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Chiral Soliton Lattice Formation in Monoaxial Helimagnet Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$

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Helical magnetic structures and their responses to external magnetic fields in Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ with a chiral crystal structure of the space group $R32$ have been investigated by resonant X-ray diffraction. It is shown that the chiral chirality is reflected in the helicity of the magnetic structure by a one-to-one relationship, indicating that an antisymmetric exchange interaction mediated via the conduction electrons exists. When a magnetic field is applied perpendicular to the helical axis (c axis), the second-harmonic peak of $(0, 0, 2q)$ develops with increasing field. The third-harmonic peak of $(0, 0, 3q)$ has also been observed for the $x=0.06$ sample. This result provides strong evidence for the formation of a chiral magnetic soliton lattice state, a periodic array of chiral twist of spins, which has been suggested by the characteristic magnetization curve. The helical ordering of magnetic octupole moments accompanying the magnetic dipole order has also been detected.

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1. Introduction

Chirality is one of the most fundamental elements of symmetry in nature. It plays an important role in various phenomena ranging from biological functions to the physical properties of inorganic substances. In magnetic materials lacking the local inversion center for the two-ion exchange interaction, a spiral magnetic order is often stabilized by the antisymmetric Dzyaloshinskii–Moriya (DM) interaction, giving rise to distinct physical properties. The simultaneous appearance of electric polarization with the spiral magnetic order is a typical manifestation of such effects. In chiral magnetic materials without both inversion and mirror symmetries, a helical magnetic order with a fixed sense of spin rotation can be stabilized. When a magnetic field is applied to such a system, a characteristic arrangement of the topological spin structure is often stabilized through competition between the Zeeman energy and the twisting force from the DM interaction. In cubic B20-type compounds such as MnSi with the space group $P2_13$, for example, the helical spin structure transforms into a hexagonal lattice condensate of magnetic skyrmions. The skyrmion state is a long-range pattern of twisted spin arrangements realized in magnetic fields, which become more stable in two-dimensional configurations in thin films.

In monoaxial chiral helimagnets such as CrNb$_2$S$_6$ (space group $P6_322$), when a magnetic field is applied perpendicular to the helical axis, the helical ground state transforms into a periodic array of incommensurate chiral spin twists, which separates the ferromagnetically aligned commensurate region. This is a nonlinear order of topological spin structure and is called a chiral soliton lattice (CSL). These materials are expected to provide a new functionality that is operated by tuning the number of skyrmions or solitons in the sample.

In the present paper, we report on the new monoaxial chiral helimagnet system of Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$, in which the CSL state is expected to be realized. The rare-earth compound YbNi$_3$Al$_9$ has a chiral crystal structure with the space group $R32$ (No. 155), which lacks both space inversion and mirror symmetries. The main block of the crystal structure is shown in Fig. 1 (drawn with VESTA). The physical properties of YbNi$_3$Al$_9$ have been studied as those of an Yb-based heavy-fermion compound. Yb ions form a two-dimensional honeycomb lattice in the c plane, which is separated by $c/3=9.121$ Å from the neighbouring Yb layer by five Al and two Ni layers. Since this is much larger than the nearest-neighbor distance of $a/\sqrt{3}=4.199$ Å within a layer, the relation between the two-dimensionality and the heavy-fermion state has also been of interest. The detailed study of this compound from the viewpoint of its chirality started with the discovery of a characteristic magnetization process that is reminiscent of a CSL state. By substituting Ni with Cu, it was discovered that the $M(H)$ curve behaves similarly to that of CrNb$_2$S$_6$, in which the CSL state has clearly been identified.

The exchange interaction in metallic YbNi$_3$Al$_9$ is considered to be of the Ruderman–Kittel–Kasuya–Yosida (RKKY)
type. Since the crystal is chiral, there must be some antisymmetric contribution to the RKKY mechanism in the form of $D_{ij} \times S_i \times S_j$, which is generally called the DM interaction.\(^{(2,3)}\) Since the microscopic mechanism given by Moriya is based on the superexchange interaction in insulators, the mechanism of the RKKY-type DM interaction is an important subject to be studied. The question is how the crystal chirality is transferred to the spin system of $f$ electrons and conduction electrons.

YbNi$_3$Al$_9$ is a metallic compound which orders at $T_N = 3.5$ K. It is reported that the magnetic structure of YbNi$_3$Al$_9$ is helical with propagation vector $(0, 0, -0.8)$ and the moments lying in the $c$ plane. By applying a magnetic field perpendicular to the $c$ axis, the helimagnetic order jumps to a ferromagnetic state at a critical field of $H_c = 1$ kOe.\(^{(22,23)}\) By substituting Ni with Cu, both $T_N$ and $H_c$ increase. An anomalous $M(H)$ curve reminiscent of a CSL state is observed for $x=0.06$.\(^{(26)}\) However, the relationship between the crystal chirality and the magnetic helicity, the Cu concentration dependence of the helimagnetic structure, and detailed dependences on the temperature and magnetic field have not yet been studied. The aim of the present study is to clarify these properties experimentally by using resonant X-ray diffraction (RXD).

Experimentally, how to observe a chiral state has long been a subject of interest. Recent progress in the transmission electron microscopy method has made it possible to capture real-space images of skyrmions and CSLs.\(^{(5–8,12)}\) It is also of fundamental importance to capture the spatially averaged structure as a Fourier transform of a real-space image by neutron and X-ray diffraction methods. Polarized neutron diffraction is a powerful method for observing the helical magnetic structure and for determining the helicity.\(^{(28,29)}\) One drawback of this method is that it is difficult to perform an experiment in magnetic fields because the neutron spin state is affected by the magnetic field. X-ray diffraction, on the other hand, can be used both at zero field and in magnetic fields without any difficulties. The helicity of a magnetic spiral can be studied by using circularly polarized X-rays.\(^{(30–32)}\) By utilizing resonance at an absorption edge of the magnetic element, the scattering cross section is enhanced, making it possible to detect signals from an ordered structure more efficiently.\(^{(33)}\) The magnetic skyrmion state in a chiral magnet has been detected by RXD.\(^{(34)}\) Furthermore, resonant scattering has sensitivity to higher-order anisotropy (multipole moments) of both magnetic and nonmagnetic nature.\(^{(35–37)}\) This sensitivity can sometimes be applied to determine crystal chirality by using a circularly polarized beam.\(^{(38–40)}\)

This paper is organized as follows. In Sect. 2, the experimental procedure is described, including the details of the circularly polarized X-ray beam. The experimental results and the analyses are described in Sect. 3. First, in Sect. 3.1, the one-to-one relationship between the crystal chirality and the helimagnetic structure is described. Comparison of the experimental results with the helimagnetic structure model is performed in Sect. 3.2. In Sects. 3.3 and 3.4, the temperature and magnetic field dependences of the helimagnetic order are presented. The resonant nature of the signal is described in Sect. 3.5. We show that the $E2$ resonance involves a signal from a magnetic octupole, which accompanies the helical order of the magnetic dipole. In Sect. 4, we discuss the origin of the octupole moment, the temperature-dependent pitch of the helical structure, and the possibility of the CSL state in Yb(Ni$_{1–x}$Cu$_x$)$_3$Al$_9$. The present study is summarized in Sect. 5.

2. Experiment

Single crystals of Yb(Ni$_{1–x}$Cu$_x$)$_3$Al$_9$ were prepared by an Al-flux method following the procedure described in the literature.\(^{(26)}\) The starting composition $x$ of Cu sealed in a quartz ampoule was set to five times the target composition $x$. The actual Cu concentration $x$ in the obtained crystal was verified by electron probe microanalysis and was confirmed to follow the relation $x \sim 0.2x'$, as reported previously.\(^{(26)}\) We also verified the sample quality by magnetic susceptibility, magnetization, and electrical resistivity measurements and obtained consistent results with those reported in the literature.\(^{(22,26)}\)

RXD experiments were performed at BL22XU at SPring-8. The $c$-plane surfaces of the samples were mirror-polished, and the samples were mounted in a vertical-field 8 T superconducting cryomagnet equipped with a $^3$He cryostat insert so that the $c$ axis was perpendicular to the magnetic field and coincided with the scattering vector $k' = k \parallel \hat{Z}$. The scattering geometry is shown in Fig. 2. The incident X-ray energy was tuned to the $L_3$ edge of Yb.

We used a diamond phase retarder system to tune the horizontally polarized incident beam to a circularly polarized...
state.\textsuperscript{41} By rotating the angle of the diamond phase plate $\theta_{PR}$ about the 220 Bragg angle $\theta_B$, where the scattering plane is tilted by 45$^\circ$, a phase difference arises between the $\sigma$ and $\pi$ components of the transmitted beam. The phase difference is approximately proportional to $1/(\theta_{PR} - \theta_B)$. This allows us to tune the incident linear polarization to right-handed circular polarization (RCP) and left-handed circular polarization (LCP) by changing $\Delta\theta_{PR} = \theta_{PR} - \theta_B$. The polarization state of the incident beam as a function of $\Delta\theta_{PR}$ is shown in Fig. 2 using the Stokes parameters $P_2 (+1$ for RCP and $-1$ for LCP) and $P_3 (+1$ for $\sigma$ and $-1$ for $\pi$ linear polarization).\textsuperscript{42} In the horizontal scattering plane configuration in the present experiment, the incident linear polarization is $\pi$ when $\Delta\theta_{PR}$ is large. $P_1 (+1$ for 45$^\circ$ and $-1$ for $-45^\circ$ linear polarization) is zero in the present setup.

We define RCP as $\varepsilon_R = (\varepsilon_{1\sigma} + i\varepsilon_{1\pi})e^{i(kr-\omega t)}$ and LCP as $\varepsilon_L = (\varepsilon_{1\sigma} - i\varepsilon_{1\pi})e^{i(kr-\omega t)}$. We verified the helicity of the incident photon after transmitting the phase retarder by measuring the resonant scattering intensity of a forbidden reflection from $P6_3\overline{2}2$-type CsCuCl$_3$, where the intensity ratio between RCP and LCP X-rays depends on the reflection index and is exactly determined by the $P6_3\overline{2}2$ space group.\textsuperscript{38}

The crystal chirality of the sample was determined by using a laboratory-based X-ray diffraction system (Bruker APEX-II) and it was also verified in the RXD experiment at the beamline. In the former method, using a Mo $K_\alpha$ X-ray beam, the Flack parameter was deduced by analyzing the intensities of many reflections, which resulted in either 0 (R) or 1 (L). Our definition of the crystal chirality is shown in Fig. 1. Then, R and L samples were selected for each Cu concentration for use with the RXD experiment. At the beamline, the energy dependences of the (1,1,24) and (1, 1, 24) fundamental Bragg peak intensities were measured around the absorption edge of Yb, which is shown in Fig. A.1 in Appendix A. The spectrum exhibited a contrasting energy dependence at the edge depending on the chirality of the crystal. It was consistent with the calculated spectrum assuming the predetermined crystal chirality, confirming that the irradiated spot of the sample in the RXD experiment has exactly the same chirality as that determined in the laboratory X-ray diffraction. It was also confirmed at the beamline that the (1,0,3n + 1) reflections are allowed and the (1, 0, 3n) and (1, 0, 3n–1) reflections are forbidden as shown in Fig. A.2. This fact guarantees the threefold symmetry of the sample about the $c$ axis. If the forbidden reflections were observed, it would have meant that the [1 1 0] axis was mixed with the $a$ axis due to the stacking fault of 60$^\circ$.

3. Results and Analysis

3.1 Crystal chirality and the helical magnetic structure

First, we demonstrate that the crystal chirality and the helicity of the helical magnetic structure have a one-to-one relationship. A typical example is shown in Fig. 3 for the R and L crystals with $x=0.06$. The reciprocal scans along (0, 0, $L$) around the (0, 0, 27) fundamental Bragg peak using RCP and LCP X-rays exhibit opposite behavior for the R and L crystals as well as those for the (0, 0, 27 – $q$) and (0, 0, 27 + $q$) peaks. In the R(L) crystal at (0, 0, 27 – $q$), the intensity is strong (weak) for LCP and weak (strong) for RCP. This relation is reversed at (0, 0, 27 + $q$). The X-ray energy of 8.944 keV corresponds to the $E_1$ (2$p$ ↔ 5$d$) resonance. The energy dependence of the intensity demonstrating the resonance feature will be shown later. In Fig. 3, the peaks are observed at an incommensurate wave vector of $q$=0.445 for the L crystal and $q$=0.425 for the R crystal. This difference in the $q$ value is due to the difference in the sample quality, i.e., a slight difference in the Cu concentration, and is unrelated to the chirality.

More detailed information can be extracted from the $\Delta\theta_{PR}$ scans, which are shown in Fig. 4. This figure shows not only the intensity relations for the RCP and LCP X-rays at (0, 0, 27 ± $q$) but also the overall feature of the incident polarization dependence as a function of $\Delta\theta_{PR}$. The incident polarization state varies with $\Delta\theta_{PR}$ as shown in the inset of Fig. 2. We again observe from this measurement that the crystal chirality and the helicity of the magnetic structure have a one-to-one relationship. In addition, the relationship does not change with the Cu concentration between $x=0$ and $x=0.06$. The solid lines in the figures represent the calculated curves expected from the helical magnetic structure with the moments lying in the $c$ plane and propagating along the $c$ axis. Next, we describe the analysis of the above experimental results.

3.2 Magnetic structure

There are two Yb atoms for the 6c site of the R32 space group: Yb-1 at $d_1 = (0, 0, z)$ and Yb-2 at $d_2 = (0, 0, z)$, where $z=0.167\sim 1/6$. In the present single-$q$ magnetic structure, the magnetic moments $\mu_{1,j}$ and $\mu_{2,j}$ of Yb-1 and Yb-2, respectively, on the $j$th lattice point at $r_j = (n_1, n_2, n_3)$, (n$_1$+2/3, n$_2$+1/3, n$_3$+1/3), and (n$_1$+1/3, n$_2$+2/3, n$_3$+2/3), where $n_1$, $n_2$, and $n_3$ are integers, are generally expressed as

$$\mu_{1,j} = m_1 e^{i q r_j} + m_2 e^{-i q r_j},$$

and

$$\mu_{2,j} = m_2 e^{i q r_j} + m_1 e^{-i q r_j},$$

where $m_1$ and $m_2$ are the magnetic amplitude vectors of Yb-1 and Yb-2, respectively. In the present case of Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_6$, since the moments are expected to be ordered within the $c$ plane, $m_1$ and $m_2$ can generally be written...
Table I. Relation among the phase $\varphi$, Fourier component $m$, scattering vector $Q$, magnetic structure factor $Z_{\text{dip}}^{(1)}$, sign of $C_2$, and crystal chirality.

<table>
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<tr>
<th>$\varphi$</th>
<th>$m$</th>
<th>$Q$</th>
<th>$Z_{\text{dip}}^{(1)}$</th>
<th>$C_2$</th>
<th>Crystal</th>
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<tr>
<td>$\pi/2$</td>
<td>$\hat{x} + i\hat{y}$</td>
<td>$(0, 0, 3n \pm q)$</td>
<td>$(1, \hat{a}, 0)$</td>
<td>$\mp$</td>
<td>R</td>
</tr>
<tr>
<td>$-\pi/2$</td>
<td>$\hat{x} - i\hat{y}$</td>
<td>$(0, 0, 3n \pm q)$</td>
<td>$(1, \hat{a}, 0)$</td>
<td>$\pm$</td>
<td>L</td>
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Fig. 4. (Color online) Incident polarization ($\Delta \theta_{\text{pr}}$) dependence of the intensities at $(0, 0, 27 \pm q)$ for $x=0$ and $x=0.06$ crystals with right and left chirality. The background has been subtracted. Solid lines are the calculations described in the text.

as $m_1 = m_1(\hat{x} + e^{i\varphi} \hat{y})$ and $m_2 = m_2 e^{i\varphi}(\hat{x} + e^{i\varphi} \hat{y})$, where $\hat{x}$ and $\hat{y}$ represent the unit vectors along the $x$ and $y$ axis, respectively, which are taken perpendicular to the $c$ axis. The irreducible representation of the $m$-vector for $q = (0, 0, q)$, where $q$ is an incommensurate value, is written as $\hat{x} \pm i\hat{y}$. Therefore, $\varphi$ is either $\pi/2$ or $-\pi/2$. The phase difference between $\mu_{1,j}$ and $\mu_{2,j}$ is represented by $\delta$. The above expression for the magnetic structure can be reduced to

$$\mu_{1,j} = m_1 [\hat{x} \cos q \cdot r_j + \hat{y} \cos (q \cdot r_j + \varphi)] ,$$

$$\mu_{2,j} = m_2 [\hat{x} \cos (q \cdot r_j + \delta) + \hat{y} \cos (q \cdot r_j + \varphi + \delta)] .$$

(2a)

(2b)

Since $\varphi = \pm\pi/2$, the above expression describes a perfect helical structure with helicity $\pm 1$ in which the adjacent Yb-1 (or Yb-2) moments on the neighboring layers along the $c$ axis make a fixed angle of $2\pi q/3$. On the other hand, the angle between the Yb-1 and Yb-2 moments within a layer, the former at $(0, 0, z)$ and the latter at $(2/3, 1/3, 1/3) + (0, 0, z)$ in Fig. 1, is described by the parameter $\delta$. This angle is reported to be $20.5^\circ$ for $x=0.43$. Note that our experimental results presented in this paper, which were collected only along the $(0, 0, L)$ line, are not sufficiently sensitive to determine the $\delta$ value.

The E1 resonant scattering amplitude from the magnetic dipole order is proportional to $(i\hat{e} \times \hat{e}) \cdot Z_{\text{dip}}^{(1)}$,

$$Z_{\text{dip}}^{(1)} = \sum_{jd} \mu_{jd} e^{-iQ \cdot (r_j + d)} ,$$

(3)

represents the magnetic structure factor at $Q = k' - k$. At $Q = (0, 0, 3n \pm q)$, $Z_{\text{dip}}^{(1)} = (1, \hat{a}, 0)$ when $\varphi = \pi/2$, and $Z_{\text{dip}}^{(1)} = (1, -\hat{a}, 0)$ when $\varphi = -\pi/2$. The scattering amplitude matrix, as defined in Appendix B, for the magnetic structure factor $(1, \pm\hat{a}, 0)$ is expressed as

$$\tilde{F}_{E1} = \begin{pmatrix} 0 & i\cos \theta \\ -i\cos \theta & \mp \sin 2\theta \end{pmatrix} .$$

(4)

Then, following the method described in Appendix B, we can calculate the coefficients $C_n$ ($n=0$–3) defined in Eq. (B-5), which express the scattering cross sections. The parameters $C_2/C_0$ and $C_3/C_0$, as normalized by the total cross section $C_0$, correspond to the intensity terms proportional to $P_2$ and $P_3$, respectively. When $C_3 > 0$, the intensity is stronger for the RCP ($\Delta \theta_{\text{pr}} > 0$). For $Q = (0, 0, 27 \pm q)$, when $\varphi = \pi/2$, $C_2/C_0 = 0.04$ and $C_3/C_0 = -0.47$ are obtained. The observed intensity is a superposition of the $P_2$ and $P_3$ terms. The experimental data in Fig. 4 show that at $Q = (0, 0, 27 + q)$, $C_2 > 0$ in the R-crystal and $C_2 < 0$ in the L-crystal. This means that $\varphi = \pi/2$ ($m = \hat{x} + i\hat{y}$) in the R-crystal and $\varphi = -\pi/2$ ($m = \hat{x} - i\hat{y}$) in the L-crystal. These relations are summarized in Table I. The magnetic structure is shown in Fig. 5 for $x=0.06$. The Yb-2 moment is not shown because the relative angle with the Yb-1 moment is unknown. The solid lines in Fig. 4 are the calculations using the $C_2/C_0$ and $C_3/C_0$ values calculated above, which agree well with the experimental data.

3.3 Temperature dependence

Figure 6 shows the $(0, 0, L)$ peak profile for $x=0$ (L) and $x=0.06$ (L) samples. With increasing $T$, the intensity decreases and vanishes at $T_N$, indicating that the resonant signal is of magnetic origin. In addition, the peak position shifts with the temperature. It is also noteworthy that the direction of the peak shift for $x=0.06$ is opposite to that for $x=0$. It depends on the Cu concentration $x$ but does not depend on the chirality of the crystal.

The parameters obtained from the $(0, 0, L)$ scans are summarized in Fig. 7. For $x=0$, the $q$ value decreases with decreasing $T$ and saturates at $\sim 0.818$ at the lowest temperature, indicating that the helical structure is incommensurate with the lattice. The $T$ dependence of the $q$ value becomes weak for $x=0.02$. Surprisingly, at $x=0.04$, the direction of the $T$ dependence is reversed and the $q$ value increases with decreases.
In addition, the shift of the $q$ value mentioned above, regardless of its direction, is almost proportional to the intensity, which reflects the development of the ordered moment. This suggests that the $q$-shift is associated with the magnitude of the ordered moment. In Fig. 7(f), we show the $x$ dependence of the $q$ value and the pitch $L_0 = c/q$ at the lowest temperature. $L_0$ should be compared with the interlayer distance of $c/3 \approx 9.1$ Å. The angle between the moments on neighboring layers is calculated as $2\pi q/3$, i.e., 98.2, 74.0, 66.4, and 53.4° for $x=0$, 0.02, 0.04, and 0.06, respectively, at the lowest temperature.

### 3.4 Magnetic field dependence

Figure 8(a) shows the magnetic field dependence of the peak profile of $(0, 0, 21 - q)$ for the $x=0.06$ (L) sample, measured at the $E2$ (2$p \leftrightarrow 4f$) resonance energy of 8.934 keV, where the signal-to-noise ratio was much higher than that at the $E1$ resonance. The energy dependence of the resonant signal will be shown later. We used the RCP photon with stronger scattering intensity for the L-crystal than the LCP photon. The result for the second-harmonic peak measured at $(0, 0, 21 - 2q)$ is shown in Fig. 8(b). With increasing $H$, the peak position shifts to the fundamental Bragg peak at $(0, 0, 21)$ and the intensity of the first-harmonic $(q)$ peak gradually decreases. On the other hand, the intensity of the second-harmonic $(2q)$ peak, which does not exist at zero field, gradually increases with increasing $H$.

The magnetic field dependence of the $q$ values and the integrated intensities of the $q$ and $2q$ peaks for $x=0.02$, 0.04, and 0.06 are summarized in Fig. 9. Although all these measurements were performed using the L-crystals, the results do not depend on the crystal chirality. For all the Cu concentrations, it is commonly observed that the $q$ value decreases with increasing $H$, which becomes more rapid at higher fields on approaching the critical field $H_c$. Note that $q$ does not decrease.

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Fig. 6. (Color online) Temperature dependence of the peak profile for $x=0$ (L) and $x=0.06$ (L).

Fig. 7. (Color online) (a)-(d) Temperature dependence of the $q$ value of the propagation vector. The vertical dashed line represents $T_N$. (e) Temperature dependence of the normalized intensity. (f) Cu concentration dependence of the $q$ value (closed circles) and the pitch $L_0 = c/q$ (open circles) at the lowest temperature.

Fig. 8. (Color online) Magnetic field dependence of the peak profile for $x=0.06$ measured with the RCP photon at the $E2$ resonance energy. (a) First harmonic peak at $(0, 0, 21 - q)$. (b) Second harmonic peak at $(0, 0, 21 - 2q)$. The field is applied perpendicular to the $c$ axis ($b^*$).
continuously to zero but jumps to zero at $H_c$. The integrated intensity of the $q$ peak gradually decreases with increasing $H$ and also jumps to zero at $H_c$. These results show that the transition at $H_c$ is of first-order. It is also a common characteristic that the $2q$ peak is gradually induced with increasing $H$. This is observed even for the $x=0.02$ sample with $\mu_0H_c=3$ kG.

Another noteworthy result is the locking-in behavior of the helimagnetic propagation vector at $q=0.375=3/8$ between 9 and 9.5 kG for $x=0.06$. As observed in Fig. 8, the peak position does not change in this field region. The $2q$ peak is also fixed at $2q=3/4$. This result shows that some coupling exists between the helimagnetic structure and the lattice, although the magnetic anisotropy in the $c$ plane is considered to be very small. There is no hysteresis in this behavior, which can be observed in both field-increasing and -decreasing processes. It is also interesting that the lock-in does not seem to exist at $q=3/7=0.4286$ at around 5 kG. This suggests that the lock-in is more associated with the $2q$ peak, which develops at high fields, than the $q$ peak existing from zero field to high fields.

At 9.5 kG, slightly below the critical field of 10 kG for the ferromagnetic state in the $x=0.06$ (L) sample, we searched for more higher-order harmonics and successfully detected the third-harmonic peak. The result is shown in Fig. 10. For all the harmonics, the scattering intensity for the RCP photon is stronger than that for the LCP photon, indicating that the magnetic helicity of the modulated structure giving the higher-harmonic is the same as that of the original helical structure of the first harmonic. The fourth-harmonic peak was too weak to be recognized above the background. The integrated intensities of the $2q$ and $3q$ peaks are approximately 6 and 50 times weaker, respectively, than that of the $q$ peak.

The $H$ dependence of the $q$ value directly shows that the pitch of the helimagnetic structure increases with increasing $H$. In addition, the appearance of the higher-harmonic peaks shows that some additional structure is superimposed with increasing $H$. It is noteworthy that the $H$ dependence of the $q$ and $2q$ peak intensities shown in Fig. 9 is very similar to the calculation for the chiral sine-Gordon model (see Fig. 25 of Ref. 10 or Fig. 13 of Ref. 11). This result, as well as the $H$ dependence of $q$ which is associated with $L_0/L_{CSL}$ (Fig. 13 of Ref. 10 or Fig. 38 of Ref. 11), strongly indicates that a CSL state is formed in Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_2$, especially for $x=0.06$.

### 3.5 Energy spectrum

Figure 11 shows the energy dependence of the $(0, 0, 27 – q)$ peak at 0 kG and the $(0, 0, 27 – 2q)$ peak at 9 kG measured for $x=0.06$ (L). The two resonant peaks are well separated at 8.934 and 8.944 keV. The former can be assigned to the $E2$ resonance ($2p \leftrightarrow 4f$) peak and the latter to the $E1$ resonance ($2p \leftrightarrow 5d$) peak. In the tail on the lower-energy side of the $(0, 0, 27 – q)$ peak we can see weak nonresonant magnetic scattering. The energy dependence for the second-harmonic peak also exhibits resonances at the $E2$ and $E1$ energies. No nonresonant signal was observed. This shows that the resonant signal of the second harmonic can be ascribed to the helimagnetic order itself and not to a possible lattice deformation induced by the magnetic order. These features of the energy dependence were commonly observed for other Cu concentrations.

### 3.6 Contribution of magnetic octupole to the $E2$ resonance

Figure 12 shows the $\Delta \theta_{PR}$ dependence of the $(0, 0, 27 – q)$ peak intensity at zero field and the $(0, 0, 27 – 2q)$ peak intensity at 9.9 kG at the $E2$ resonance energy. We notice that the $\Delta \theta_{PR}$ dependence appears to be different from that in Fig. 4 for the $E1$ resonance. The $E2$ intensity is strongly enhanced when $\Delta \theta_{PR}$ is tuned to the LCP or RCP position. The result that the two $\Delta \theta_{PR}$ dependences are very similar shows that the structure factors for the $q$ and $2q$ peaks are almost the same. By fitting these $\Delta \theta_{PR}$ dependences using Eq. (B.5), we obtain three parameters, $C_0$, $C_2$, and $C_3$. The parameters obtained for various $Q$ vectors for the first harmonic peak from $(0, 0, 6 \pm q)$ to $(0, 0, 30 \pm q)$ for the $x=0.06$ (R) sample are shown in Fig. 13. The parameters $C_2$ and $C_3$ are normalized by $C_0$. Note that the sign of $C_2$ in Fig. 13 is opposite to the one deduced from Fig. 12 because the crystal chirality is opposite. With respect to the $E1$ resonance, the $Q$-dependence data in Fig. 13(a) can be well reproduced by the scattering amplitude.
of the magnetic dipole, \(i (\mathbf{e} \times \mathbf{x}) \cdot \mathbf{Z}_{\text{dip}}^{(1)}\), as explained in §3.2. The calculated \(Q\)-dependences of the parameters are shown by the lines in Fig. 13(a).

The problem is that the results of the E2 resonance in Figs. 12(a) and 13(b) cannot be reproduced by the scattering from the magnetic dipole moment. Using Eq. (B-10), the E2 scattering-amplitude matrix for the magnetic dipole with the structure factor \((1, \pm i, 0)\) is expressed as

\[
\mathbf{F}_{\text{E2}} = \begin{pmatrix}
\frac{\pi}{2} \sin 2\theta & i \cos 3\theta \\
-\frac{\pi}{2} \cos 2\theta & \frac{\pi}{2} \sin 3\theta
\end{pmatrix}.
\]

For \(Q = (0, 0, 27 \pm q)\), when \(\varphi = \pi/2\) for the R-crystal in the present case, \(C_2/C_0 = 0.79\) and \(C_3/C_0 = 0.51\) are obtained by calculation. However, the sign of \(C_2\) is opposite to the experimental result. In addition, since the \(\cos 3\theta\) in \(\mathbf{F}_{\text{E2}}\) and \(\mathbf{F}_{\text{R}}\) changes sign at \(\theta = \pi/6\), \(C_2\) in Fig. 13(b) should change sign around \(L=20\), which clearly disagrees with the experimental result.\(^{45}\) Therefore, we cannot explain the E2 resonance by only the scattering from the magnetic dipole.

The \(Q\)-dependence of \(C_2\) and \(C_3\) for E2 can be reproduced by considering the scattering from the magnetic octupole. We use the following model. First, the structure factor of the magnetic dipole (rank-1) for \(Q = (0, 0, 3n \pm q)\) for the R-crystal is represented by

\[
\mathbf{Z}_{\text{dip}}^{(1)} = (1, \pm i, 0).
\]

Second, we take into account the current from the magnetic dipole moment. Using Eqs. (7a) and (7b) the dipole and octupole order, should be written as

\[
\mathbf{Z}_{\text{dip}}^{(3)} = \sqrt{3}Ae^{i\phi}(1, \pm i, 0),
\]

\[
\mathbf{Z}_{\text{dip}}^{(3)} = \sqrt{5}Ae^{i\phi}(1, \pm i, 0),
\]

where \(A\) and \(\phi\) represent the relative amplitude and phase, respectively, of the octupole structure factor with respect to those of \(\mathbf{Z}_{\text{dip}}^{(3)}\). By putting \(A = 0.46\) and \(\phi = -0.79\pi\), the data are well explained as shown by the calculated curves in Fig. 13(b). The \(\Delta \theta_{\text{RCP}}\) dependence in Fig. 12(a) can also be reproduced by using these parameters.

The detailed relationship of the coefficients between Eqs. (7a) and (7b) originates from the reducible representation of the order parameter in the \(D_3\) point group.\(^{46}\) Although we use the cubic coordinates for the intensity calculation, we should analyze the order parameter using the hexagonal coordinates. The in-plane dipole moments, \(J_x\) and \(J_y\), for example, belong to the two-dimensional \(E_u\) representation in the \(D_3\) point group. The octupole moments with the \(E_u\) representation, on the other hand, are expressed as linear combinations of \(T_{1x}\) and \(T_{3y}\). They are written as \(T_{1x} = (\sqrt{7}T_{1x}^{(1)} - \sqrt{3}T_{1x}^{(2)})\) and \(T_{3y} = (\sqrt{3}T_{3y}^{(1)} + \sqrt{3}T_{3y}^{(2)})\). Therefore, the ordered structure of the octupole moments given by Eqs. (7a) and (7b) is equivalent to the helical octupole ordering expressed by \(T_{1x}^{(1)} + iT_{1x}^{(2)}\), which has the same symmetry as the helical magnetic dipole order expressed by \(J_x + iJ_y\). Although the opposite sign of \(Z_{\text{dip}}^{(3)}\) in Eq. (7b) is a rather tricky result, it is not surprising.

Other representations are given by \(T_{1x}^{(1)} = (\sqrt{7}T_{1x}^{(1)} - \sqrt{3}T_{1x}^{(2)})\) and \(T_{1x}^{(2)} = (\sqrt{3}T_{1x}^{(1)} + \sqrt{3}T_{1x}^{(2)})\) which also constitute another \(E_u\) representation in the \(D_3\) group. Although
these moments generally need to be included, the data were
successively explained without taking them into account.

4. Discussion

4.1 Helical order of octupole moments

The ground multiplet of \( J = \frac{7}{2} \) for \( \text{Yb}^{3+} \) splits into four
Kramers doublets in the crystalline electric field of \( \text{YbNi}_3\text{Al}_9 \),
represented by the point group \( D_3 \). Since the magnetic
moments preferentially lie in the \( c \) plane, the crystal field
ground state is likely to be composed mainly of \( \left\{ j, \pm \frac{1}{2} \right\} \), which
is isotropic in the \( c \) plane. In this two-dimensional space of
\( \left\{ j, \pm \frac{1}{2} \right\} \), the \( x \)-component matrices of \( J_x \) (\( E_u \) dipole)
and \( T_y^q \) \([x(5z^2-r^2)]\)-type, \( E_u \) octupole) are expressed in the same form as

\[
J_x = 2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad T_y^q = -15 \sqrt{3} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.
\]

Therefore, when a magnetic dipole moment \( \langle J_x \rangle \) is induced,
the \( \langle T_y^q \rangle \) octupole arises simultaneously. When a helical mag-
netic dipole order of \( \langle J_x + i J_y \rangle \) occurs, the helical magnetic oc-
tupole order of \( \langle T_y^q + i T_y^q \rangle \) with the same helicity also
arises. The matrix elements of the \( T_{57}^q \) and \( T_{67}^q \)
 octupoles \( (E_u) \), \( T_{57}^q \) \((A_{2u}) \), and \( T_{57}^q \) \((A_{1u}) \) all vanish in the \( \left\{ j, \pm \frac{1}{2} \right\} \) space. This is
the reason we did not need to include these moments in the
analysis in §3.6. Also, there is no degree of freedom for the
quadrupole (rank-2) moments, which guarantees the reason-
ing that the orbital contribution is not included in the second-
harmonic signal.

The \( T^q \)-type magnetic octupole reflects an aspherical charge
distribution of the \( \left\{ j, \pm \frac{1}{2} \right\} \) states. Figure 14 shows
schematics of the magnetic charge distributions.\(^{47}\) The
superposition of the \( J_x \)-dipole and the \( T^q \)-octupole, shown in
Figs. 14(a) and 14(b), respectively, results in the magnetic
charge distribution shown in Fig. 14(c). We see a lower mag-
netic moment density along the \( c \) (\( z \)) axis, which is associated
with the lower charge density of the \( \left\{ j, \pm \frac{1}{2} \right\} \) state along the \( c \)
axis as shown in Fig. 14(d).

At the present stage, it is not clear whether the octupole
moments affect any physical property in \( \text{YbNi}_{1-x}\text{Cu}_x\text{Al}_9 \).
It should be remarked, however, that the strength of the inter-
ionic multipolar interaction is rank-independent in the RKKY
mechanism.\(^{48,49}\) As a result, the higher-rank multipoles play
important roles in the physical properties and can equally be
introduced as primary order parameter, as is typically realized in the
cubic \( \text{Ce}_x\text{La}_{1-x}\text{B}_6 \) system, in which the dipole, quadrupole,
and octupole moments are active as independent degrees of
freedom.\(^{50,51}\) In \( \text{YbNi}_{1-x}\text{Cu}_x\text{Al}_9 \), by contrast, the active
moments in the doublet ground state are \( \langle J_x, J_y \rangle \) or \( \langle T_y^q, T_y^q \rangle \),
which both belong to the \( E_u \) representation and are not
independent. The issue is how much the physical properties are
affected by the octupolar interaction in comparison with the dipolar interaction.

4.2 Temperature-dependent helical magnetic structure

As shown in Fig. 7, the propagation vector changes with
Fig. 14. (Color online) Magnetic charge distributions representing (a) a
dipole and the \( q \)-octupole, shown in
magnetic charge density of the \( J(72, \pm 12) \) state
of \( \text{Yb}^{3+} \), possessing a magnetic dipole moment \( \langle J_x \rangle \).\(^{47}\)

3
2
1
0
1
2
3
4
5
the octupole interaction in comparison with the dipolar interaction.
Fig. 15. (Color online) (a) Comparison of the experimental data of $q(H)/q(0)$ for $x = 0.06$ with the $L_0/L_{CSL}$ curve obtained from the chiral sine-Gordon (SG) model.$^{10,11}$ $\mu_0H_{C0}$ is set to 11.5 kG. (b) Comparison of the experimentally obtained intensity ratios of $I_{3q}/I_q$ (filled circles) and $I_{q}/I_q$ (open square) with the calculated ratio for the sine-Gordon model using $\mu_0H_{C0}=10.5$ kG.

Fig. 16. (Color online) (a)-(c) Magnetic structures of Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ for $x=0.06$ (L) in magnetic fields expected from the chiral sine-Gordon model. Only the moments on Yb-1 sites are shown. (a) Helimagnetic ordered state at zero field with $q=0.445$ and the helical pitch of $L=6.7c_0$. This is the same as Fig. 5. (b) CSL state for $H/H_{C0}=0.4$, corresponding to $q=3/7$ and $L=7c_0$ at around 5 kG. (c) CSL state for $H/H_{C0}=0.8$, corresponding to $q=3/8$ and $L=8c_0$ between 9.0 and 9.5 kG. (d) CSL state for continuous one-dimensional spin model corresponding to (c), $H/H_{C0}=0.8$.

In Fig. 16(b) and (c), we compare the $H$ dependence of the normalized propagation vector $q(H)/q(0)$ for $x = 0.06$ with the calculation of $L_0/L_{CSL}$ for the sine-Gordon model. $^{10,11}$ We introduced a critical field of $\mu_0H_{C0}=11.5$ kG so that the data fit the calculation. The data points closely follow the theoretical curve up to $H/H_{C0} \sim 0.85$, where the first-order transition to the ferromagnetic state takes place. In Fig. 16(b), we compare the intensity ratios of $I_{3q}/I_q$ and $I_{q}/I_q$ with the theoretical curve by using a slightly different $\mu_0H_{C0}$ of 10.5 kG. These intensity ratios also closely follow the theoretical curve. Although the calculation is for neutron diffraction, the result can almost equally be applied to the intensity of RXD. These agreements between the experiment and theory strongly indicate that the CSL state is actually formed in the Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ system.

4.4 Magnetic exchange and DM interactions

There are many problems concerning the magnetic exchange and DM interactions in this system. The sine-Gordon theory is based on the following one-dimensional model for a layered monoaxial chiral helimagnet with ferromagnetic nearest-neighbor exchange and DM interaction:

$$\mathcal{H} = -J_1 \sum_i S_i \cdot S_{i+1} - D \cdot \sum_i S_i \times S_{i+1} - \sum_i S_i \cdot \mathbf{H},$$

where $S_i$ lies in the $xy$ plane, $D$ is along the $z$ axis, and $\mathbf{H}$ is applied in the $xy$ plane. At $H = 0$, a helimagnetic order with $q_0 = c_0^{-1} \arctan(D/J_1)$ is formed, where $c_0$ is the interlayer distance. If we simply apply this model to Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ to obtain $q_0$ values of 0.42, 0.54, and 0.63 for $x=0.06$, 0.04, and 0.02, $D/J_1$ is required to be 1.2, 2.1, and 3.9, respectively.
which are unrealistically large. For $x=0$, in addition, it is impossible to reproduce $q_0=0.82$ from this model because the angle between spins on neighboring layers is larger than $90^\circ$. To explain these large $q_0$ values, it is necessary to include more long-range exchange interactions mediated by the conduction electrons. It is more reasonable to consider that $q_0$ is determined mainly by $J_1 (> 0)$, $J_2 (< 0)$, and further interactions, with which $J(q)$ takes a maximum at $q_0$. If we consider $J_1$ and $J_2$, for example, $J(q) = J_1 \cos q_0 + J_2 \cos 2q_0$, and $q_0$ is given by $q_0^2\arccos(-J_1/4J_2)$. The degeneracy of $\pi q_0$ is lifted by the DM term.

However, there still remains a problem. If $q_0$ is determined by the maximum of $J(q)$, it is expected that $T_N \propto J(q_0)$ and $H_C \propto J(q_0) - J(0)$. When $q_0$ approaches 0 (ferromagnetic state) with increasing Cu concentration, $J(q_0)$ - $J(0)$ should also become small because $J(q)$ is a symmetric function of $q$. However, while $T_N=6.5$ K for $x=0.06$ is twice as large as that for $x=0$, $\mu_0 H_C=10$ kG for $x=0.06$ is ten times as large as that for $x=0$. These facts are not explained by the simplistic model above and show that the situation behind the helimagnetic order of Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ is not so simple.

Firstly, the interaction between Yb-1 and Yb-2 moments should be considered. More importantly, the fact that $H_C$ significantly increases with increasing $x$, i.e., with decreasing $q_0$ and $J(q_0) - J(0)$, suggests that the nonlinear effect of the RKKY formation in magnetic fields plays an important role in keeping the helimagnetic structure and preventing the system from undergoing a transition to the ferromagnetic state. The possibility of the DM interaction increasing with increasing Cu concentration should also be considered.

5. Summary

We performed resonant X-ray diffraction experiments to investigate the helical magnetic structure of Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ with the space group R32, which lacks both inversion and mirror symmetries and allows the existence of left- and right-handed crystal structures.

- We showed that the magnetic structure is described by an incommensurate propagation vector $(0,0,q)$, where $q=0.818, 0.617, 0.553$, and $0.445$ for $x=0.00, 0.02, 0.04$, and $0.06$, respectively, at the lowest temperature. The magnetic moments lie in the $c$ plane.

- We clarified that the helicity of the magnetic structure has a one-to-one relation with the crystal chirality, indicating that an antisymmetric exchange interaction mediated by the conduction electrons exists, i.e., the RKKY mechanism. A theoretical study is required to provide further insight into the physical mechanism.

- When a magnetic field is applied perpendicular to the helical axis, the $q$ value decreases (the helical pitch increases) and, simultaneously, the higher-harmonic peaks of $2q$ and $3q$ are induced with increasing field. This behavior, especially for the $x=0.06$ case, coincides with the calculation for the chiral sine-Gordon model, which describes the formation of the chiral soliton lattice (CSL) state in a monoaxial helimagnet. This coincidence provides strong evidence for the CSL formation in Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$, which has been suggested by magnetization measurement. However, since the helical pitch is not much longer than the interlayer spacing, it is questionable if the spin arrangement could be approximated as a continuous medium. The applicability of the sine-Gordon model to Yb(Ni$_{1-x}$Cu$_x$)$_3$Al$_9$ remains a question. The lock-in phenomenon at $q = 3/8$ and the first-order transition to the ferromagnetic state also are important issues to be studied.

- We observed an anomalous temperature dependence of the propagation vector. The $q$ value changes with temperature by an amount almost in proportion to the magnetic order parameter, which we ascribed to the change in the exchange interaction with the development of the ordered moment. It is not understood, however, why the $q$ value decreases with decreasing $T$ for $x < 0.03$, but this is reversed for $x > 0.03$.

- The helical ordering of the magnetic octupole moment was detected, which arises simultaneously with the helical ordering of the magnetic dipole moment, reflecting the anisotropic charge density of the crystal field ground state of Yb$^{3+}$, consisting mainly of $|7/2, \pm 1/2\rangle$.

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Appendix A: Confirmation of the Crystal Structure

A.1 Crystal chirality

The crystal chirality of the sample, especially the spot where the X-ray beam is irradiated in the RXD experiment, can be confirmed at the beamline by measuring the energy dependence of an appropriate fundamental Bragg peak as shown in Fig. A-1. The structure factor of the $(1,1,24)$ fundamental reflection for the right-handed crystal is expressed as $F_{R,(1,1,24)}(\omega) = A_{AI}f_{AI}(\omega) + A_{Ni}f_{Ni}(\omega) + A_{Yb}f_{Yb}(\omega)$, where $A_{AI} = 0.24 + 24.6i$, $A_{Ni} = -8.6 + 14.9i$, and $A_{Yb} = 6.0$. $F_{L,(1,1,24)}$ also has the same expression. For $F_{R,(1,1,24)}$ and $F_{R,(1,1,24)}$, we take the complex conjugates for $A_{AI}$ and $A_{Ni}$. When $f_{Yb}(\omega) = f_{0,Yb} + f_{1,Yb}(\omega) + f_{2,Yb}(\omega)$ exhibits an anomalous dispersion around the absorption edge, the intensity of the Bragg reflection also exhibits a strong energy dependence. Since the intensities for the right- and left-handed crystals are expressed as $|F_{R,(1,1,24)}(\omega)|^2$ and $|F_{L,(1,1,24)}(\omega)|^2$, respectively, they exhibit different energy dependences due to the different interference effect. As shown in Fig. A-1, the relative relation of the intensity is reversed for the $(1,1,24)$ reflection. The relationship of the intensity is consistent with the calculated spectrum assuming the predetermined crystal chirality.

A.2 Threefold symmetry about the $c$ axis

Figure A-2 shows the rocking scans of the $(1,0,L)$ reflections for the $x=0.06$ (L) sample. Only the $(1,0,3n+1)$ reflection is allowed in the $(1,0,L)$ reflections in the R32 space group. These data guarantee the threefold symmetry of this
Appendix B: Formalism of Resonant X-ray Scattering

We use the scattering-amplitude-operator method to analyze the experimental results. We consider a $2 \times 2$ matrix $\hat{F}$, consisting of four elements of the scattering amplitudes for $\sigma\sigma'$, $\pi\pi'$, $\sigma\pi'$, and $\pi\sigma'$:

$$\hat{F} = \begin{pmatrix} F_{\sigma\sigma'} & F_{\sigma\pi'} \\ F_{\pi\sigma'} & F_{\pi\pi'} \end{pmatrix}. \quad (B-1)$$

By using the identity matrix $\hat{I}$ and the Pauli matrix $\hat{\sigma}$, $\hat{F}$ can generally be expressed as

$$\hat{F} = \beta \hat{I} + \alpha \cdot \hat{\sigma} = \begin{pmatrix} \beta + \alpha_3 & \alpha_1 - i \alpha_2 \\ \alpha_1 + i \alpha_2 & \beta - \alpha_3 \end{pmatrix}. \quad (B-2)$$

Once we know the matrix $\hat{F}$, the scattering cross section $(d\sigma/d\Omega)$ can be calculated by

$$\left(\frac{d\sigma}{d\Omega}\right) = \text{Tr}[\hat{\mu}^\dagger \hat{F} \hat{F}].$$

$$= \beta^* \beta + \alpha^* \cdot \alpha + \beta^*(\mathbf{P} \cdot \mathbf{a}) + (\mathbf{P} \cdot \mathbf{a}^*) \beta$$

$$+ i \mathbf{P} \cdot (\mathbf{a}^* \times \mathbf{a}), \quad (B-3)$$

where $\hat{\mu} = (\hat{I} + \mathbf{P} \cdot \hat{\sigma})/2$ represents the density matrix and the Stokes vector $\mathbf{P} = (P_1, P_2, P_3)$ represents the polarization state of the incident photon. $P_1$, $P_2$, and $P_3$ represent the degrees of $+45^\circ$ ($P_1 = 1$) or $-45^\circ$ ($P_1 = -1$) linear polarization, right ($P_2 = 1$) or left ($P_2 = -1$)-handed circular polarization, and the $\sigma$ ($P_3 = 1$) or $\pi$ ($P_3 = -1$) linear polarization state, respectively.

Using the elements of Eq. (B-1), the scattering cross section is expressed as

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{2}\left|\langle F_{\sigma\sigma'}^2 + |F_{\sigma\pi'}|^2 + |F_{\pi\sigma'}|^2 + |F_{\pi\pi'}|^2 \rangle \right|^2$$

$$+ P_1 \text{Re}\{F_{\sigma\sigma'}^* F_{\sigma\pi'} + F_{\sigma\pi'}^* F_{\pi\sigma'} \}$$

$$+ P_2 \text{Im}\{F_{\sigma\pi'}^* F_{\sigma\sigma'} + F_{\sigma\sigma'}^* F_{\pi\pi'} \} \quad (B-4)$$

$$+ \frac{1}{2} P_3 (|F_{\pi\pi'}|^2 + |F_{\pi\sigma'}|^2 - |F_{\sigma\pi'}|^2 - |F_{\sigma\sigma'}|^2).$$

Therefore, the cross section for the incident beam described by $(P_1, P_2, P_3)$ can generally be written as

$$\left(\frac{d\sigma}{d\Omega}\right) = C_0 + C_1 P_1 + C_2 P_2 + C_3 P_3,$$  

which can be used as a fitting function for the $\Delta\theta_{\text{pp}}$ scan with the four parameters of $C_n \ (n = 0 \sim 3)$.

The four elements of Eq. (B-1) at an X-ray energy $E = h\omega$ near the resonance energy are expressed as

$$F_{\varepsilon k}'(\omega) = F_{E1,\varepsilon k}'(\omega) + F_{E2,\varepsilon k}'(\omega). \quad (B-6)$$

$F_{E1,\varepsilon k}'(\omega)$ and $F_{E2,\varepsilon k}'(\omega)$ for a scattering process from the photon state $(\varepsilon, k)$ to $(\varepsilon', k')$ are expressed as

$$F_{E1,\varepsilon k}'(\omega) = \sum_{\nu=0}^{2} a_{E1}^{(\nu)}(\omega) \sum_{\Gamma} X_{E1,\varepsilon k}'^{(\nu)}(\varepsilon, k) \cdot (Z_{\Gamma}^{(\nu)}) \quad (B-7)$$

$$F_{E2,\varepsilon k}'(\omega) = \sum_{\nu=0}^{4} a_{E2}^{(\nu)}(\omega) \sum_{\Gamma} X_{E2,\varepsilon k}'^{(\nu)}(\varepsilon, k) \cdot (Z_{\Gamma}^{(\nu)}) \quad (B-8)$$

$\langle Z_{\Gamma}^{(\nu)} \rangle$ represents the structure factor of the rank-$\nu$ multipole moment of the irreducible representation $\Gamma$ in the cubic coordinates. $X_{E1,\varepsilon k}'^{(\nu)}$ is the geometrical factor corresponding to $\langle Z_{\Gamma}^{(\nu)} \rangle$.

For the rank-1 dipole moment with the $T_{1u}$ representation,

$$X_{E1,\varepsilon k}^{(1)} = \frac{i}{\sqrt{2}}(\varepsilon' \times \varepsilon), \quad (B-9)$$

$$X_{E2,\varepsilon k}^{(1)} = \frac{i}{2 \sqrt{10}} [(k' \cdot k)(\varepsilon' \times \varepsilon) + (\varepsilon' \cdot k)(k' \times k)$$

$$+ (k' \cdot k)(\varepsilon' \times \varepsilon) + (\varepsilon' \cdot k)(k' \times \varepsilon)]. \quad (B-10)$$

See Ref. 36 for $X_{E2}^{(3)}$. The scattering amplitude is obtained by taking the scalar product of $X_{\Gamma}^{(\nu)}$ and $(Z_{\Gamma}^{(\nu)})$.

The same result is obtained by using the spherical tensor method. By transforming $(Z_{\Gamma}^{(\nu)})$ in the cubic representation to $(T_{\ell q}^{(\nu)})$ in the spherical representation,

$$F_{E1,\varepsilon k}'(\omega) = \sum_{\nu=0}^{2} a_{E1}^{(\nu)}(\omega) \sum_{q=-\nu}^{\nu} (-1)^q X_{E1,\varepsilon k}'^{(\nu)}(T_{q}^{(\nu)}), \quad (B-11)$$

Fig. A1. (Color online) X-ray energy dependence of the (1,1,24) and (1,1,24) fundamental reflections for the right- and left-handed crystals for $x=0.06$ around the $L_5$ absorption edge of Yb. Solid lines are the guides for the eye.

Fig. A2. (Color online) Rocking scans of the (1,0,16), (1,0,17), and (1,0,18) reflections for the $x=0.06$ (L) sample.
where the geometrical factors of $\alpha_{E1,q}^{(v)}$ and $X_{E2,q}^{(v)}$ are also expressed in the spherical representation as

$$
X_{E1,q}^{(v)} = \sum_{p,p'=-1}^{1} \epsilon_{p}^{'\prime} \epsilon_{p'}^{'\prime} \langle 1| p 1' | q \rangle v q , \tag{B-13}
$$

$$
X_{E2,q}^{(v)} = \sum_{p,p'=-1}^{1} \epsilon_{p}^{'\prime} \epsilon_{p'}^{'\prime} \langle 2| p 2' | q \rangle v q , \tag{B-14}
$$

$$
h_{m}^{'\prime} = \sum_{p,p'=-1}^{1} \epsilon_{p}^{'\prime} \epsilon_{p'}^{'\prime} \langle 1| p 1' | 2m \rangle , \tag{B-15}
$$

$$
h_{m}^{'\prime} = \sum_{p,p'=-1}^{1} \epsilon_{p}^{'\prime} \epsilon_{p'}^{'\prime} \langle 1| p 1' | 2m \rangle . \tag{B-16}
$$

It is important that the spectral functions of $\alpha_{E1,q}^{(v)}$ and $\alpha_{E2,q}^{(v)}$ are rank-dependent, in the data analysis, each of them may be approximated by the form

$$
\alpha^{(v)}(\omega) = \frac{\epsilon_{\phi}^{'}}{\hbar \omega - \Delta + i\gamma} , \tag{B-17}
$$

where $\Delta$, $\gamma$, and $\phi$ are the resonance energy, lifetime broadening effect, and phase factor, respectively.
60) (Supplemental material) A simple calculation assuming \( J_1 \) and \( J_2 \) is provided online in Fig. S2.
Table S.1. Irreducible representation (Irrep.), operator notation, and basis functions of the dipole (rank-1) and octupole (rank-3) moments in the $O_b$ and $D_3$ point groups.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Irrep.</th>
<th>Notation</th>
<th>Basis Function</th>
<th>Irrep.</th>
<th>Notation</th>
<th>Basis Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$T_{1u}$</td>
<td>$J_1$</td>
<td>$x$</td>
<td>$E_u$</td>
<td>$J_z$</td>
<td>$x$</td>
</tr>
<tr>
<td></td>
<td>$J_z$</td>
<td>$y$</td>
<td></td>
<td>$J_y$</td>
<td>$y$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$T_{2u}$</td>
<td>$T_1^a$</td>
<td>$x(5x^2 - 3y^2)/2$</td>
<td>$T_2^a$</td>
<td>$y(5y^2 - 3z^2)/2$</td>
<td>$T_3^a$</td>
</tr>
<tr>
<td></td>
<td>$T_2^b$</td>
<td>$J_1$</td>
<td>$\sqrt{15}(x^2 - z^2)/2$</td>
<td>$T_2^c$</td>
<td>$J_1$</td>
<td>$\sqrt{15}(y^2 - x^2)/2$</td>
</tr>
<tr>
<td></td>
<td>$T_{1u}$</td>
<td>$T_{1u}$</td>
<td>$\sqrt{15}(x^2 - z^2)/2$</td>
<td>$T_{2u}$</td>
<td>$T_{2u}$</td>
<td>$\sqrt{15}(y^2 - x^2)/2$</td>
</tr>
</tbody>
</table>

Fig. S.1. Comparison of the disagreeing calculation with the $L = 3n \pm q$ dependence data of the parameters $C_2/C_0$ at zero field, which was obtained from the $\Delta \theta_{bg}$ scans for the $x=0.06$ (R) sample at the E2 resonance energy. Solid, dashed, and dot-dashed curves represent the calculation of $C_2/C_0 (L = 3n \pm q)$, $C_2/C_0 (L = 3n - q)$, and $C_2/C_0 (L = 3n + q)$, respectively, for models of (a) $J_1 \pm iJ_2$ dipole (rank-1) only and (b) $(T_2^a \pm iT_2^c)$ octupole (rank-3) only. The data can be explained by mixing these two scattering contributions as described in the main text.

Fig. S.2. A simple calculation of $J(q)$ for one dimensional spin chain with nearest-neighbor exchange $J_1$ and next-nearest-neighbor exchange $J_2$. $J_1$ and $J_2$ are taken so that $q_0 = c_0^{1/2} \arccos(-J_1/(4J_2))$, where $J(q) = J_1 \cos q_0 + J_2 \cos 2q_0$ takes the maximum, reproduces the experimental value and $J(q_0)$ is proportional to $T_N$. The degeneracy at $\pm q_0$ will be lifted by including the DM term. In this model, without considering any nonlinear effect such as CSL formation, $H_C$ will be proportional to $J(q_0) - J(0)$. However, it is contradictory to the experimental result.