Neutron scattering study of a one-dimensional XY antiferromagnet Cs_2CoCl_4

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The magnetic behavior of Cs_2CoCl_4 is studied by quasielastic neutron scattering techniques. The one-dimensional (1D) character along the orthorhombic b axis is established by the observation of a sheetlike structure in the static correlation function $S(\vec{Q})$. The temperature dependence of the inverse correlation length $\kappa \sim 0.88 k_B T/|J|$ between 0.32 and 0.65 K is consistent with the recent theoretical calculation of the κ for the in-plane component of spins in a 1D XY system with $S=\frac{1}{2}$. In addition, the modulation of the 1D sheet of $S(\vec{Q})$ was found in the paramagnetic phase. With a basis on a simplified model of competing interactions we show that the 1D short-range order is driven to an incommensurate state due to the interchain exchange interactions.

I. INTRODUCTION

In recent years, a study of one-dimensional (1D) magnets has attracted a great deal of interest from the experimentalists.[1,2] A variety of compounds has been found in which the magnetic ions behave as a set of magnetic chains, and both static and dynamical properties have been studied extensively. However, there are few materials which are known to behave as a 1D XY magnet with $S=\frac{1}{2}$, for which interesting quantum effects are expected in its dynamical properties.[3–5]

Recent measurements of the heat capacity[6] and magnetic susceptibility[7] suggest that the compound Cs_2CoCl_4 might be one of the rare examples of 1D XY antiferromagnet with the effective spin $S=\frac{1}{2}$. Stimulated by these reports, we studied the static spin correlation at low temperatures using neutron scattering techniques. The purpose of our study is to clarify to what extent the static spin correlation function $S(\vec{Q})$ of Cs_2CoCl_4 reflects the properties of a 1D XY model with $S=\frac{1}{2}$. We found that in quasielastic scattering Cs_2CoCl_4 exhibits a sheetlike structure characteristic of the one-dimensional behavior. From the width of the sheet, we determined the temperature dependence of the inverse correlation length κ in Cs_2CoCl_4, and compared it with the recent calculations by Tonegawa of the temperature dependences of both the in-plane correlation length κ_x and the out-of-plane correlation length κ_z in a 1D XY magnet with $S=\frac{1}{2}$.

Another aspect of this study is an effect of the interchain coupling J'. This compound contains two nonequivalent chains shifted by half a lattice unit with respect to each other[6] as shown in Fig. 1. For a finite value of J' an incommensurate spin ordering may be favorable for such a system rather than a simple antiferromagnetic ordering. Based on a simplified model of a body-centered orthorhombic lattice with the finite interchain coupling, we show that Cs_2CoCl_4 can have a helical spin ordering. Such a model is consistent with the fact that the static spin-correlation function $S(\vec{Q})$ of Cs_2CoCl_4 exhibits a systematic modulation from the commensurate positions even in the paramagnetic phase.

II. PRELIMINARY DETAILS

The compound Cs_2CoCl_4 has the orthorhombic structure[8] of a β-K_2SO_4 type, whose unit cell contains four Co ions surrounded by the tetrahedrons of the chlorine atoms. In the tetrahedral cubic environment the orbital ground state for the Co ions is a singlet with $S=\frac{3}{2}$. An axial dis-

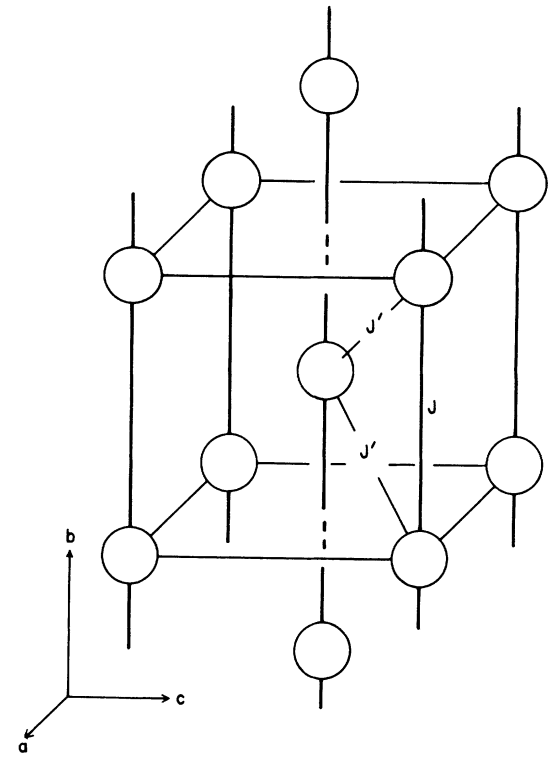

FIG. 1. Simplified model of the spin lattice for Cs_2CoCl_4.

tortion and the spin-orbit coupling split this state into two Kramers doublets with a separation of about 15 K.[8] The inspection of possible superexchange paths suggests that the exchange interaction in the b axis direction is considerably stronger than those in other directions.[6] Consequently, the magnetic behavior of Cs_2CoCl_4 at sufficiently low temperatures may be described by a 1D anisotropic exchange Hamiltonian with an effective spin $S=\frac{1}{2}$,

$$\mathcal{H}=-2J\sum(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y+\eta S_i^zS_{i+1}^z)\ . \qquad (1)$$

Algra *et al.*[6] reported that the specific-heat data between 0.3 and 1 K could be fitted to the calculated specific heat of the 1D Hamiltonian, Eq. (1), with an antiferromagnetic exchange $J/k_B=-1.35$ K and an anisotropy parameter $\eta=0.25$. They observed the onset of a three-dimensional (3D) long-range order at $T_N=0.222\pm0.005$ K. Duxbury *et al.*[7] reported that the c-axis susceptibility was fitted to the transverse susceptibility of the Hamiltonian, Eq. (1), with a reasonable agreement over the range $1\ \text{K}<T<2.5$ K. Specifically, they could improve the fits by including some Ising-type anisotropy, i.e., a finite $\eta=0.25$ in Eq. (1) as was used with the specific-heat data.

It should be noted that there is a fundamental difficulty in the measurements of the magnetic properties in Cs_2CoCl_4 due to the rather complicated crystallographic structure of this compound.[7] In Cs_2CoCl_4 with the β-K_2SO_4-type structure there are two nonequivalent Co-ion sites.[9] Although the easy planes in each chain are parallel, the easy planes in adjacent chains make a large angle with one another. Consequently, the bulk properties are mostly the superposition of the local properties of the two nonequivalent easy planes. Duxbury *et al.*[7] pointed out, for example, that there is no special direction where the susceptibility along the out-of-plane direction ($\vec{H}$ perpendicular to the easy plane: $\chi_\perp$) can be observed separately from $\chi_{||}$. In the case of the neutron scattering experiments, we encounter a similar limitation. In principle, the neutron scattering technique allows us to observe only the fluctuations perpendicular to the scattering vector.[10] Therefore, we can observe the pure transverse fluctuations in an Ising system by setting the scattering vector parallel to the magnetic moments. Unfortunately, however, in the neutron scattering experiments on Cs_2CoCl_4 we always observe a mixture of the in-plane and the out-of-plane fluctuations due to the coexistence of two different easy planes.

III. EXPERIMENTAL DETAILS

A single crystal of Cs_2CoCl_4 grown by us was used for the neutron scattering study. High-purity $CoCl_2$ is produced from the metallic cobalt in a flowing HCl gas, and is melted with CsCl powder in a silica tube. A single crystal of Cs_2CoCl_4 is grown by the standard Bridgman technique. The size of the crystal used is about $7\times7\times10\ \text{mm}^3$ and the lattice constants at $T=0.3$ K are $a_0=9.71$ Å, $b_0=7.27$ Å, and $c_0=12.73$ Å. The preliminary measurements were carried out at JRR-2, in the Japan Atomic Energy Research Institute (JAERI), Tokai, Ibaraki, Japan, while most of the measurements for $0.3\ \text{K}<T<0.6$ K were performed at the Brookhaven National Laboratory High-Flux Beam Reactor.

The sample crystal was mounted in a pumped He^3 cryostat with the b^* axis or the a^* axis vertical to give the $(hk0)$ or the $(0kl)$ scattering plane, respectively. A (002) reflection of a pyrolytic graphite (PG) was used for both monochrometer and analyzer. A PG filter was placed before the monochrometer to eliminate the higher-order contaminations. The spectrometer was operated in a triple-axis configuration with an incident neutron energy of 14.8 meV, and the collimators were 20′-40′-40′-40′ for the $(hk0)$ zone and 40′-20′-20′-40′ for the $(0kl)$ zone, which gives a momentum resolution of 0.053 Å^{-1} in the longitudinal direction and 0.027 Å^{-1} in the transverse direction. The energy resolution of these spectrometer configurations is approximately 0.6 meV, giving a sufficient energy integration over the quasielastic scattering, because the spin-wave excitation energy at the zone boundary was determined to be 0.35 meV from our measurements.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the $(hk0)$ reciprocal plane for Cs_2CoCl_4. The ridge of the quasielastic scattering was observed at the half-integer values of k at $T=0.4$ K. The scans across the ridge around $k=0.5b^*$ with different h values are shown on the left-hand side of Fig. 3, while four ridges with increasing order of k are shown on the right-hand side of Fig. 3. A similar ridge was also found in the $(0kl)$ zone, indicating a sheetlike quasielastic scattering perpendicular to the b^* axis. It is clear that the spins in Cs_2CoCl_4 behave basically like a set of antiferromagnetic chains oriented along the b axis.

An interesting feature of the peaks shown in Fig. 3 is the systematic shifts of their positions from the half-integer values of k. The ridges observed in the $(0kl)$ zone exhibit similar modulation. To illustrate such modulations perpendicular to the chain direction, we plotted in Fig. 4 the peak positions, the peak intensities, and the full width at half maximum of the ridges observed in both the $(hk0)$ and the $(0kl)$ zones. Peak positions reach maxima

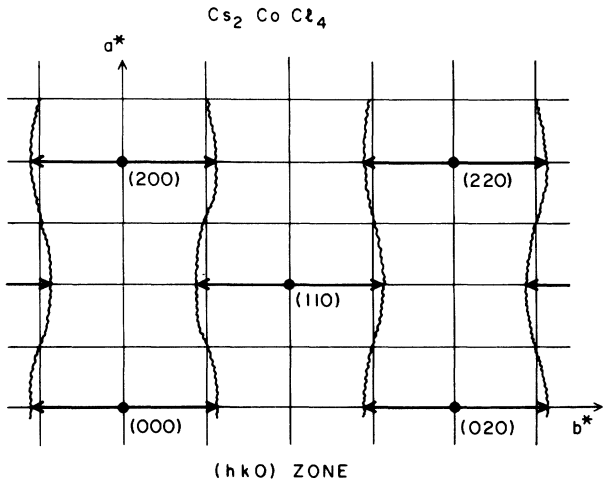

FIG. 2. $(hk0)$ scattering plane for Cs_2CoCl_4. Solid circles show the positions of the nuclear Bragg reflections.

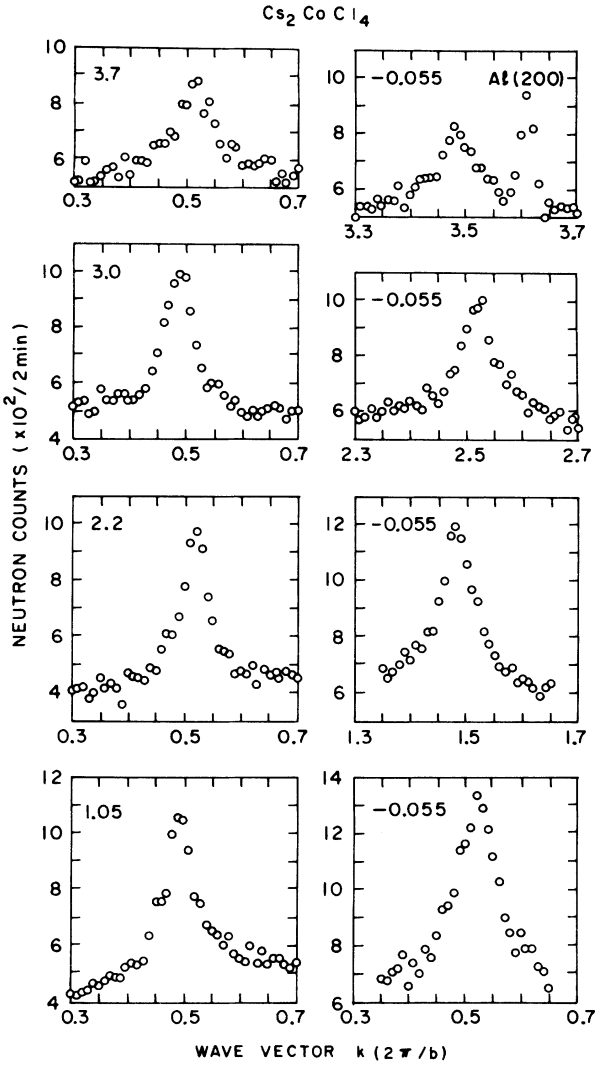

FIG. 3. Neutron profiles observed in a $(hk0)$ zone at $T=0.4$ K, where the number in each panel gives h.

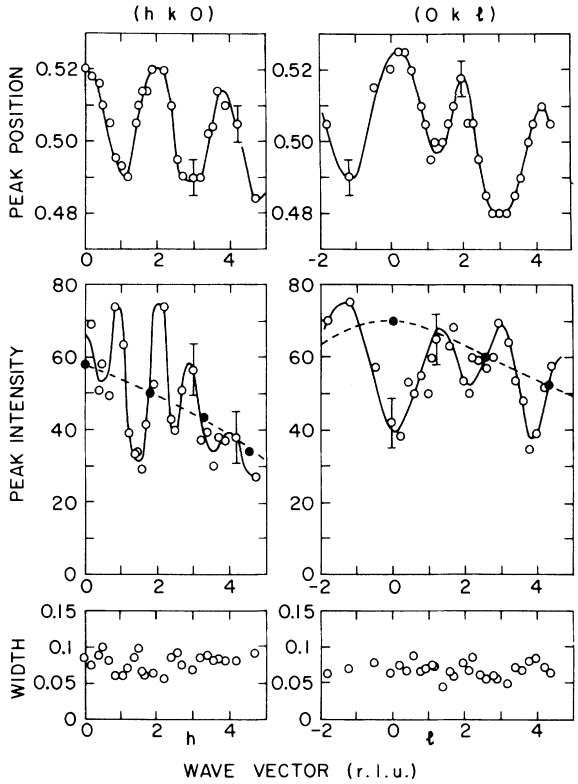

FIG. 4. Scattering vector dependences of the peak position, the peak intensity, and the width of the static correlation function $S(\vec{Q})$ perpendicular to the chain direction at $T=0.4$ K. Solid lines are guides to the eyes. A dashed line with solid circles gives the magnetic form factor of Co ions.

at even integers of h or k while they reach minima at odd integers. These plots clearly demonstrate the incommensurate feature of the diffuse scattering in Cs_2CoCl_4. A possible mechanism for this modulation will be given in a later section. The two middle panels show the relative change of the ridge intensity along the h or the l directions, where the effective volume of the sample is corrected by normalizing the incoherent background intensity. Solid circles show the Q dependence of the ridge intensity along the $[0k0]$ direction, giving the magnetic form factor of the Co ion. The oscillation of the ridge intensity may be interpreted as the precursor of the onset of a 3D long-range order due to the interchain exchanges.

The temperature dependence of the ridge width was measured between 0.32 and 0.65 K, and the inverse correlation length κ of the chain was evaluated. As shown in Fig. 5, κ shows the linear dependence on temperature in this temperature range. With the use of the exchange constant $|J|/k_B=1.45$ K obtained by the bulk susceptibility measurements,[7] κ is expressed in reciprocal-lattice vector units (r.l.u.) as

$$\begin{aligned}&\kappa\sim 0.097T \text{ (r.l.u.)},\\ &\kappa\sim 0.609T \ (b_0^{-1}\text{units}),\\ &\kappa\sim 0.884k_BT/|J| .\end{aligned} \tag{2}$$

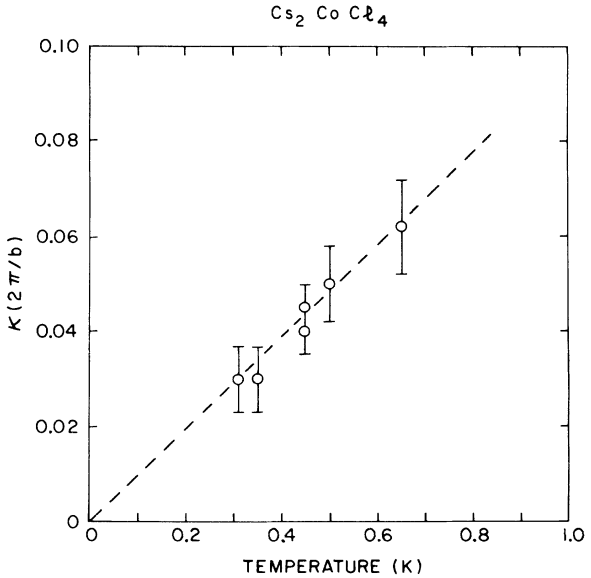

FIG. 5. Temperature dependence of the inverse correlation length κ in Cs_2CoCl_4.

According to the recent calculation on a 1D XY model with $S=\frac{1}{2}$ by Tonegawa,[4] the inverse correlation length κ_x for the in-plane component of spins follows $\kappa_x \sim 0.785 k_B T/|J|$ at the low temperatures, while the κ_z for the out-of-plane component of spins follows $\kappa_z \sim 3.14 k_B T/|J|$. Therefore, the observed κ in Cs_2CoCl_4 is in reasonable agreement with the temperature dependence of the κ_x. Note that the observed κ in our experiment is a mixture of S_{xx} and S_{zz}. Calculations[3,5] show that the amplitude of the S_{xx} near the sheet position is substantially stronger than that of the S_{zz}. Consequently, the intensity from κ_z is presumably masked by that from the S_{xx}. We attempted to observe the out-of-plane component κ_z separately from κ_x at the ridge. Since κ_z is roughly four times larger than κ_x, we expected that the ridge width becomes broader at larger h or l where the relative weight of the out-of-plane component increases in the scattering function. However, no appreciable change of the width was found.

Now we return to a discussion on the modulation of the diffuse scattering. The deviation of the ridge peak from the half-integer value is schematically shown by wavy curves in Fig. 2. This modulation may be understood by following model. The chemical unit cell of Cs_2CoCl_4 contains eight Co ions which form four chains along the b axis.[6] Two chains are shifted by $b_0/2$ with respect to the other two chains. Consequently, the configuration of the Co ions is very close to a body-centered orthorhombic lattice shown in Fig. 1. The important interactions are the intrachain exchange J, with two nearest-neighbor (NN) ions along the b axis, and the interchain exchange J', with eight next-nearest-neighbor (NNN) ions at the corners. When J and J' are both negative, they favor spins to align antiparallel to the nearest-neighbor spins and to the second-nearest-neighbor spins, but spins can never satisfy these conditions at the same time. A simplified model Hamiltonian for such a case may be written as

$$\mathcal{H}=-\sum_{\mathrm{NN}} J(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \eta S_i^z S_{i+1}^z) - \sum_{\mathrm{NNN}} J' \vec{S}_i \cdot \vec{S}_j \ . \tag{3}$$

The first term results in an antiferromagnetic configuration in the chains, whereas the second term causes the spins to rotate within the easy plane and stabilizes the incommensurate configuration. This spin structure is nothing but the helical structure along the b axis with a long period.[11] Because the second term is small, as seen from the good 1D character of Cs_2CoCl_4, the shift from the half-integer (commensurate value) is expected to be small.

The neutron scattering intensity which is proportional to $S(\vec{Q})$ takes maxima where $J(\vec{q})$ has minima. $J(\vec{q})$ is evaluated by taking the summation of the exchanges over the interacting neighbor spins for Cs_2CoCl_4:

$$J(\vec{q})=\sum_{\vec{r}} J(\vec{r}) e^{i\vec{q}\cdot\vec{r}} = 2J\cos(q_y)+8J'\cos(q_x/2)\cos(q_y/2)\cos(q_z/2) \ . \tag{4}$$

For example, we consider the wave-vector dependence along the k direction in the $(hk0)$ zone. Since the derivative of $J(\vec{q})$ with respect to q_y is written as

$$\frac{\partial J}{\partial q_y} = -2J\sin q_y - 4J'\cos(q_x/2)\sin(q_y/2)\cos(q_z/2), \tag{5}$$

the intensity maxima will occur at $\vec{q}$ which satisfies the following equation:

$$\sin(q_y/2)[J\cos(q_y/2)+J'\cos(q_x/2)\cos(q_z/2)]=0 \ . \tag{6}$$

Specifically, for the $[0k0]$ direction, the peaks will appear at

$$q_y = 2\cos^{-1}(-J'/J) \ . \tag{7}$$

It is easily seen from Eq. (7) that when J' vanishes, the chain exhibits the antiferromagnetic configuration, whereas a finite J' causes the shift of the peak of the quasielastic scattering $S(\vec{Q})$. From the observed peak position,

$$q_y \approx (0.515 \pm 0.005)\pi \ , \tag{8}$$

the ratio of J' to J is estimated to be 0.0471 ± 0.016. The peak position dependences on either h or 1 can be understood in the same manner. We illustrated the contour of $J(\vec{q})$ in the $(hk0)$ zone in Fig. 6 which is in good agreement with our observations.

Finally, we shall briefly discuss the spin waves in Cs_2CoCl_4. We carried out a limited number of inelastic scattering scans to study spin-wave excitations. The spectrometer was operated in a constant-Q mode with a final neutron energy of 4.4 meV and the collimators were all 40′, which gives an energy resolution of 0.11 meV (full width at half maximum). The spin-wave excitations were observed at $\vec{Q}=(0,1.5+\zeta,0)$ and $\vec{Q}=(2,0.5+\zeta,0)$ at

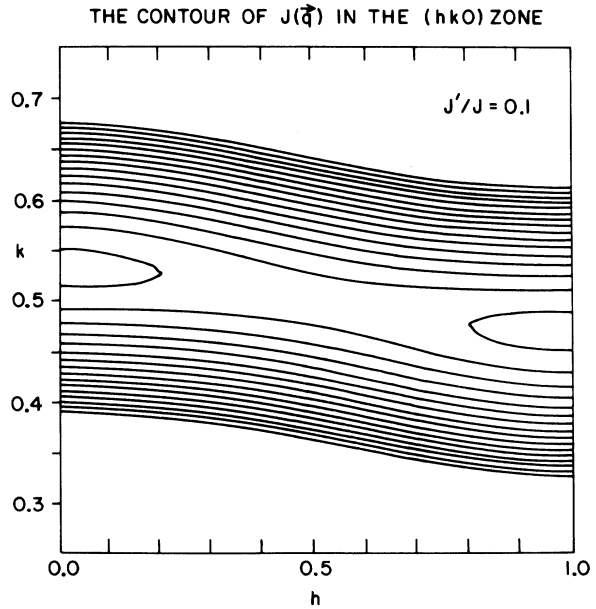

FIG. 6. Contour of $J(\vec{q})$ in the $(hk0)$ zone given by Eq. (4).

$T=0.3$ K. At the zone boundary, the well-defined spin-wave (SW) excitation was observed at 0.35 ± 0.05 meV.

The excitation spectrum of the 1D XY-Heisenberg antiferromagnet, Eq. (1), is expected to be a continuum[3,5] and its lower and upper boundaries are given by

$$E_{\text{lower}}(\zeta)=|I\sin 2\pi\zeta|\ ,\quad E_{\text{upper}}(\zeta)=2|I\sin\pi\zeta|\ , \tag{9}$$

where $I=(\pi J\sin\mu)/\mu$ and $\mu=\cos^{-1}\eta$. By assuming that the most spectral weight is concentrated in a region close to the lower boundary because of the antiferromagnetic nature of Cs_2CoCl_4, we estimated the J_{SW} with the use of $\eta=0.25$ and obtained

$$J_{SW}/k_B\simeq-1.76\pm0.25\ \text{K}\ . \tag{10}$$

Although this figure is slightly larger than the J values obtained from other measurements,[6,7] it certainly determines the upper limit of J. We also studied the line shapes of spin-wave excitations at the zone center in detail to detect the excitation continuum of the 1D chain. However, no sign of such a continuum was observed.

V. CONCLUSION

We confirmed that Cs_2CoCl_4 behaves as a 1D XY antiferromagnet with $S=\frac{1}{2}$. The inverse correlation length κ shows the linear dependence on the temperature between 0.3 and 0.6 K, with a slope consistent with the κ_x of the 1D XY model with $S=\frac{1}{2}$. Because of the weak interchain coupling, the sheet of the critical scattering was driven to the incommensurate position, and the helical spin structure along the chain direction is stabilized. A part of the work has been presented elsewhere.[12]

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