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Magnetic Structure of $CsCoCl_3$

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Neutron diffraction measurements were carried out on single crystals of $CsCoCl_3$, a quasi-one-dimensional antiferromagnet of Ising-like spins, in the long range ordered region. The determined magnetic structure at 4.2 K is composed of antiferromagnetic stacking of ferrimagnetic c-plane with three sublattices as determined by Melamud *et al.* The spins are aligned along c-axis and were evaluated to be 3.11 μ_B at 0 K by extrapolation. Unusual temperature dependence of magnetic reflection intensity was observed and interpreted as a partial disordering transition in which one of the three sublattices in a c-plane loses its magnetization above 13.5 K resulting in antiferromagnetic c-planes. This transition is discussed in connection with the antiferro-ferrimagnetic transition in the triangular Ising lattice. The critical exponent of the magnetization was found to be 0.34 around the Néel temperature 20.82 K.

§1. Introduction

Since Achiwa found the one-dimensional features in the magnetic properties of hexagonal ABX_3-type compounds, a number of magnetic studies have been carried out on these compounds. Due to the interchain magnetic interaction, these compounds undergo a magnetic transition into a long range ordered state at a temperature much below the temperature of maximum magnetic susceptibility or maximum specific heat characteristic of one-dimensional antiferromagnet. The intrachain short range ordering develops below these temperatures of maxima which give a measure of the intrachain magnetic interaction. The interchain interaction is estimated to be order of 10^{-2} weaker than the intrachain interaction in most of these compounds.[1,2] Not only the magnetic ion configuration in the lattice but also the antiferromagnetic short range ordering in the chains weaken the interchain interaction. The decoupling of the interchain interaction by the short range ordering is not effective in $CsCuCl_3$ because it exceptionally has modulated ferromagnetic chains.[3]

Even if the magnetic interaction is predominantly one-dimensional, the transition into a long range ordered state shows usually three-dimensional critical behavior. The magnetic properties in the long range ordered state inherit, however, the low dimensional character and are expected to yield informations about the magnetic interaction.

In a quasi-one-dimensional system, the short range order develops predominantly along the magnetic chains. When the short range order is well-developed at low temperatures, each magnetic chain would behave like a magnetic moment as a whole. The resultant magnetic structure in the plane perpendicular to the magnetic chains is often correlated to the two-dimensional spin system.

For example, neutron diffraction studies of $CsNiCl_3$[4–6] revealed that the spins in the c-plane perpendicular to the magnetic chains form a triangular structure. Triangular Heisenberg lattice with an antiferromagnetic interaction has the ground state of a triangular spin structure. It may, therefore, be concluded that the magnetic interaction between the magnetic chains is antiferromagnetic in Cs $NiCl_3$.

The same situation is expected in Ising-like spin system containing Co^{++} ions. Melamud *et al.*[7] determined the magnetic structure at 4.2 K by a neutron diffraction experiment on $CsCoCl_3$. The magnetic structure was composed of an antiferromagnetic stacking of collinear spin planes in which one third of spins are aligned oppositely to the remainder. The spin arrangement in the plane is exactly the ground state of triangular Ising lattice with an antiferromagnetic nearest neighbor interaction together with a weak ferromagnetic second neighbor interaction.

In the course of neutron diffraction study of $CsCoCl_3$, we found previously an anomalous temperature dependence of magnetic reflection intensity and Melamud *et al.*[7] and Yelon *et al.*[8] reported also the anomaly in $CsCoCl_3$ and $CsCoBr_3$, respectively. A recent calculation based on the molecular field approximation by one of the authors[9] showed a possible transition from a ferrimagnetic state into a partially disordered antiferromagnetic state below the Néel temperature in a two-dimensional triangular Ising lattice. According to the above-mentioned conjecture, the result may be applicable to the Co^{++} ion systems in hexagonal ABX_3-type compounds of which *c*-plane is a triangular lattice and the anomaly of the neutron diffraction intensity is possibly connected with the transition.

The present investigation was undertaken to study more closely the anomalous behavior of $CsCoCl_3$ by neutron diffraction measurements. The results will be discussed in connection with the transition in a triangular Ising lattice.

§2. Experimental

Neutron diffraction experiments were performed by the use of a conventional two-axis spectrometer at Research Reactor Institute of Kyoto University. Wave length of 1.02 Å was utilized. Specimen was cooled down to 2 K in a cryostat whose temperature was regulated within 0.1 K during a measurement.

Specimen was prepared from CsCl and $CoCl_2$ by melting. Pulverized specimen of about 20 g was used for powder diffraction measurements. Single crystals were grown in evacuated silica tubes by the Bridgman method. In the present investigation, six single crystals with dimensions of $8\sim10\times5\sim7\times3\sim5$ mm^3 were used because of fragmentary machine time of spectrometer. The $\lambda/2$ contribution was found to be 0.2~0.3%.

Extinction coefficient was determined for every crystal after Zachariasen's method[10] using absorption coefficient 0.708 cm^{-1}. The temperature factor for nuclear scattering yielded Debye temperature of 160 K consistently with the specific heat measurements.[11] Spherical magnetic form factors evaluated by Watson and Freeman[12] were used for the calculation of the magnetic structure factors.

§3. Results

The observed and the calculated structure factors of powder diffraction at 77 K and 4.2 K are compared in Table I. The reflection planes are indexed with respect to the chemical unit cell. The weighted *R*-factors in Tables are denfied by $R=\{\Sigma\omega(F^2_{\text{obs}}-F^2_{\text{cal}})^2/\Sigma\omega F^4_{\text{obs}}\}^{1/2}$.

Table II gives the nuclear structure factors obtained from the single crystal measurements.

Table I. Comparison of the observed and the calculated structure factors of powder diffraction of $CsCoCl_3$.

			77 K		4.2 K	
h	*k*	*l*	F^2_{obs}	F^2_{cal}	F^2_{obs}	F^2_{cal}
1	0	0	1.80	1.94	1.34	1.96
1/3	1/3	1	—	—	0.24	0.23
1	0	1	0.10	0.19	0.23	0.19
2/3	2/3	1	—	—	0.53	0.48
4/3	1/3	1	—	—	0.49	0.53
2	0	0	7.22	7.74	9.00	8.20
0	0	2	36.5	38.1	40.0	40.5
2	0	1	32.5	31.7	34.8	34.1
1	1	2	6.00	1.36		
2	1	1	9.32	8.69		
			$R=0.20$		$R=0.07$ $S_1=\ 2.90\,\mu_B$ $S_2=\ 2.90\,\mu_B$ $S_3=-3.05\,\mu_B$	

Table II. Comparison of the observed and the calculated nuclear structure factors of single crystal diffraction of $CsCoCl_3$. The observed values were reduced to those at 0 K using the Debye temperature, 160 K.

h	*k*	*l*	F^2_{obs}	F^2_{cal}
1	1	0	0.02	0.05
2	2	0	52.7	48.9
3	3	0	0.09	0.24
4	4	0	38.3	35.6
0	0	2	42.4	40.5
1	1	2	1.55	1.51
2	2	2	32.9	35.9
3	3	2	0.41	0.27
0	0	4	55.7	54.2
1	1	4	0.05	0.05
2	2	4	40.3	48.9
0	0	6	45.9	40.5
1	1	6	1.47	1.51
			$R=0.10$	

Table III. Comparison of the observed and the calculated magnetic structure factors of single crystal diffraction of $CsCoCl_3$.

			4.2 K		7.6 K		13.6 K	
h	k	l	F^2_{obs}	F^2_{cal}	F^2_{obs}	F^2_{cal}	F^2_{obs}	F^2_{cal}
0	0	1	0.000	0.000				
1/3	1/3	1	0.225	0.204	0.169	0.175	0.275	0.253
2/3	2/3	1	0.428	0.406	0.364	0.367	0.531	0.532
1	1	1	0.107	0.095	0.007	0.011	0.000	0.000
4/3	4/3	1	0.340	0.394	0.313	0.357	0.422	0.516
5/3	5/3	1	0.242	0.309				
7/3	7/3	1	0.139	0.156				
8/3	8/3	1	0.076	0.101				
1/3	1/3	3	0.000	0.011				
2/3	2/3	3	0.034	0.036				
4/3	4/3	3	0.094	0.074				
2	2	3	0.007	0.013				
1/3	1/3	5	0.006	0.001				
2/3	2/3	5	0.012	0.003				
			$R=$	0.17	$R=$	0.07	$R=$	0.11
			$S_1=$	2.66 μ_B	$S_1=$	1.70 μ_B	$S_1=$	0.00 μ_B
			$S_2=$	2.66 μ_B	$S_2=$	2.34 μ_B	$S_2=$	3.61 μ_B
			$S_3=$	-2.80 μ_B	$S_3=$	-3.21 μ_B	$S_3=$	-3.61 μ_B

As the measurements were carried out at various temperatures, the observed values were reduced to those at 0 K using the obtained Debye temperature, 160 K and are in good agreement with the calculated ones for the reported structure[13] isomorphous to $CsNiCl_3$. The values of the nuclear scattering lengths used are 0.55×10^{-12} cm and 0.25×10^{-12} cm and 0.96×10^{-12} cm for Cs,[14] Co[15] and Cl,[15] respectively. In the structure, Co atoms form a flat simple hexagonal lattice constituting magnetic chains along c-axis.

Magnetic structure factors at 4.2 K, 7.6 K and 13.6 K were obtained after corrections of the $\lambda/2$ mixing and the extinction as listed in Table III together with the calculated values. Magnetic reflections were observed in ($h/3$ $k/3$ l) plane, where integers, h and k are not a multiple of 3, and l is odd. This indicates that the magnetic unit cell is three times as large as the chemical one and that the spins in a chain are arranged antiferromagnetically. Each magnetic unit cell contains six Co atoms. In the structure, the magnetizations of sublattices neighboring along the c-axis have the same magnitude but the opposite direction with each other; $S_4=-S_1$, $S_5=-S_2$ and $S_6=-S_3$. In consequence, only three sublattice magnetizations S_1, S_2 and S_3 should be taken into consideration.

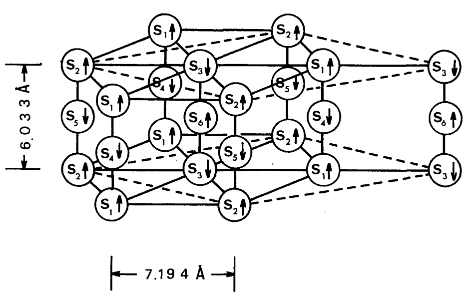

Fig. 1. Magnetic structure of $CsCoCl_3$. Dotted lines show magnetic unit cell. In the high temperature phase, spins of sublattices 1 and 4 are uncorrelated to those of other sublattices.

At 4.2 K, another type of magnetic reflections (h k l) for odd l was observed. If a c-plane would have no net magnetization, the (h k l) reflection should vanish. An antiferromagnetic stacking of ferrimagnetic c-planes with spins parallel to the c-axis as shown in Fig. 1 gave the best fitting of the calculated values to the data. The determined magnetic structure is the same obtained by Melamud *et al.*[7] Canting of spins from the c-axis did not improve the fitting. In the determined structure, the sublattice magnetization S_3 is aligned oppositely to the other two which were assumed to be eaual. This assumption is necessary because the individual magnetization of the three sublattices can not be determined definitely from the $(h/3\ k/3\ l)$ and the $(h\ k\ l)$ reflection intensities and only two independent equations relating the three sublattice magnetizations to each other are obtained therefrom.

At 13.6 K, the $(h\ k\ l)$ reflection vanishes and each c-plane should be antiferromagnetic, or $S_1+S_2+S_3=0$. Among possibilities like triangular spin structures, the best fitting to the observed magnetic structure factors was obtained by the partially disordered collinear spin structure. The R-factor for the triangular spin structures could not be reduced to a value smaller than 0.22. In the determined structure, one of the three sublattices loses its magnetization resulting antiferromagnetic c-plane of the other two sublattices, that is, $S_1=0$ and $S_2=-S_3$. But it is to be noted that the short range ordering in each magnetic chain remains unaltered. It may, therefore, be more suitable to say that the spins in one-third of magnetic chains are uncorrelated to those in the other two-thirds. Another model with $S_1=S_2=-S_3/2$ giving the same structure factors is rather artificial and quite unlikely.

In the magnetic structure at 7.6 K, three sublattice magnetizations are different from

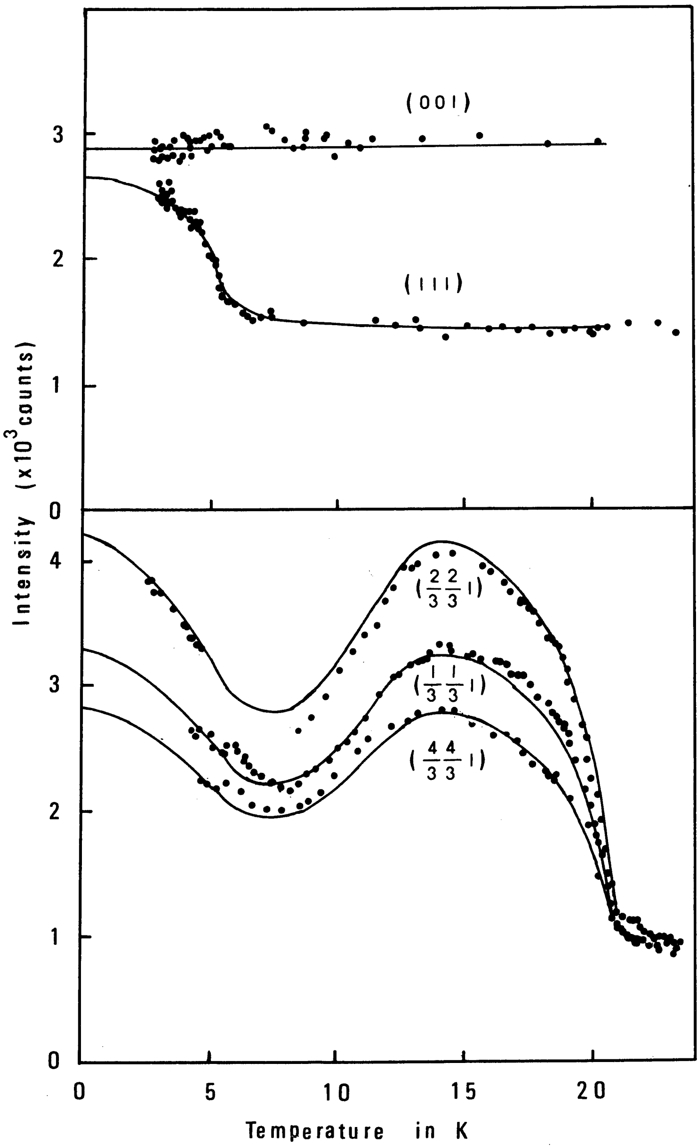

Fig. 2. Temperature dependence of peak intensity of typical magnetic reflections. Solid curves are calculated values for sublattice magnetizations given in Fig. 3.

each other. The structure is an intermediate one between the high temperature structure and the low temperature one. Individual magnetization was determined so as to be compatible with temperature variation.

The temperature dependences of the diffraction peak intensities for some typical planes were measured as shown in Fig. 2. Figure 3 shows the probable temperature dependences of sublattice magnetizations on the basis of the model in the following section. Other possibilities compatible with the data yield also similar characteristic temperature dependences to the one in Fig. 3. The solid curves in Fig. 2 are the reflection intensity for the sublattice magnetization in Fig. 3. The calculated values were normalized at 4.2 K to the observed one. As seen in Fig. 3, the transition into partially disordered phase is completed at 13.5 K. The region between 5.5 K and 13.5 K is the intermediate region where three sublattice magnetizations have different magnitude from each other.

The magnetic moments at 4.2 K were evaluated from the single crystal diffraction to be $2.66\pm0.1\ \mu_B$ for S_1 and S_2 and $2.80\pm0.1\ \mu_B$ for S_3. Powder diffraction gave slightly larger values; $2.90\pm0.25\ \mu_B$ and $3.05\pm0.25\ \mu_B$, respectively. Melamud *et al.* obtained $2.3\ \mu_B$ from the single crystal diffraction and $3.0\ \mu_B$ from the powder diffraction.[7] The magnetic moment extrapolated to 0 K is $3.24\pm0.15\ \mu_B$ irrespective of sublattice.

The Néel temperature was determined to be 20.82 ± 0.10 K from $(h/3\ k/3\ l)$ reflections in good agreement with the temperature of specific heat anomaly, 20.85 K,[11] although Melamud *et al.*[7] determined it to be 21.5 K. The magnetic peak intensities observed in the vicinity of the Néel temperature are shown in Fig. 4. The evaluated critical exponent for magnetization has an average of 0.34 ± 0.01 which may possibly be affected by critical scattering. Theoretical values for three-dimensional and two-dimensional Ising lattices are 0.312 and 0.125,[16] and the experimental values for Ising-like antiferromagnets, $CsCoBr_3$[8] and $CsCoCl_3\cdot2H_2O$[17] are 0.306 and 0.44, respectively.

§4. Discussions

The present results are featured by the extraordinary temperature dependence of sublattice magnetizations. This temperature dependence is interpreted by the partial disordering transition.

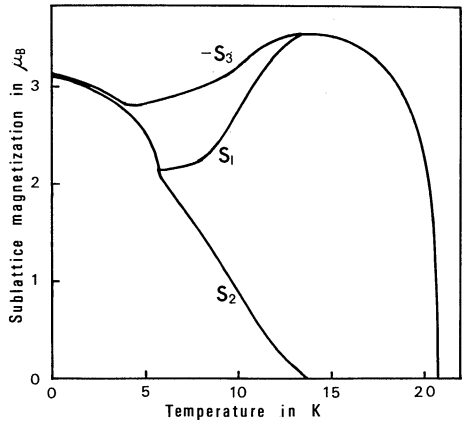

Fig. 3. Probable temperature dependence of sublattice magnetizations.

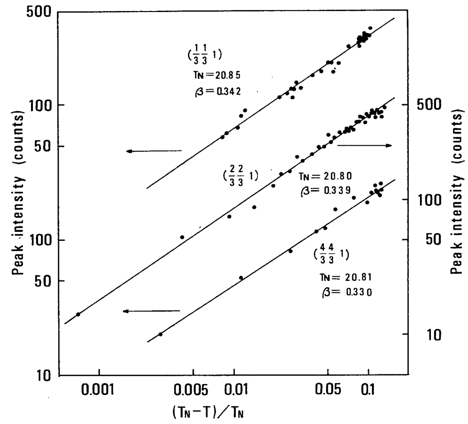

Fig. 4. Temperature dependence of peak intensity in the vicinity of the Néel temperature.

The g-factor of Co^{++} ions in $CsCoCl_3$ is very anisotropic; $g_{//}=7.4\pm0.3$ and $g_\perp=4.3\pm0.2$ for fictitious spin $S=1/2$.[1] The spin wave spectrum obtained by an inelastic neutron diffraction study gave the fraction of x-y component of the exchange interaction to be 9.4%.[18] These facts indicate the Ising character of the present system.

The magnitude of the intrachain exchange interaction was estimated from the magnetic susceptibility[1] and the spin wave spectrum[18] to be -86 K and -74.7 K, respectively, so that well-developed ordering in the magnetic chains is expected at the Néel temperature.

The residual magnetic entropy at the Néel temperature was evaluated to be 21% from the specific heat measurements.[11)] Owing to the well-developed short range ordering in the chains, we may regard each magnetic chain approximately as a magnetic moment below the Néel temperature. Consequently, it may be sufficient to take into consideration of two-dimensional ordering of the magnetic chains and $CsCoCl_3$ may be correlated to the triangular Ising lattice. Actually, the determined *c*-plane structure of the low temperature phase is identical to the ground state of the triangular Ising lattice with antiferromagnetic nearest neighbor interaction J_1 and ferromagnetic second neighbor interaction J_2.

A second-order transition from a ferrimagnetic state to a partially disordered antiferromagnetic state was predicted in a triangular Ising lattice.[9)] In the system with $0>J_2/J_1>-0.8$, the partially disordered antiferromagnetic state which has a slightly higher energy than the ferrimagnetic ground state becomes stable at high temperatures due to large entropy. In the ferrimagnetic state, one of three sublattices has an opposite magnetization to the other two with an equal magnitude. As temperature is raised, a transition into the antiferromagnetic state in which one of the latter two sublattices is disordered, occurs through an intermediate state with three different sublattice magnetizations. The J_2 stabilizes the ferrimagnetic state and the transition temperature rises as $|J_2/J_1|$ is increased.

Figure 5 shows an example of the temperature dependences of sublattice magnetizations for $J_2/J_1=-0.4$ calculated by the molecular field approximation. These theoretical curves have common features to the observed one given in Fig. 3. It is concluded that the partial disordering transition in $CsCoCl_3$ is a kind of the antiferro-ferrimagnetic transition in the triangular Ising lattice.

The notable differences between Fig. 3 and Fig. 5 are the width of the intermediate region and the marked increase of the magnitude of S_3 in the high temperature phase. The magnitude of S_3 in Fig. 5 decreases monotonically with increasing temperature. These disagreements are not explainable at present, but may be due to the difference in spin-flip between single spin and almost ordered magnetic chain.

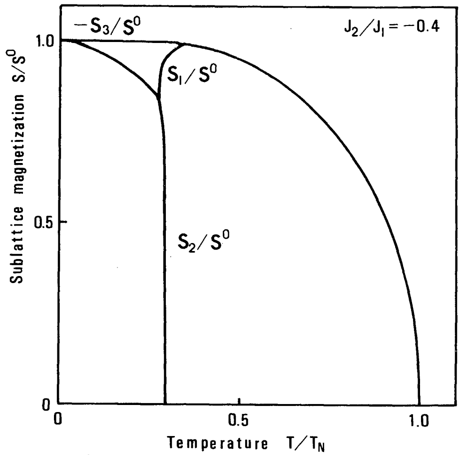

Fig. 5. Calculated temperature dependence of sublattice magnetizations of triangular Ising lattice with antiferromagnetic nearest neighbor interaction J_1 and ferromagnetic second neighbor interaction J_2.

The broad hump of the temperature dependence curve of the (2/3 2/3 1) reflection around 14 K shown in Fig. 2 is difinitely higher than that of the reported one[7)] indexed as (2 0 1). Only one single crystal measured in the present study gave the hump as low as the reported one. The hump seems possibly to be sensitive to the condition of the crystal.

Any anomaly of the specific heat due to the partial disordering transition has not been detected so far.[11)] The absence of the anomaly is rather plausible if one considers the spin number associated to the transition is order of $N^{2/3}$ for total spin number N, because of well-developed short range order.

An isomorphous compounds $RbCoCl_3$ and $CsCoBr_3$ are expected to show an analogous magnetic behavior. Actually, $RbCoCl_3$ has the same magnetic structure to that of CsCo Cl_3 at low temperatures.[19)] In $CsCoBr_3$ a similar temperature dependence of neutron diffraction intensity has been reported[8)] although the broad humps in the temperature dependence curves of $(h/3\ h/3\ l)$ are less prominent than in $CsCoCl_3$. The deduced magnetic structures are the same to the present ones except a small canting of spin from the *c*-axis. The definite difference in the analysis is in the intermediate region between the two phases. According to the paper, the two phases coexist in the region. But if the partial disordering model is applicable to $CsCoCl_3$, the transition should be of second order and is not compatible with the coexistence of the two phases. The present experiment, however, can not confirm the character of the transition.

The magnetic moment evaluated by the extrapolation to 0 K amounts to 3.11 μ_B as compared $g_{//}S=3.70\,\mu_B$ for the ground state. The difference between these two values may be partly attributed to spin contraction which is prominent in low dimensional and low spin state. In $CsNiCl_3$, the difference is unexpectedly large.$^{6)}$ It is notable that the sublattice magnetizations at 13.6 K are almost equal to that of the ground state.

If energy difference between triangular spin structure and partially disordered collinear spin structure is small enough by some causes in triangular Heisenberg lattice, a partial disordering analogous to the present one is possibly to occur due to entropy gain at high temperatures. The magnetic transition found just below the Néel temperature in $CsNiCl_3$$^{20-22)}$ may possibly be attributed to the transition from the triangular spin structure into a partially disordered collinear spin structure. The experimental results so far obtained, NMR, specific heat and neutron diffraction, are compatible to this conjecture.

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