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Magnetic Ordering and Low Ni^{2+} Moment in CsNiCl_3[†]

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The magnetic structure of CsNiCl_3 has been carefully reexamined by single-crystal neutron diffraction techniques in view of an apparent inconsistency between previous powder neutron diffraction results and a recent NMR investigation. Intensity data were collected from two different-sized crystals taken from the sample used in the NMR study, and corrected for absorption and extinction effects. These data confirm that there is an antiferromagnetic transition at 4.3 °K to the triangular arrangement of moments deduced in the previous study. In the region between 4.3 and 2.7 °K the sublattice magnetization has a critical exponent β of 0.27 ± 0.03. A particularly striking result is that the magnitude of the Ni^{2+} moment extrapolated to 0 °K is only $(1.0_5 \pm 0.1)\mu_B$, indicative of very substantial zero-point deviation effects.

I. INTRODUCTION

A great deal of attention is currently being focused on double halides which exhibit one- or two-dimensional magnetic properties. One of these is CsNiCl_3, in which there are chains of octahedrally coordinated Ni^{2+} ions along the c axis which are separated in the basal plane by about 7 Å. At low temperatures the compound shows many of the characteristics of a linear antiferromagnet.[1]

Recent powder[2] and single-crystal[3] neutron diffraction studies have shown that the compound undergoes an antiferromagnetic transition at about 4.5 °K to an ordered structure in which the moments form a triangular array. However, single-crystal NMR data appear to be consistent with a collinear structure and not with this arrangement.[4] In view of the rather limited scope of the previous neutron studies, and in order to check whether the properties are sensitive to differences in sample composition as appears to be the case in isostructural RbNiCl_3,[2,5] accurate neutron data have been obtained from high-purity crystal samples of CsNiCl_3 grown by Peirce[6] for the NMR experiments. The results are in excellent agreement with the triangular model if the spin plane is assumed to be oriented perpendicular to the basal plane. Sample differences can therefore be ruled out as a possible explanation. Of particular interest is the fact that an abnormally low value of $1.05\mu_B$ is obtained for the Ni^{2+} moment extrapolated to 0 °K.

II. NUCLEAR STRUCTURE REFINEMENT

The CsNiCl_3 crystal was one obtained from the melt by the Bridgman technique. A fragment from this measuring approximately 8×5×4 mm was used initially; however, when it became apparent at an early stage that substantial corrections for extinction and absorption were required, a more extensive set of data was collected from a much smaller piece measuring about 3×1.5×1.5 mm. In each case, the c axis lay roughly along the longest edge.

The crystals were mounted with their (100) cleavage faces horizontal on a pedestal inside aluminum sample holders filled with helium gas to provide adequate thermal conductivity. Temperatures were measured by means of a germanium resistor buried in a copper block to which the sample holder was attached. Data from the (hhl) zone were first collected with neutrons of 1.03-Å wavelength from the larger of the two crystals at 1.83 and 50 °K. Within statistical limits, the intensities at the nuclear positions were identical at the two temperatures. The measured values were corrected for absorption, which is quite appreciable in this material ($\mu \sim 0.7\ \mathrm{cm}^{-1}$). A rough comparison of observed and calculated intensities revealed that the strong peaks were appreciably affected by extinction, and a least-squares fit to the data was carried out with an extinction coefficient included as a variable parameter.[7,8] Final values of the parameters which were varied are listed in Table I, and include an instrumental constant k for scaling the calculated

TABLE I. Final parameter values obtained from refinement of nuclear intensity data from CsNiCl_3. Standard errors are given in parentheses and refer to the least significant digit(s). The weighted R factor R_w is $[\sum w(I_{\mathrm{obs}}-I_{\mathrm{calc}})^2/\sum w(I_{\mathrm{obs}})^2]^{1/2}$.

	Larger crystal (50 °K)	Smaller crystal (1.67 °K)
x_{Cl}	0.1545(20)	0.1548(1)
$B_{\text{over-all}}$ (Å^2)	...	0.25(4)
Extinction coefficient	$0.75(28)\times10^3$	$1.69(17)\times10^3$
Scale constant	6.82(40)	0.2382(49)
R_w	0.100	0.035

TABLE II. Comparison of observed and calculated nuclear intensities for $CsNiCl_3$. I_{obs} is the observed intensity corrected for absorption and I_{corr} is I_{obs} corrected for extinction. Scattering lengths taken as 0.55, 1.03, and 0.963×10^{-12} cm for Cs(Ref. 9), Ni(Ref. 10), and Cl (Ref. 10), respectively. Parameters as in Table I.

	Larger crystal			Smaller crystal		
hkl	I_{obs}	I_{corr}	I_{calc}	I_{obs}	I_{corr}	I_{calc}
110	338	356	382	11.8	12.3	13.1
002	3874	5221	4151	116.1	143.8	142.9
112	1117	1239	1080	34.5	37.2	36.9
220	4036	7228	8084	175.7	291.2	272.7
222	1428	1726	1885	53.1	61.6	63.0
004	5441	8546	7504	177.7	247.8	247.4
114	161	164	156	5.4	5.5	5.1
330				10.2	10.5	10.7
224				132.6	180.8	176.5
332				9.7	10.0	9.9
006				43.3	47.4	49.0
116				15.9	16.4	15.9
334				8.4	8.6	8.5
440				80.8	100.4	109.1

to the observed intensities. These are listed in Table II.

A more extensive set of data was obtained at 1.67 °K from the smaller of the two crystals. Several equivalent pairs of reflections of the type (*hhl*) and ($hh\bar{l}$) were measured and found to agree within 5% in each case. Final least-squares parameters and corresponding intensities are listed in Tables I and II, respectively, and agreement is seen to be very satisfactory. It is to be noted that the extinction coefficient is considerably larger for the smaller crystal, reflecting a higher degree of perfection which was also apparent from the reduced width of the rocking curve.

III. MAGNETIC STRUCTURE REFINEMENT

At the lower temperatures a number of additional peaks of the type $(\frac{1}{3}h\frac{1}{3}hl)$ with $h \neq 3n$ and $l = 2n+1$ were observed. (All indices in the paper are based on the chemical unit cell.) This is a characteristic feature of the triangular structure found previously. The intensities were quite small compared to those of the nuclear peaks, the strongest magnetic peak having less than 0.5% of the intensity of the strongest nuclear peak. The intensities of eleven reflections from the smaller crystal were measured at 1.67 °K. Equivalent pairs $(\frac{1}{3}h\frac{1}{3}hl)$ and $(\frac{1}{3}h\frac{1}{3}h\bar{l})$ were found to agree to within 5–10%. The mean values were corrected for absorption, extinction effects being completely negligible. A more limited set of data was obtained at 1.83 °K from the larger crystal and corrected in a similar fashion.

Attempts were made to fit the data to a number of different magnetic models by least-squares analysis. The form factor $f(x)$ was assumed to have the form $f_0(Kx)$, where f_0 is the free atom spherical form factor,[11] x is $(\sin\theta)/\lambda$ and K is a scaling constant. This is a simple empirical way of allowing for differences between observed and calculated form-factor curves which might arise from covalency effects,[12] for example, and gives good results in the case of NiO.[13] Both the moment and K were treated as variables in the least-squares analysis, and the other variables, including the instrumental scale constant, were fixed at the values determined by the nuclear refinement.

The results of the various refinements are summarized in Table III. Model I represents the triangular configuration with the moments lying in the (001) plane. In models II*a* and II*b* the moments are assumed to lie in a plane perpendicular to (001), with model II*a* corresponding to the case in which there are equal fractions of equivalent domains. Model II*b* corresponds to the single-domain case, in which the orientation of the spin plane is an additional variable which can also be determined. Models III, IV*a*, and IV*b* describe sinusoidal arrangements with the same periodicity as the triangular structure, but in which only the components along one direction are ordered. In model III, this direction is the *c* axis, while models IV*a* and IV*b* are the multidomain and single-domain cases, respectively, with the spin direction lying in the basal plane. Once again, in the latter case, the spin direction can be determined. These various arrangements are depicted schematically in Fig. 1.

One other model which also gives magnetic peaks in these positions is the collinear arrangement V shown in Fig. 1. However, as previously noted, this structure can be ruled out because of the absence of a significant magnetic contribution to the (111) reflection. This is a forbidden nuclear reflection, but some multiple Bragg scattering was observed. There was no significant difference in intensities at 1.67 and 5 °K, the statistical error being less than 10% of the required intensity for this model. There do not appear to be any other collinear structures which can account for the ob-

TABLE III. Final values of moment (μ), form-factor scaling coefficient (K), and weighted R factor (R_w) for the various magnetic models described in text for the smaller $CsNiCl_3$ crystal at 1.67 °K. See also Fig. 1.

Model	Orientation	$\mu(\mu_B)$	K	R_w
I	(001)	0.79(4)	0.91(7)	0.293
II*a* (multidomain)	⊥(001)	0.93(2)	0.85(2)	0.094
II*b* (single domain)	⊥(001)[a]	0.92(2)	0.85(2)	0.093
III	[001]	1.55(17)	0.99(16)	0.510
IV*a* (multidomain)	⊥[001]	1.12(6)	0.91(7)	0.294
IV*b* (single domain)	⊥[001][b]	1.02(3)	0.87(4)	0.158

[a] Normal to spin plane at 39° to [110].

[b] Spin direction at 90° to [110].

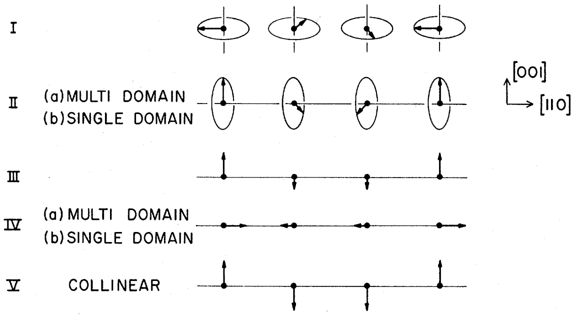

FIG. 1. Various magnetic models described in text. Each moment is antiparallel to adjacent c-axis neighbors.

served magnetic reflections.

From Table III it is evident that model II, the triangular arrangement with the moments oriented in a plane perpendicular to (001), gives significantly the best agreement. It is to be noted that with this crystal orientation, the data do not allow a choice to be made between the multidomain and the single-domain cases; in fact, if the normal to the spin plane is inclined at 45° to [110], the calculated structure factor expressions are identical. As noted previously, it is also impossible from a neutron diffraction experiment to determine the absolute direction of the moments within the spin plane.

The final magnetic parameter values for both crystals are summarized in Table IV, and the corresponding intensities in Table V. Figure 2 shows the observed and calculated form-factor values.

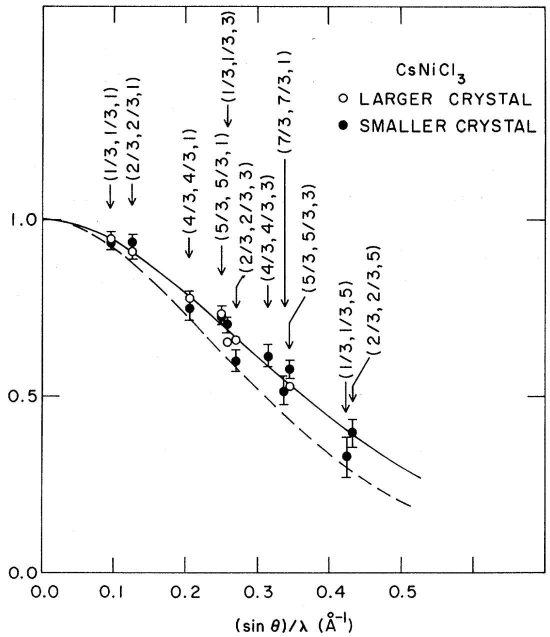

FIG. 2. Experimental form-factor values for Ni^{2+} in $CsNiCl_3$ for triangular model II*a*. Broken line is the theoretical $\langle j_0 \rangle$ curve (Ref. 11). Solid line is this curve with $(\sin\theta)/\lambda$ scaled by 0.85 as described in text. Error bars for larger crystal are about the size of the circles.

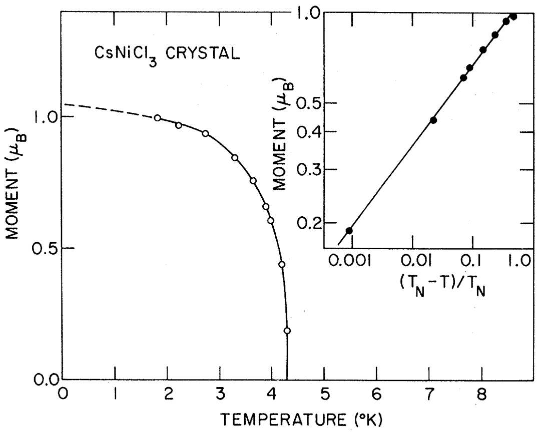

FIG. 3. Variation of Ni^{2+} moment in $CsNiCl_3$ with temperature. Insert illustrates the fit to the expression $M(T) \propto (1 - T/4.29)^{0.27}$.

The errors listed in the moments do not include possible errors in the instrumental scale constants, which were fixed during the refinements of the magnetic data. If these are taken into account, the two sets of data compare quite well.

IV. TEMPERATURE DEPENDENCE OF MAGNETIC MOMENT

The intensity of the $(\frac{1}{3}\frac{1}{3}1)$ reflection from the larger crystal was measured as a function of temperature, and the temperature dependence of the sublattice magnetization is plotted in Fig. 3. Very rough corrections for critical scattering have been made to the two points closest to T_N. In the region between 2.7 and 4.3 °K, the data can be fitted well to an expression of the type $M(T) \propto (1 - T/T_N)^{\beta}$. A least-squares fit of the data yields $T_N = 4.29$ °K and $\beta = 0.27$. The absolute error limits, which are considerably larger than the standard deviations, are in the region of ±0.1 °K and ±0.03, respectively. Mekata *et al.*[3] obtained a value of 0.35±0.05 for β from the temperature dependence of the peak intensity.

TABLE IV. Final parameter values obtained from refinement of magnetic intensity data from $CsNiCl_3$. Standard errors are given in parentheses and refer to the least significant digit.

	Larger crystal (1.83 °K)	Smaller crystal (1.67 °K)
$\mu(\mu_B)$	1.00(2)	0.93(2)
K	0.87(3)	0.85(2)
R_w	0.031	0.094

TABLE V. Comparison of observed and calculated magnetic intensities for $CsNiCl_3$. I_{obs} is the observed intensity corrected for absorption. I_{calc} has been calculated for model II*a* with the parameters listed in Table IV. Intensities are on the same relative basis as the nuclear ones in Table II. All indices are based on the chemical unit cell.

	Larger crystal (1.83 °K)		Smaller crystal (1.67 °K)	
hkl	I_{obs}	I_{calc}	I_{obs}	I_{calc}
$\frac{1}{3}\frac{1}{3}1$	22.1	21.9	0.665	0.671
$\frac{2}{3}\frac{2}{3}1$	18.0	17.9	0.578	0.546
$\frac{4}{3}\frac{4}{3}1$	9.0	9.1	0.251	0.278
$\frac{5}{3}\frac{5}{3}1$	6.9	6.3	0.199	0.190
$\frac{1}{3}\frac{1}{3}3$	3.7	4.1	0.128	0.123
$\frac{2}{3}\frac{2}{3}3$	3.8	3.8	0.092	0.115
$\frac{4}{3}\frac{4}{3}3$	...	...	0.091	0.084
$\frac{7}{3}\frac{7}{3}1$	...	...	0.075	0.085
$\frac{5}{3}\frac{5}{3}3$	2.3	2.2	0.078	0.067
$\frac{1}{3}\frac{1}{3}5$	...	...	0.017	0.025
$\frac{2}{3}\frac{2}{3}5$	...	...	0.025	0.024

The temperature dependence data in Fig. 3 yield a value for the Ni^{2+} moment extrapolated to 0 °K which is clearly about $1.05\mu_B$, with over-all error limits certainly no higher than $\pm 0.1\mu_B$. This is a strikingly low figure, appreciably less than the value of $1.5\mu_B$ recorded in the previous powder study. However, the powder figure is subject to rather large errors in view of the weak magnetic scattering and uncertainties in the background. The observed moment is also lower than the figure of $1.3\mu_B$ at 2 °K obtained by Mekata *et al.* by direct comparison of the relative intensities of $(\frac{1}{3}\frac{1}{3}1)$ and (220). Because of the presence of substantial extinction effects, the same procedure for the larger of the two crystals in the present case would yield a value around $1.5\mu_B$.

Ni^{2+} with roughly octahedral coordination in simple predominantly ionic compounds is normally found to have a moment around $2\mu_B$. While covalency effects can certainly be expected to produce some reduction in its moment,[12] the general similarity of the observed form factor with that of Ni^{2+} in NiO[13] would indicate that these fall far short of accounting for the low observed value of $1.05\mu_B$. A more likely explanation is the existence of very pronounced zero-point spin deviation effects amounting to some 40–45% which reflect the basically one-dimensional nature of the magnetic order. It is hoped that a study of $CsMnBr_3$ which is currently in progress will provide further evidence of such effects.

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