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Zero-field random-field effect in diluted triangular lattice antiferromagnet $CuFe_{1-x}Al_xO_2$

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Abstract

We performed neutron scattering experiments on a diluted triangular lattice antiferromagnet (TLA), $CuFe_{1-x}Al_xO_2$ with $x = 0.10$. The detailed analysis of the scattering profiles revealed that the scattering function of magnetic reflection is described as the sum of a Lorentzian term and a Lorentzian-squared term with anisotropic width. The Lorentzian-squared term dominating at low temperature is indicative of the domain state in the prototypical random-field Ising model. Taking account of the sinusoidally amplitude-modulated magnetic structure with incommensurate wavenumber in $CuFe_{1-x}Al_xO_2$ with $x = 0.10$, we conclude that the effective random field arises even at zero field, owing to the combination of site-random magnetic vacancies and the sinusoidal structure that is regarded as a partially disordered (PD) structure in a wide sense, as reported in the typical three-sublattice PD phase of a diluted Ising TLA, $CsCo_{0.83}Mg_{0.17}Br_3$ (van Duijn *et al* 2004 *Phys. Rev. Lett.* **92** 077202). While the previous study revealed the existence of a domain state in $CsCo_{0.83}Mg_{0.17}Br_3$ by detecting magnetic reflections specific to the spin configuration near the domain walls, our present study revealed the existence of a domain state in $CuFe_{1-x}Al_xO_2$ ($x = 0.10$) by determination of the functional form of the scattering function.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The effect of geometrical spin frustration on magnetic phase transitions and critical phenomena in triangular lattice antiferromagnets (TLAs) has been extensively investigated both experimentally and theoretically [1]. Owing to competing interactions, a TLA exhibits a variety of magnetically ordered states such as long-period collinear Néel states or disordered

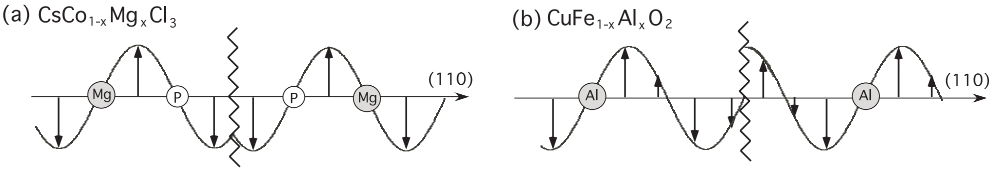

Figure 1. Schematic drawing of the domain state generated by nonmagnetic impurity in (a) the PD phase of $CsCo_{1-x}Mg_xX_3$ (X = Cl, Br) and (b) the oblique partially disordered (OPD) phase of $CuFe_{1-x}Al_xO_2$ with $x > 0.05$. ((a) is a commensurate three-sublattice structure, while (b) is a sinusoidally amplitude-modulated structure with incommensurate wavenumber (∼0.19)). Circles labelled as 'P', 'Mg' and 'Al' depict the disordered sites, nonmagnetic Mg^{2+} ions and nonmagnetic Al^{3+} ions, respectively. Vertical zigzag lines denote domain walls.

spin-glass-like states. One of the unusual magnetic ordering in TLAs is the partially disordered (PD) state in which one of the sublattices is disordered. This PD state appears in several ABX_3-type Ising TLAs (such as $CsCoCl_3$ or $CsCoBr_3$) [1, 2]. The most remarkable feature of the PD state is its high sensitivity to nonmagnetic impurity. For example, neutron and magnetic susceptibility measurements on $CsCo_{1-x}Mg_xCl_3$ [3] have revealed that only 0.2% dilution of magnetic Co^{2+} sites with nonmagnetic impurity wipes out the low-temperature ferrimagnetic phase, and extends the high-temperature PD phase to the low-temperature region. A neutron scattering study on a further diluted system, $CsCo_{0.83}Mg_{0.17}Br_3$ [4], revealed that an only 17% dilution destroys the long-range magnetic ordering, and produces a domain state whose local spin structure is a three-sublattice PD structure. This high sensitivity to nonmagnetic impurity of the PD state has been interpreted in terms of the effective random-field effect caused by site-random magnetic vacancies and the PD structure. As has been argued in a previous study [4], the disordered site coincides with a magnetic vacancy so as to minimize the loss of exchange energy, as illustrated in figure 1(a). Consequently, domains nucleated by site-random magnetic vacancies compete with each other at the domain walls, and the long-range magnetic ordering is destroyed. This indicates that the random-field domain state arises even at zero field, owing to the combination of site-random magnetic vacancies and PD magnetic structure. In the previous study on $CsCo_{0.83}Mg_{0.17}Br_3$, however, the functional form of the structure factor specific to the random field effect (namely Lorentzian-squared) was not discussed; instead evidence of a domain state obtained by detecting the magnetic reflections specific to the spin configuration near the domain walls was presented.

In the present experiments, we performed neutron scattering measurements on the diluted TLA $CuFe_{1-x}Al_xO_2$ with $x > 0.05$. The delafossite-type compound $CuFeO_2$ is one of the model materials of TLAs, and it has been extensively investigated in the last decade [5]. Recent studies on the diluted system $CuFe_{1-x}Al_xO_2$ with $x < 0.050$ [6] have revealed that various magnetically ordered phases compete with each other in the low Al^{3+} concentration region of $x < 0.050$ (see figure 2(a)), reflecting partial release of frustration. Among the various magnetically ordered phases, two phases have the sinusoidally amplitude-modulated structure with an incommensurate wavenumber that is regarded as a PD structure in a wide sense: one is the partially disordered (PD) phase that is thermally induced from the four-sublattice (4-sub) phase or impurity-induced low-temperature (LT) phase, and the other is the oblique partially disordered (OPD) phase that appears in the high Al^{3+} concentration region. Since the PD phase of $CuFe_{1-x}Al_xO_2$ decays with increasing substitution, we now pay attention to the OPD phase whose magnetic structure is a sinusoidal structure with an incommensurate wavenumber and magnetic moments canted by ∼50° from the *c*-axis [7], as shown in the inset of figure 2(a). Since the magnetic structure of the OPD phase can be regarded as a PD structure

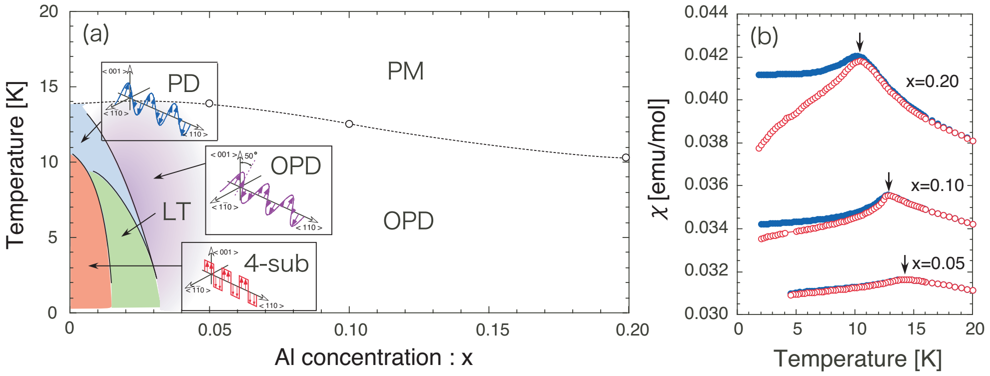

Figure 2. (a) x–T magnetic phase diagram of $CuFe_{1-x}Al_xO_2$ based on a previous study on $CuFe_{1-x}Al_xO_2$ with $x < 0.05$. The circular symbols in the region of $x > 0.05$ denote the anomalies found in the magnetic susceptibility measurements. (b) Temperature dependence of magnetic susceptibility (parallel to the hexagonal ⟨001⟩ axis) of the samples with $x = 0.05$ [8], 0.10 and 0.20. The vertical arrows denote the transition temperature, T_N. The open and closed symbols denote results obtained in measurements after zero-field cooling and applied-field (100 Oe) cooling, respectively.

in a classical spin system with Ising symmetry, it is expected that the nonmagnetic impurities nucleate domains by locking the phase of the sinusoidal modulation as illustrated in figure 1(b). The results of magnetic susceptibility measurements on the samples with $x = 0.05$, 0.10 and 0.20 show that no other phase transition was induced by further dilution, although the spin-glass-like hysteresis depending on the cooling process (zero-field cooling or cooling under an applied field) is enhanced as x increases (see figure 2(b)). This implies that the OPD state is stable in the region of $x > 0.05$, and the zero-field random-field effect is expected to be remarkable with increasing substitution of nonmagnetic impurity.

2. Experimental results and discussions

2.1. Experimental details and preliminary measurements

Single crystals of $CuFe_{1-x}Al_xO_2$ with $x = 0.05$, 0.10 and 0.20 of nominal composition were prepared by the floating zone technique. Some preliminary neutron scattering measurements on these samples were made using a triple-axis spectrometer, HQR, installed at the guide hall of JRR-3M in JAERI. For all samples, only the magnetic reflection corresponding to the magnetic ordering of the OPD state whose propagation wavevector is $(q_{\mathrm{OPD}}, q_{\mathrm{OPD}}, 1.5)$ was found below T_N ($T_N^{x=0.05} \sim 14.0$ K, $T_N^{x=0.10} \sim 12.8$ K, $T_N^{x=0.20} \sim 10.2$ K). q_{OPD} ($\sim$0.19) is almost independent of temperature, although it depends slightly on x. The typical profiles of $(h, h, 1.5)$ reciprocal lattice scans on each sample at the lowest temperature ($T = 2.0$ K) are shown in figures 3(a)–(c). We found that the width of the scattering profiles broadens with increasing Al^{3+} concentration as shown in figures 3(b) and (c), while the width of the scattering profile is very close to the resolution limit for the sample with $x = 0.05$, as shown in figure 3(a). These results qualitatively indicate that the long-range magnetic ordering is destroyed by substitution of nonmagnetic impurity. For more quantitative analysis in the present study, we selected the sample with $x = 0.10$ in which the zero-field random-field effect is considered to be clearly observed.

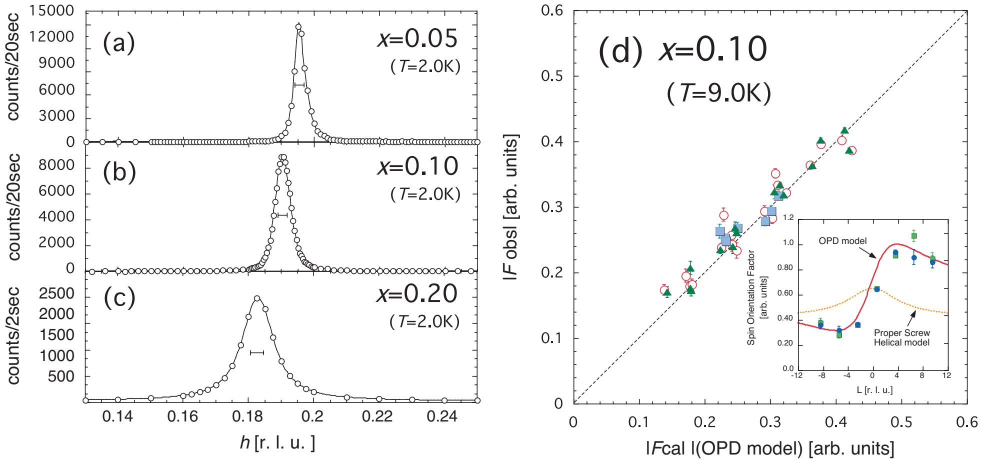

Figure 3. Typical scattering profiles for the samples with (a) $x = 0.05$, (b) $x = 0.10$ and (c) $x = 0.20$ in the $(h, h, 1.5)$ reciprocal lattice scans at $T = 2.0$ K. The horizontal bars indicate the experimental resolution. (d) Relationship between the observed structure factors ($|F_{\text{obs}}|$) and calculated structure factors ($|F_{\text{cal}}|$) for the OPD model. The magnetic reflections belonging to three equivalent $\langle 110\rangle$, $\langle 1\bar{2}0\rangle$ and $\langle \bar{2}10\rangle$ domains are depicted by circular, triangular and square symbols, respectively. The inset of (d) shows the index l-dependence of spin orientation factors along $(-q_{\text{OPD}}, 1 - q_{\text{OPD}}, 1)$ (green square) and $(q_{\text{OPD}}, 1 - 2q_{\text{OPD}}, 1)$ (blue circle). The solid and dotted lines denote the calculated spin orientation factor for the OPD structure and proper screw-type helical structure, respectively.

First, in order to confirm the magnetic structure of the sample with $x = 0.10$, a neutron diffraction measurement was carried out with the four-circle neutron diffractometer (FONDER) [9] installed at the guide hall of JRR-3M in JAERI. The wavelength of the neutron beam was 1.24 Å, obtained by a Ge311 monochromator. The sample was mounted in a closed-cycle He-gas refrigerator. We observed 41 magnetic reflections among three equivalent magnetic domains with the hexagonal threefold symmetry.

Next, in order to determine the functional form of the scattering function, $S(q)$, a neutron scattering experiment on the sample with $x = 0.10$ was carried out with the triple-axis neutron spectrometer HQR in a triple-axis configuration. The samples were mounted in a ^{4}He pumped cryostat with the hexagonal $\langle 1\bar{1}0\rangle$ axis vertical making (h, h, l) reflections accessible for measurements. The incident neutron wavelength of 2.44 Å was obtained using pyrolytic graphite monochromators. Collimation open-’40-’40-’60 was employed.

2.2. Magnetic structure analysis using four-circle neutron diffractometers

We determined the magnetic structure of the sample with $x = 0.10$ at $T = 9.0$ K. The magnetic structure analysis method used here is the same as that used in the previous study [7]. We first performed a crystal structure analysis to obtain the extinction parameter and the scale factor. Subsequently, we performed a magnetic structure analysis. In both of the crystal and the magnetic structure analyses, we performed absorption correction using the program DABEX, and determined the structure by a least-squares method. The result of the analysis is shown in figure 3(d). We found that the magnetic structure of the sample with $x = 0.10$ is the OPD structure which appears in the ground state of the sample with $x = 0.050$ [7].

The reliability factor of the present analysis was $R(F) = 6.00\%$, and this value is comparable to that of our previous analysis for $x = 0.05$ [7]. This result reveals that the OPD

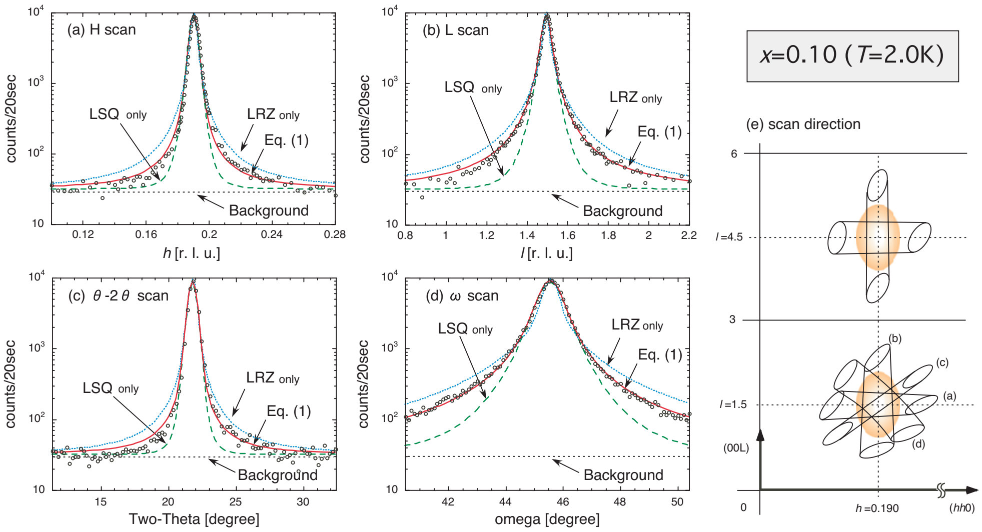

Figure 4. ((a)–(d)) Scattering profiles of the (q_{OPD}, q_{OPD}, 1.5) reflection at 2 K, where $q_{\mathrm{OPD}} = 0.190$. The results of MPD analysis for the functional form of Lorentzian (dotted lines), Lorentzian-squared (dashed lines) and equation (1) (solid lines) are shown. (e) The scan directions in the reciprocal lattice space of $\mathrm{CuFe}_{1-x}\mathrm{Al}_x\mathrm{O}_2$. Schematic drawing of anisotropic $S(q)$, resolution function and scan direction corresponding to (a)–(d) are shown.

magnetic structure is stable in the region $x > 0.05$, while the magnetic ordering markedly changes with the amount of nonmagnetic impurity in the region $x < 0.05$ [6].

2.3. Scattering profile analysis using triple-axis neutron spectrometer

In order to confirm the zero-field random-field effect quantitatively, we performed a detailed analysis of the scattering profiles for the sample with $x = 0.10$. At $T = 2.0$ K, we obtained scattering profiles of (q_{OPD}, q_{OPD}, 1.5) reflections with q_{OPD} ($\sim$0.19) along the four directions shown in figure 4(e). Next, we numerically calculated the scattering profiles for these four directions by convoluting a functional form of $S(q)$ with the measured resolution function, and simultaneously fitted them to the measured profiles. We refer to this analysis as 'multi-profile-deconvolution (MPD)'. Trying several functional form of $S(q)$, we found that the $S(q)$ of an OPD reflection is well described by the sum of a Lorentzian-squared (LSQ) term and a Lorentzian (LRZ) term with anisotropic width as follows:

$$S(q) = \frac{A}{(1 + \frac{qa^2+qb^2}{\kappa ab^2} + \frac{qc^2}{\kappa c^2})^2} + \frac{B}{1 + \frac{qa^2+qb^2}{\kappa ab^2} + \frac{qc^2}{\kappa c^2}} \qquad (1)$$

where q_a, q_b and q_c are the reduced wavenumbers representing the distance from the peak centre of the OPD reflection, along $\langle 110\rangle$, $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ axes, respectively. The fitted profiles are shown in figures 4(a)–(d). From the results of MPD analysis with equation (1), $B/A = 0.068$, $\kappa_{ab} = 0.001\,56$ [r.l.u.] and $\kappa_c = 0.0237$ [reciprocal lattice unit (r.l.u.)] were determined. Note that the two different profiles around the (q_{OPD}, q_{OPD}, 4.5) reflection whose scan directions are shown in figure 4(e) are also fitted well by equation (1) with almost the same parameters described in equation (1). Here, we would like to emphasize that the MPD analysis is necessary for the determination of anisotropic scattering function mentioned above.

If the deconvolution analysis is performed individually for each profile, the parameters of $S(q)$ cannot be determined uniquely. Only a simultaneous deconvolution analysis for the profiles along more than two directions can evaluate the anisotropic spin correlation accurately.

The LSQ term dominating at $T = 2.0$ K ($B/A = 0.068$) is indicative of the domain state in the prototypical random-field Ising model, and suggests that the system consists of a large number of domains. It should be noted that these analysis results were reproduced in the two-axis mode, suggesting that the energy integration in the triple-axis configuration is sufficient to obtain an instantaneous correlation function, $S(q)$, in this system.

As mentioned in the introduction, the argument that a nonmagnetic impurity and the three-sublattice partially disordered magnetic structure generate a domain state is illustrated in figure 1(a). A simple energy consideration of the spin configuration around an impurity ion reveals that a nonmagnetic impurity will be preferentially coincident with the disordered sublattice in order to minimize the loss of exchange energy. As a result, domains nucleated by site-random magnetic vacancies must generate domain walls running between them. Although the OPD structure in $\mathrm{CuFe_{1-x}Al_xO_2}$ is not the prototypical three-sublattice PD structure, there must be $\mathrm{Fe^{3+}}$ sites that play the role of a paramagnetic sublattice in a prototypical PD state. Hence, the nonmagnetic impurity must lock the phase of sinusoidal modulation of the OPD phase, and generate domain walls as illustrated in figure 1(b). The anisotropic spin correlation ($\kappa_c/\kappa_{ab} \sim 15.2$) is due to the two-dimensional character of the antiferromagnetic interaction in this system [10]. In order to minimize the loss of the strongest exchange energy within the triangular lattice plane, the phases of sinusoidal modulations on each plane are strongly affected by the configurations of nonmagnetic impurity ion on each plane. Consequently, the spin correlation along the c-axis is destroyed more easily, than that in the triangular lattice plane. In contrast, the spin correlation length along the c-axis is longer than that on the triangular lattice plane ($\kappa_c/\kappa_{ab} \sim 0.35$) in $\mathrm{CsCo_{0.83}Mg_{0.17}Br_3}$ [4] in which the exchange interaction along the c-axis is dominant.

The temperature dependences of A, B, κ_{ab} and κ_c in equation (1) are shown in figures 5(c)–(e). These parameters were obtained by MPD analysis with equation (1) for the scans along two directions (specifically, (a) and (b) in figure 4(e)). Below $T = 12.0$ K, the LSQ term is dominant ($A \gg B$), and κ_{ab} and κ_c are independent of temperature. Above $T = 12.0$ K, the LRZ term is dominant ($A \sim 0$), and κ_{ab} and κ_c rapidly increase with increasing temperature. According to the previous neutron scattering study [11], the LRZ term corresponds to critical scattering, and the LSQ term corresponds to the scattering from the domain state. Thus, the meaning of κ^{-1} is the thermal correlation length when the LRZ term is dominant, and is the geometrical correlation length of the domain structure when the LSQ term is dominant. In the present analysis, κ_{ab}^{-1} and κ_c^{-1} exhibit the typical temperature dependence of thermal correlation length above $T = 12.0$ K, while these are independent of temperature below $T = 12.0$ K due to the formation of the domain state. These results are consistent with those previous studies on the conventional random field effect in a diluted Ising antiferromagnet under an applied field [12, 13].

3. Conclusion

We performed neutron scattering measurements on a diluted TLA $\mathrm{CuFe_{1-x}Al_xO_2}$ ($x = 0.10$). The MPD analysis revealed that the scattering function of magnetic reflections of the sample with $x = 0.10$ is not described as a δ-function indicating the long-range ordering, but as the sum of an LRZ term and an LSQ term with anisotropic width. The Lorentzian-squared term dominating at low temperature indicates that the system breaks into a large number of microdomains. Taking account of the experimentally confirmed OPD magnetic structure in

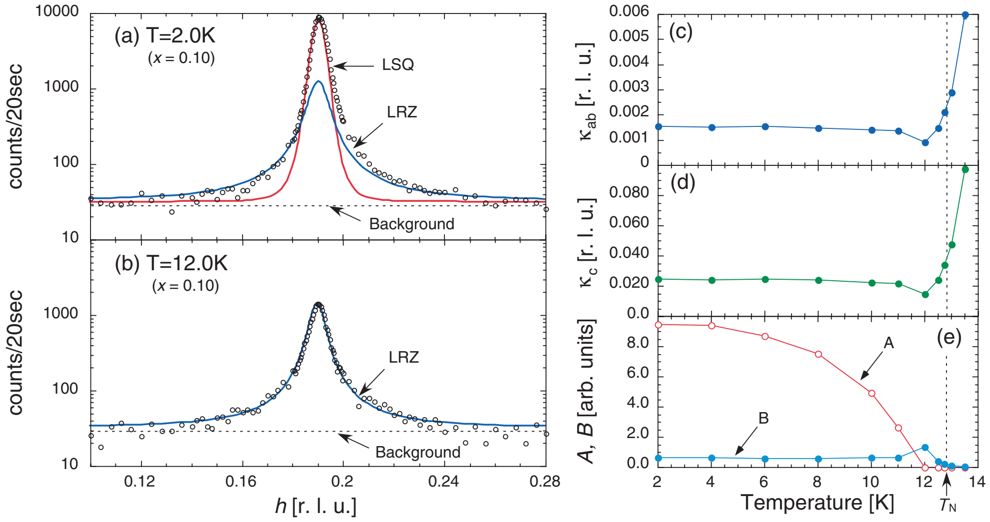

Figure 5. Typical scattering profiles of $(h, h, 1.5)$ reciprocal lattice scans at (a) $T = 2.0$ K and (b) $T = 12.0$ K. The solid lines indicate the contribution of the LRZ term and the LSQ term. At 12 K, the scattering profiles are purely LRZ. Temperature dependences of (c) κ_{ab}, (d) κ_c and (e) A, B in equation (1), obtained by MPD analysis. The dotted line and vertical arrow denote T_N determined by magnetic susceptibility measurements.

CuFe$_{1-x}$Al$_x$O$_2$ with $x = 0.10$, we conclude that the effective random field arises even at zero field, owing to the combination of site-random magnetic vacancies and the sinusoidal structure that is regarded as a PD structure in a wide sense. The anisotropic spin correlation ($\kappa_c/\kappa_{ab} \sim 15.2$) is due to the two-dimensional character of the antiferromagnetic interaction in this system [10]. While the previous study revealed the existence of a domain state in CsCo$_{0.83}$Mg$_{0.17}$Br$_3$ by detecting magnetic reflections specific to the spin configuration near the domain walls [4], our present study revealed the existence of a domain state in CuFe$_{1-x}$Al$_x$O$_2$ ($x = 0.10$) by determination of the functional form of the scattering function.

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