption was corrected by the DABEX software. We have performed least-square fitting analysis, in which we used the established magnetic structural parameters of the elliptic helical magnetic structure presented in ref. 13 and refined the volume fractions, \( V_{(110)} \), \( V_{(1\bar{2}0)} \) and \( V_{(2\bar{1}0)} \). The comparison between the observed magnetic structure factor \( F_{\text{obs}} \) and the calculated values \( F_{\text{cal}} \) is shown in Fig. 2(d). The reliability factor was obtained to be 7.4%, and the volume fractions of the three magnetic domains were determined to be \( V_{(110)} : V_{(1\bar{2}0)} : V_{(2\bar{1}0)} = 0.88 : 0.07 : 0.05 \). This shows that the uniaxial bias-stress of 5 MPa applied onto the [1\( \bar{T}0 \)] surface successfully produces almost mono-domain state.
3.2 Spherical neutron polarimetry

Our tasks to study the spin-mediated piezoelectric effect are (i) obtaining the uniaxial-stress $p$ variation of magnetic structural parameters characterizing elliptic helical magnetic ordering in the (110)-domain such as the direction of helical axis, the ellipticity, propagation wave number $q$ and the spin phase shift $\delta$ (see figure 4 (b)), and (ii) obtaining the $p$-dependence of $P_0^{(110)}(p)$ which can be deduced through the relation of

$$P_0^{(110)}(p) \sim P(p)/(D_{(110)}(p)V_{(110)}(p)) \quad .$$

This relation would be applicable under almost mono-domain state in which the (100)-domain dominates over the (120)- and (\overline{2}10)-domains. To determine the magnetic structural parameters of the direction of helical axis and the ellipticity, spherical neutron polarimetry was carried out at the triple-axis spectrometer TAS-1 with the CRYOPAD option installed at JRR-3 in JAEA. The sample was mounted in the uniaxial stress device inserted in the pumped $^4$He cryostat, as shown in figure 2 (a)–(c). For $p=5$ (bias) and 80 MPa, we measured polarization matrix terms at seven different magnetic Bragg reflections belonging to the (110)-domain at $T=2$ K. As a result, it was turned out that the magnetic structural parameters are consistent with our previous results [13] and dose not show any clear uniaxial stress dependences within the experimental accuracy.

3.3 Polarized neutron diffraction with in-situ pyroelectric measurement

In order to obtain the uniaxial stress $p$ dependence of the asymmetry $D_{(110)}(p)$, the volume fraction $V_{(110)}(p)$, the propagation wave number $q(p)$, the spin phase shift $\delta(p)$ and the macroscopic ferroelectric polarization $P(p)$ along the [110] direction, polarized neutron-diffraction and in-situ pyroelectric measurements were carried out at the triple-axis neutron spectrometer PONTA installed at JRR-3 in the JAEA. The sample was mounted in the uniaxial stress device inserted in the pumped $^4$He cryostat, as shown in figure 2 (a)–(c).

In the in-situ pyroelectric measurements, as shown in the figure 3 (a), the temperature variation of the ferroelectric polarization $P$ along the [110] direction, which were obtained by time-integration of the observed pyroelectric current, shows pronounced uniaxial stress dependence of ferroelectric phase transition temperature $T_c$ as well as in the value of $P$ at low temperature. As is clearly seen in the inset of figure 3 (a), uniaxial-stress enhancement of the ferroelectric polarization $P$ at $T=2$ K was observed. It should be noted that this enhancement of $P$ was reversible in the $p$-range of 5 MPa (bias) ~ 100 MPa and also reproducible over off-bench pyroelectric measurements in between successive neutron experiments.

In the present polarized neutron-diffraction experiment, we measured only two magnetic Bragg reflections of $(q,q,\frac{1}{2})$ and $(\frac{1}{2}+q,\frac{1}{2}+q,\frac{1}{2})$. As shown in Fig.3 (b), these reflections can be assigned as $\hat{\tau} + \hat{Q}$ and $\hat{\tau} - \hat{Q}$ reflections, where $\hat{\tau}$ is a reciprocal lattice vector and $\hat{Q} = (q,q,\frac{1}{2})$ is the magnetic propagation vector. The scattering cross-section for these reflections is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{\hat{\tau} \pm \hat{Q}} \approx S(\hat{k})\{(\mu_{x\perp}^2 + \mu_{z\perp}^2)[V_{(110)}^{RH} + V_{(110)}^{LH}] + 2\mu_{x\perp}\mu_{z\perp} (\hat{p}_N \bullet \hat{k})[V_{(110)}^{RH} - V_{(110)}^{LH}]\} .$$

Here $S(\hat{k})$ is a factor dependent on the magnetic form factor $f(\hat{k})$ and the spin phase shift $\delta$, and is expressed by

$$S(\hat{k}) \sim f(\hat{k})^{2} \pm e^{i\delta} \quad ,$$

where + and – signs correspond to $(q,q,\frac{1}{2})$ and $(\frac{1}{2}+q,\frac{1}{2}+q,\frac{1}{2})$ reflections, respectively. $\mu_{x\perp}$ and $\mu_{z\perp}$ are the length of the spin components projected onto the plane normal to the scattering vector. $\hat{p}_N$ and $\hat{k}$ are unit vectors of neutron polarization vector and the scattering vector, respectively.

From equation (3), $D_{(110)}$ is approximately given by \(\frac{I_{ON}-I_{OFF}}{I_{ON}+I_{OFF}}\) for the two magnetic Bragg
reflections [13], where \( p_0 \sim 0.975 \) is the instrumental beam polarization of the incident neutrons. \( I_{ON} \) and \( I_{OFF} \) are the intensities of a magnetic Bragg reflection measured when the spin flipper is ON (\( P_N \bullet \hat{k} = 1 \)) and OFF (\( P_N \bullet \hat{k} = -1 \)), respectively. As is seen in large difference in between flipper On- and flipper Off- intensities shown in figure 3 (c), the deduced asymmetry \( D_{(110)}(p) \) was close to 1, suggesting that the poling-electric-field \( E_P = 250 \text{ KV/m} \) is strong enough to achieve a almost spin-helicity-mono-domain state. The asymmetry \( D_{(110)}(p) \) is almost the uniaxial stress \( p \)-independent, as is seen in figure 3 (d).

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As shown in figure 3 (c), with increasing the stress, the intensity at \((q,q,\frac{1}{2})\) Bragg reflection increases, whereas the intensity at \((\frac{1}{2}-q,\frac{1}{2}-q,\frac{1}{2})\) Bragg reflection decreases. Taking accounts of equation (4), these clearly indicate that the spin phase shift \( \delta \) becomes small as the stress \( p \) increasing. In deducing the \( p \)-variation of volume fraction \( V_{(110)}(p) \) and spin phase shift \( \delta(p) \), we analyzed integrated intensity-data set, paying attention to that integrated intensity-data set at \( p=5 \text{ MPa} \) contain the information of \( \delta(p=5\text{MPa}) \sim 73^\circ \) [13] and \( V_{(110)}(p=5\text{MPa}) \sim 0.88 \) (see section 3.1). While the volume fraction \( V_{(110)}(p) \) is almost the uniaxial stress \( p \)-independent as shown in figure 3 (d), the spin phase shift \( \delta(p) \) shows pronounced \( p \)-variation as shown in figure 4 (a).

**Figure 3.** (a) Temperature variations of \( P \) measured on heating after cooling process with poling electric field \( E_p=250 \text{ KV/m} \) at \( p =5, 40 \) and 80 MPa. The inset shows uniaxial stress dependence of \( P \) at \( T=2.0 \text{ K} \). (b) The location of the magnetic reflections surveyed in the present polarized neutron measurement using PONTA spectrometer in the (HHL) scattering zone. (c) The diffraction profiles of \((H,H,\frac{1}{2})\) reciprocal lattice scans for the \((q,q,\frac{1}{2})\) and \((\frac{1}{2}-q,\frac{1}{2}-q,\frac{1}{2})\) magnetic Bragg reflections at \( T=2\text{K} \). (d) Uniaxial stress \( p \) dependence of \( D_{(110)} \) and \( V_{(110)} \). The solid lines are guides to the eyes.

### 3.4 Discussion

To summarize the results up to here, as for the task (i) obtaining the uniaxial-stress \( p \) variation of magnetic structural parameters characterizing elliptic helical magnetic ordering in the (110)-domain, it was turned out that only the spin phase shift \( \delta \) among magnetic structural parameters shows
pronounced $p$-variation as shown in figure 4 (a). And, as for the task (ii) obtaining the $p$-dependence of $P_0^{(110)}$ by equation (2), as is clearly seen in figure 4 (c-1), uniaxial-stress enhancement of the ferroelectric polarization $P_0^{(110)}$ at $T=2$ K was found as the spin-mediated piezoelectric effect.

According to the calculation on the basis of $d$-$p$ hybridization mechanism proposed by Arima [6], the ferroelectric polarization along $[110]$ direction $P_0^{(110)}$ has magnetic structural parameters dependences as is described by

$$P_0^{(110)} = C \sin(4\pi q) \{ \sin(2(\theta_1 - \theta_2 - \delta)) + \sin(2(\theta_1 - \theta_2 + \delta)) \}, \quad (5)$$

where finite ellipticity $\mu_x/\mu_z \approx 0.9$ [13] was neglected and the original expression (the equation 6 in ref. 6) is extending to the case that Fe$_1$ site and Fe$_2$ site are not equivalent, as shown in figure 4 (b). Putting the almost $p$-independent propagation wave number $q(p)$ shown in figure 4 (a), the value of $\theta_1 - \theta_2 \approx 100^\circ$ [6] and $p$-dependent phase shift $\delta(p)$, we obtained the relative variation $R$ of calculated $P_0^{(110)}$ to that at $p=5$MPa, as shown in figure 4 (c-1). Thus, the uniaxial-stress variation of magnetic structural parameters characterizing helical magnetic ordering suggests decreasing of the ferroelectric polarization according to the calculation on the basis of $d$-$p$ hybridization mechanism. Therefore, it is suggested that the enhancement of ferroelectric polarization seen in the figure 4 (c-1) originates not in variation of the magnetic structure but in the enhancement of the microscopic $d$-$p$ hybridization coupling constants [6] which are contained in the coefficient $C$ in equation (5).

As already mentioned, ferroelectric (magnetic) phase transition temperature $T_c$ significantly increases under application of uniaxial stress. This is the evidence that uniaxial stress slightly modifies the competing exchange interactions in this frustrated magnetic system, which can be also seen in pronounced uniaxial stress variation of the spin phase shift $\delta(p)$. Therefore, the enhancement of the microscopic $d$-$p$ hybridization coupling constants contained in the coefficient $C$ would be similarly expected.

**Figure 4.** (a) Uniaxial stress $p$ dependence of the magnetic propagation wave number $q$ and the spin phase shift $\delta$. (b) A Fe$_4$O$_2$ cluster used for the calculating the local electric dipole moment for the proper helical magnetic structure with finite phase shift $\delta$. As the spin phase difference is depicted between Fe sites, Fe$_1$ site and Fe$_2$ site are not equivalent, and there is the spin phase shift $\delta$ in between. (c-1) Uniaxial stress $p$ dependence of $P_0$ and the relative variation $R$ of calculated ferroelectric polarization based on $d$-$p$ hybridization model to that at $p=5$MPa. (c-2) Uniaxial stress $p$ dependence of enhancement factor defined by $P_0(p)/P_0(p=5$MPa$)/R$. The solid lines are guides to the eyes.
Finally, let us mention the smallness of the uniaxial stress of ~100 MPa providing the spin-mediated piezoelectric effect. This is in contrast to the 100 time larger isotropic high pressure ~10 GPa which is necessary to suppress the long-range ordering accompanied by spontaneous lattice distortion [17]. Key point would be that $[\bar{1}10]$-uniaxial stress is anisotropic and conjugate to the anisotropic spontaneous lattice distortion. To conclude, using spin-driven magneto-electric multiferroic CuFeO$_2$, we have demonstrated uniaxial stress control of the ferroelectric polarization via the modification of the magnetic structure as spin-mediated piezoelectric effect, in which the microscopic d-p hybridization coupling constants are suggested to be enhanced.

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