\[ S_i \cdot S_j \] on each bond. This phenomenon may be called ‘spin-driven’ bond order.

It is also known that the spin-lattice coupling effect also plays a crucial role in magnetic-field-induced phase transitions in Cr-spinel oxides, which exhibit 1/2-magnetization plateau phases under applied magnetic fields of up to 13.4 T. Previous theoretical studies have pointed out that the symmetry-lowering structural transitions result in bond-order states in which exchange interactions among the nearest neighbor bonds in a tetrahedron are enhanced or reduced reflecting the magnetic orderings, specifically the spin correlation \( \langle S_i \cdot S_j \rangle \) on each bond. This phenomenon may be called ‘spin-driven’ bond order.

In this paper, we report inelastic neutron scattering (INS) measurements on a triangular lattice antiferromagnet CuFeO\(_2\) (CFO), which is a typical example of geometrically frustrated spin systems, under applied magnetic fields of up to 13.4 T. We have observed spin-wave spectra in a magnetic field-induced 1/5-magnetization plateau phase, which appears above \( T \approx 12.5 \) T below \( T \approx 10 \) K.\[ N_1 \]

CFO has been extensively investigated as a geometrically frustrated magnet from 1990s.\[ N_1 \] The crystal structure of CFO is shown in the inset of Fig. (a); the magnetic Fe\(^{3+}\) ions are arranged in equilateral triangular lattice layers, which are separated by O\(^{2-}\)-magnetic Fe\(^{3+}\)-O\(^{2-}\) dumbbells. The Curie-Weiss temperature of this system has been estimated to be \( \Theta_{\text{CW}} \approx -100 \) K.\[ N_1 \] On the other hand, CFO undergoes a magnetic phase transition from the paramagnetic (PM) phase to an incommensurate collinear magnetic phase, which is referred to as the partially disordered (PD) phase, at \( T_{N1} = 14 \) K in zero magnetic field. The large difference between \( T_{N1} \) and \( |\Theta_{\text{CW}}| \) indicates the existence of the strong spin frustration in this system. The magnetic phase transition at \( T_{N1} \) is accompanied by a structural transition from the original trigonal structure to a monoclinic structure so that the geometrical frustration is partly relieved. With further decreasing temperature from \( T_{N1} \), the system enters a collinear four-sublattice (4SL) antiferromagnetic ground state at \( T_{N2} \approx 11.2 \) K. The spin arrangement in the 4SL phase is shown in Fig. (h). When a magnetic field is applied along the c axis at low temperatures, CFO exhibits successive magnetic phase transitions, as shown in the \( H-T \) magnetic phase diagram in Fig. (a). The first-field-induced phase is referred to as the ferro-...
electric incommensurate-magnetic (FE-ICM) phase. The magnetic structure in this phase is a distorted screw-type structure\textsuperscript{14,15} which breaks the inversion symmetry of the system and accounts for the ferroelectricity in this phase\textsuperscript{16} The second-field-induced phase is the 1/5-magnetization plateau phase. Figure 1(i) shows the spin arrangement on a triangular lattice layer in this phase.\textsuperscript{17} Because the magnetic unit cell has five spins on its basal plane, this phase has been referred to as the five sublattice (5SL) phase.

Interestingly, these magnetic-field-induced phase transitions are accompanied by distinct changes in crystal structure\textsuperscript{12,13,19} This indicates that the spin-lattice coupling effect plays an important role for the field-induced transitions in CFO.\textsuperscript{20} Terada et al. have explained the field-induced lattice deformations in terms of changes in Fe-O-Fe bonding angle.\textsuperscript{18,21} They have pointed out that the antiferromagnetic (AF) NN interaction is enhanced by increasing the bonding angle, and vice versa.\textsuperscript{21} As a result, positions of the Fe\textsuperscript{3+} and O\textsuperscript{2-} ions are shifted so as to lower the exchange energy in each of the magnetically ordered phases. Moreover, in CFO, an O\textsuperscript{2-} ion is surrounded by three Fe\textsuperscript{3+} ions, and thus a displacement of an O\textsuperscript{2-} ion can affect three Fe-O-Fe bonds. This situation can lead to a variety of bond-order states associated with the magnetic orderings.

Recently, we have identified the bond order in the 4SL phase.\textsuperscript{22} By means of INS measurements using a single crystal of CFO, we have revealed that the NN exchange interaction, $J_1$, splits into two interactions of $J_1^{(1)}$ and $J_1^{(2)}$; $J_1^{(1)}$ is a strong AF interaction connecting antiferromagnetically coupled NN spins and $J_1^{(2)}$ is a weak AF interaction connecting ferromagnetically coupled NN spins, as shown in Fig. 1(h). The atomic displacements associated with this bond order result in doubling of the unit cell along the [110] direction, which is consistent with the previous x-ray diffraction results.\textsuperscript{12,13,19} A similar bond order and resulting atomic displacements were also found in the FE-ICM phase (see Fig. 1(i) and Refs. 16, 10, 23, 24). On the other hand, in the 5SL phase, the changes in exchange interactions were not directly observed because of the difficulty of measuring the spin-wave spectra under high magnetic fields. In order to understand the role of the spin-lattice coupling effect in the field-induced transitions in this system, however, it is indispensible to determine the exchange interactions in the 5SL phase. In the present study, we have thus performed INS measure-
ments on CFO under applied magnetic fields of up to 13.4 T.

II. EXPERIMENT

The neutron scattering experiment was carried out using the chopper spectrometer LET at the ISIS spallation neutron source. The detector coverage used in this experiment was from −30° to 50°. We used a vertical field superconducting cryomagnet whose maximum field is 13.5 T. The vertical open-angle of the magnet is from −10° to 15°. A number of incident energies ($E_i$) were selected by the multi-$E_i$ method. In the present analysis, we mainly used data measured with $E_i = 3.6$ and 8.6 meV, for which the energy resolutions are estimated to be 0.049 and 0.17 meV, respectively. A single crystal of CFO was grown by the floating zone method and was cut into a plate shape with dimensions of 22, 5.0 and 3.7 mm for [001], [110] and [1¯10] direction, respectively. During the experiment, we applied uniaxial pressure of ∼5 MPa on the [110] surfaces of the sample using a duralumin clamp. This is because CFO has three magnetic domains in the magnetically ordered phases owing to the threefold rotational symmetry about the $c$ axis, and volume fractions of the three domains can be controlled by a small uniaxial pressure applied in the triangular lattice plane. The sample with the uniaxial-pressure clamp was mounted in the cryomagnet so that the $c$ axis is parallel to the magnetic field. By measuring elastic magnetic Bragg reflections in the 5SL phase, we found that the magnetic domain having the magnetic modulation vector parallel to the [110] direction has the volume fraction of 64%, and dominates over the other two domains (14% and 22%). The huge combined data set were handled by the HORACE software of ISIS.

III. RESULTS AND DISCUSSIONS

Figures (I) c), (I) e), and (I) f) show the INS spectra measured with $E_i = 8.6$ meV, in the 4SL ($H = 0$ T), FE-ICM (10 T), and 5SL (13.4 T) phases, respectively. These spectra were measured by setting the angle between the (110) direction of the crystal and the direction of the incident neutrons to $68° \sim 73°$, as shown in Fig. (I) b). The observed data were projected on to the ($-h, 1 - h, 1/2$) line, on which magnetic Bragg reflections appear in all the three phases. In zero magnetic field, we found a distinct spin-wave branch lying in the energy range of $E = 2 \sim 3.5$ meV, as shown in Fig. (I) c). This corresponds to the higher energy branch observed in the previous INS measurements in the 4SL phase. This spin-wave spectrum also indicates that the inelastic scattering signals from the two minority domains were negligible in the present experiment, because the observed spectrum is almost the same as that in the nearly ‘single-domain’ 4SL phase in Ref. 27. In Fig. (I) d), we show a calculated INS spectrum along the ($-h, 1 - h, 1/2$) line in the single-domain 4SL phase, which also qualitatively agrees with the present result. In the FE-ICM phase, the excitation spectrum became rather diffusive, as shown in Fig. (I) e). This is characteristic of the incommensurate and non-collinear magnetic ordering in the FE-ICM phase, and is similar to the magnetic excitation spectra observed in the FE-ICM phase of CuFe$_1-x$Ga$_x$O$_2$ ($x = 0.035$). In the 5SL phase, we found that distinct spin-wave branches were retrieved, as shown in Fig. (I) f).

In Fig. (I) a), we show the spin-wave excitation spectrum along the ($h, h, 0$) line measured with $E_i = 3.6$ meV at $H = 13.4$ T and $T = 1.7$ K. The observed spectrum seems to be consistent with a theoretical prediction by Haraldsen et al, in which the spin-wave excitations under applied magnetic fields were calculated using Monte Carlo simulations and variational method for two dimensional triangular lattice. However, in CFO, exchange interactions between adjacent triangular lattice layers are quite important as was pointed out in the previous theoretical study by Fishman et al. In the present study, we have thus employed the three dimensional magnetic structure of the 5SL phase to calculate the spin-wave spectra.

Figure (I) c) shows the magnetic structure in the 5SL phase. The magnetic unit cell in the 5SL phase contains two triangular lattice layers, each of which has five spins, and therefore, the 5SL phase actually has ten sublattices. To calculate the spin-wave spectrum in the 5SL phase, we have employed a conventional linear spin-
gyromagnetic ratio, $g$, is a uniaxial anisotropy. The applied magnetic field and the Bohr magneton, respectively. Similarly to our previous work on the spin-wave excitations in the 4SL phase, nearest, second, and third neighbor exchange interactions within the triangular lattice layers ($J_1$, $J_2$ and $J_3$), and an exchange interaction between the adjacent layers ($J_z$) are employed in Eq. (1). As for $J_1$, we have introduced the spin-lattice coupling effect in the same spirit as the previous works on the 4SL and FE-ICM phases. The displacements of each O$^{2-}$ ion are assumed from the spin arrangements of the three neighboring Fe$^{3+}$ ions. Hereby, $J_1$ splits into four different NN interactions, $J_1^{(1)}$, $J_1^{(2)}$, $J_1^{(3)}$ and $J_1^{(4)}$ as shown in Fig. 2(b)).

The procedure of the spin-wave calculation for the 5SL phase is essentially the same as those in the previous works on the 4SL phase. We have applied a Holstein-Primakoff $1/S$ expansion about the classical limit to the Hamiltonian of Eq. (1). We express the spins, $S_i$, on each sublattice using Fourier transformed boson operators. By solving the Heisenberg equation of motion for the boson operators, the spin-wave dispersion relations and the INS cross section were calculated. To obtain the resolution-convoluted neutron scattering spectra, the experimental resolutions for $E_i = 3.6$ and $8.6$ meV were taken into account. The Hamiltonian parameters were adjusted so that the calculations reproduce the observed data, and finally, the best fit was obtained for the parameters shown in Table 1. The calculated spectra for the $(h, h, 0)$ and $(-h, -h, 1/2)$ lines with $E_i = 3.6$ and $8.6$ meV are shown in Fig. 2(b) and 2(g), respectively.

Comparing the parameters for the 5SL phase with those in the 4SL and FE-ICM phases, we have found that $J_1^{(1)}$ and $J_1^{(3)}$ are nearly common in all the three phases. This is consistent with the fact that the spin arrangements and the oxygen displacements associated with $J_1^{(1)}$ and $J_1^{(2)}$ in the 5SL phase are the same as those in the 4SL phase, as shown in Figs. 2(b) and 2(g)). As for $J_1^{(3)}$ and $J_1^{(4)}$, their magnitudes are found to be smaller than that of $J_1^{(1)}$. This is also reasonable because they connect two ferromagnetically coupled spins. In addition, the exchange paths of $J_1^{(3)}$ and $J_1^{(4)}$ include the O$^{2-}$ ions surrounded by three up spins, and the Fe-O-Fe bonding angles between the three up spins are expected to remain the same as each other. Therefore, the 'reductions' in magnitudes of $J_1^{(3)}$ and $J_1^{(4)}$ are expected to be smaller than that of $J_1^{(2)}$. We have found that the experimentally determined parameters are in good agreement with this scenario. This is the direct evidence for the spin-driven bond order in the 5SL phase. Moreover, the present results have also demonstrated that the field-induced phase transition from the FE-ICM phase to the 5SL phase is accompanied by the bond-order transition.

In summary, we have investigated the spin-wave excitations and the spin-lattice coupling in the 5SL phase of CFO, by means of the INS measurements under applied field of 13.4 T. Comparing the observed spin-wave spectra with the calculations including the spin-lattice coupling effects for the NN exchange interactions, we have revealed that CFO exhibits the spin-driven bond order in the 5SL phase. It should be emphasized that we have constructed the model of the bond order by taking into account the fact that an O$^{2-}$ ion belongs to three Fe-O-Fe bonds in CFO. The present results suggest the importance of topology of exchange-interactions paths for understanding the exotic spin-lattice coupling phenomena, specifically spin-driven bond order, in geometrically frustrated magnets.

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### Table 1: The Hamiltonian parameters in the 4SL phase (from Ref. 22) and the FE-ICM phase (from Ref. 23) and the 5SL phase (in meV).

| magnetic phase | sample           | $J_1^{(1)}$ | $J_1^{(2)}$ | $J_1^{(3)}$ | $J_1^{(4)}$ | $J_2$ | $J_3$ | $J_z$ | $D$ | Ref. |
|---------------|-----------------|-------------|-------------|-------------|-------------|-------|-------|-------|-----|-----|
| 4SL ($H = 0$ T) | CuFeO$_2$       | -0.176      | -0.060      | -           | -0.041      | -0.142| -0.071| 0.064 |     | 22  |
| FE-ICM ($H = 0$ T) | CuFe$_{1-x}$Ga$_x$O$_2$ ($x = 0.035$) | -0.169 | -0.066 | -           | -0.070      | -0.098| -0.070| 0.014 |     | 23  |
| 5SL ($H = 13.4$ T) | CuFeO$_2$       | -0.18       | -0.06       | -0.10       | -0.14       | -0.06  | -0.15 | 0.064 |     | This work |
