to reflect different effective Debye temperatures seem capable of producing the curve in Fig. 2, nor of giving an entropy change of $R\ln(2S+1)$ for each material. The ac method has been essential for the observation of the extremely small peaks at the ordering temperatures and the high resolution possible has facilitated the extraction of the broad magnetic contribution to the specific heat.

We conclude that thermodynamic measurements give further evidence that the ordering of the planar antiferromagnets K_2MnF_4 and K_2NiF_4 is of the Stanley–Kaplan type, with the anisotropy and three-dimensional nature of the ordered phase making only minor modifications in the over-all behavior.

Note added in proof. Yamada[22] has recently obtained similar results for the two-dimensional Heisenberg ferromagnet K_2CuF_4. The specific heat of that material does not fall on the curve of Fig. 7, but rather, resembles the curve of Fig. 5 with $\eta \cong 0.25$.

ACKNOWLEDGMENT

One of us (M. B. S.) wishes to acknowledge the hospitality of the Institute for Solid State Physics, University of Tokyo, where a portion of this research was performed while the author was a visiting scientist.

†Supported in part by the ARPA under Contract No. HC-15-67-C-0221 and by the National Science Foundation under Grant No. GH33750.

*Alfred P. Sloan Research Fellow.

[1]N. D. Mermin and H. Wagner, Phys. Rev. Letters 17, 1133 (1966).

[2]H. E. Stanley and T. A. Kaplan, Phys. Rev. Letters 17, 913 (1966).

[3]R. Birgeneau *et al.*, Phys. Rev. B 1, 2211 (1970); Phys. Rev. B 3, 1736 (1971).

[4]H. Ikeda and K. Hirakawa, J. Phys. Soc. Japan 33, 393 (1972); and (unpublished).

[5]M. E. Lines, Phys. Rev. 164, 736 (1967).

[6]M. E. Lines, Phys. Rev. B 3, 1749 (1971).

[7]V. Mubayi and R. V. Lange, Phys. Rev. 178, 882 (1969).

[8]Y. Kuramoto, Progr. Theoret. Phys. 46, 1293 (1971).

[9]M. B. Salamon and I. Hatta, Phys. Letters 36A, 85 (1971).

[10]L. P. Kadanoff *et al.*, Rev. Mod. Phys. 39, 395 (1967).

[11]M. B. Salamon, Phys. Rev. B 2, 214 (1970).

[12]P. R. Garnier, Ph.D. thesis (University of Illinois, 1972) (unpublished).

[13]D. J. Breed, Physica 37, 35 (1967).

[14]K. G. Srivastava, Phys. Letters 4, 55 (1963).

[15]M. Suzuki, Physics Letters 35A, 23 (1971).

[16]R. J. Birgeneau, F. DeRosa, and H. J. Guggenheim, Solid State Commun. 8, 13 (1970).

[17]M. E. Fisher and R. Burford, Phys. Rev. 156, 583 (1967).

[18]G. S. Joyce, Phys. Rev. 146, 349 (1966).

[19]J. D. Gunton and M. J. Buckingham, Phys. Rev. 166, 152 (1968).

[20]E. P. Maarshall, A. C. Botterman, S. Vega, and A. R. Miedema, Physica 41, 473 (1969).

[21]H. E. Stanley, Phys. Rev. Letters 20, 150 (1968).

[22]I. Yamada, J. Phys. Soc. Japan 33, 979 (1972).

PHYSICAL REVIEW B VOLUME 7, NUMBER 5 1 MARCH 1973

Magnetic Transitions in $CsNiCl_3$†

W. B. Yelon and D. E. Cox

Brookhaven National Laboratory, Upton, New York 11973

(Received 28 August 1972)

Recent NMR and specific-heat measurements have revealed the presence of magnetic phase transitions in $CsNiCl_3$ at 4.85 and 4.4 °K. Previous neutron-diffraction studies have revealed only one transition and we have, therefore reexamined a single crystal of $CsNiCl_3$ in the temperature range 1.6–5.0 °K by means of this technique. The use of neutrons of wavelength of 2.46 instead of 1.03Å gives improved resolution and peak-to-background ratio, and our study confirms the presence of two magnetic phase transitions. The first of these corresponds to the onset of antiferromagnetic order and the second is interpreted as a 90° reorientation of the basal-plane component of the magnetic moment. In addition, the triangular structure observed at 1.6 °K has been found to undergo considerable modification as the temperature approaches 4.4 °K.

I. INTRODUCTION

Previous neutron-diffraction studies[1–3] of $CsNiCl_3$, which exhibits many of the characteristics of a one-dimensional antiferromagnet, have revealed a magnetic structure in which there are linear antiferromagnetic chains along the hexagonal c axis coupled together in a triangular array with the moments lying in a plane perpendicular to the basal plane. The Néel temperature derived from

these measurements has been reported as 4.6 [2] and 4.3 °K,[3] and an interesting feature is the anomalously low value of about 1 μ_B at 0 °K observed for the Ni^{2+} moment.

Recent NMR[4] and specific-heat[5] measurements have revealed the presence of two magnetic transitions, however; the first at 4.85 °K and the second at 4.40 °K. In this region, the neutron-diffraction measurements suffer from a combination of weak signal and quite high background, and the temperature dependence of the magnetic scattering in this range was interpreted as being indicative of critical-type behavior. In the present paper, we describe a more detailed high-resolution neutron investigation in which the data were obtained with neutrons of wavelength 2.46 Å from the larger of the two crystals used in the previous study,[3] and we have confirmed the existence of two transitions. The low-temperature triangular structure observed at 1.6 °K undergoes considerable modification as the temperature is increased and the unusual temperature dependence of the perpendicular component is interpreted as arising from a 90° reorientation of this component within the basal plane, consistent with the NMR data. The results illustrate that the magnetic structures of materials of this type must depend upon a delicate balance between anisotropy, crystal field effects, and weak basal-plane exchange.

II. STRUCTURE REFINEMENT

Data were taken in the (*hhl*) zone at a number of temperatures between 1.6 and 5.0 °K. The improved resolution resulting from the use of longer-wavelength neutrons (2.46 Å) is accompanied by a significant improvement in a peak-to-background ratio in comparison to the previous studies of $CsNiCl_3$. Against this, however, is the fact that far fewer reflections were accessible and a complete nuclear structure refinement was not possible. The data were therefore fitted with only the scale factor and extinction as variable parameters. The over-all temperature factor and Cl positional parameter were held fixed at the values determined in the previous study.[3] Nuclear intensities were measured at several temperatures and no dependence on temperature was observed.

Magnetic peaks were observed only at positions $(\frac{1}{3}h\ \frac{1}{3}h\ l)$ with l odd and $h \neq 3n$. At a number of temperatures, data were taken for both $(\frac{1}{3}h\ \frac{1}{3}h\ l)$ and $(\frac{1}{3}\bar{h}\ \frac{1}{3}\bar{h}\ l)$ reflections, and were found to agree within 5 to 10%. Eight inequivalent magnetic reflections, of which two had less than the observable minimum intensity, were studied. The temperature dependence of the intensities of the three strongest magnetic peaks is shown in Fig. 1(a). Of particular significance is the fact that the ratio between the intensities of $(\frac{1}{3}\ \frac{1}{3}\ 1)$ and $(\frac{4}{3}\ \frac{4}{3}\ 1)$ is constant [Fig. 1(b)] above 4.4 °K, but decreases continuously as the temperature is lowered.

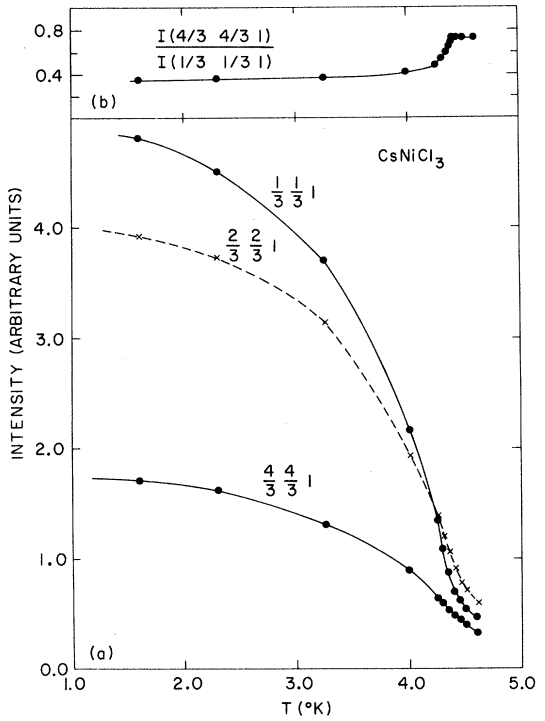

FIG. 1. (a) Intensities of the three strongest magnetic peaks in $CaNiCl_3$ as a function of temperature. (b) The ratio of intensities of the $(\frac{1}{3}\ \frac{1}{3}\ 1)$ and $(\frac{4}{3}\ \frac{4}{3}\ 1)$ reflections showing a sharp change around 4 °K and a constant ratio above 4.4 °K.

Previous experience with the low-temperature structures of $CsNiCl_3$ and $RbNiCl_3$ [6] suggested that the data might be fitted to the modified triangular model (I) shown in Fig. 2, in which it is assumed that there are equal fractions of equivalent domains. In this case, since the intensity of the (111) reflection was found to be zero, the c-axis component of the moment on site II (μ_{II_z}) must equal $-\frac{1}{2}\mu_I$ within experimental error limits. Therefore there are only two parameters to be fitted, μ_I and θ (or $\mu_\perp$), as the orientation of the basal-plane component cannot be determined from neutron data in a multi-domain crystal. At all temperatures studied, this model gave a satisfactory fit to the data (Table I) with weighted R factors $\{R_W = [\sum W(I_{obs} - I_{calc})^2 / \sum W(I_{obs})^2]^{1/2}\}$ between 5 and 8%, and the results are shown in Figs. 3(a) and 3(b). In these calculations, the theoretical Watson–Freeman form factor was adjusted by a scaling factor [$f_{scaled} = f(\kappa \sin\theta/\lambda)$, with κ held fixed at the value of 0.88 determined in the previous study[3]].

The most prominent features in Fig. 3 are the apparent change in behavior at 4.4 °K, the difference in the ordered moments on sites I and II, particularly above 3 °K, and the low Ni^{2+} saturation

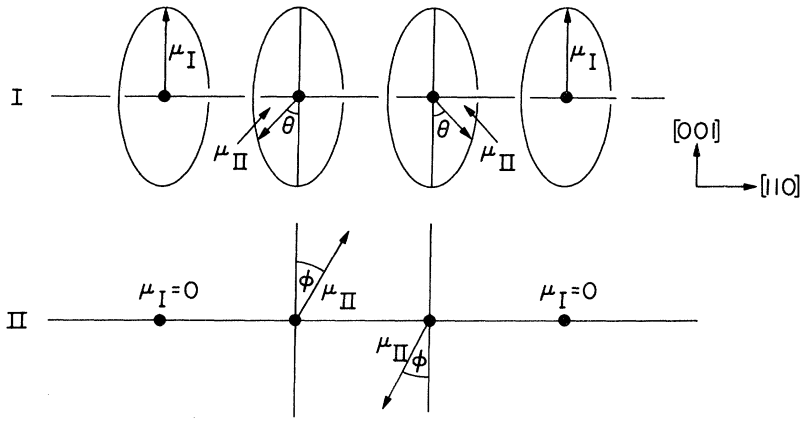

FIG. 2. Two possible models for the $CsNiCl_3$ structure. Model I, with θ varying, describes all the experimental data with a physically plausible structure, but model II gives precisely the same fits to the experimental data.

moment ($1.05\mu_B$). For this model, the intensity ratio of $(\frac{1}{3}\frac{1}{3}1)$ and $(\frac{4}{3}\frac{4}{3}1)$ depends only upon the angle θ, and the sharp break in this ratio at 4.4 °K [Fig. 1(b)] taken in conjunction with the results shown in Fig. 3 is clear evidence of a phase transition, and is consistent with the observation of a specific-heat anomaly at 4.4 °K.

The exact nature of this transition cannot be determined unequivocally from the neutron data. However, a possible explanation is suggested by the NMR results.[4] Below 4.85 °K, a hyperfine field perpendicular to the c axis ($H_\perp$) is observed on one set of Cs sites (labeled Cs_I in Fig. 4). Below 4.4 °K, a parallel component ($H_\parallel$) is also observed on these sites. For this component to be zero, the perpendicular component of the Ni moments ($\mu_\perp$) must be either disordered above 4.4 °K or correlated in such a way that the dipole field at the Cs_I site cancels out. A model consistent with the neutron data is shown in Fig. 4(a) in which $\mu_\perp$ is oriented along the y axis of the c-centered orthorhombic cell which can be derived from the hexagonal cell as outlined in the figure. The magnetic space group consistent with this description is orthorhombic, $C22'2_1'$. A 90° rotation of $\mu_\perp$ to the x axis of the orthorhombic cell (which is equivalent to a change from the [110] to the [100] direction of the hexagonal chemical cell) could then account both for the observed specific-heat anomaly and the appearance of $H_\parallel$ at 4.4 °K. The magnetic space group for this low-temperature structure is also orthorhombic, $Cm'c2_1'$. The temperature dependence of $H_\perp$ and $H_\parallel$ observed in the NMR experiments is in excellent agreement with that of $\mu_\parallel$ and $\mu_\perp$ in the neutron study (solid circles in Fig. 3).

It should be noted that the model discussed is not only one that can account for the data. For example, if the components of the moments in the basal plane did not form a collinear structure, but

TABLE I. Comparison of the observed and calculated intensities of the magnetic reflections in $CsNiCl_3$ at 4.5 and 2.3 °K, temperatures above and below the second (spin-reorientation) phase transition.

$h\,h\,l$	4.5 °K		1.6 °K	
	calc	obs	calc	obs
$\frac{1}{3}\frac{1}{3}1$	0.59	0.56	4.15	4.81
$\frac{2}{3}\frac{2}{3}1$	0.67	0.73	3.42	3.92
1 1 1	0.0	0.0	0.0	0.0
$\frac{4}{3}\frac{4}{3}1$	0.43	0.40	1.87	1.70
$\frac{5}{3}\frac{5}{3}1$	0.32	0.32	1.36	1.35
2 2 1	0.0	0.0	0.0	0.0
$\frac{1}{3}\frac{1}{3}3$	0.086	0.090	0.89	0.84
$\frac{2}{3}\frac{2}{3}3$	0.099	0.096	0.85	0.79
	$R_W=0.06$		$R_W=0.09$	

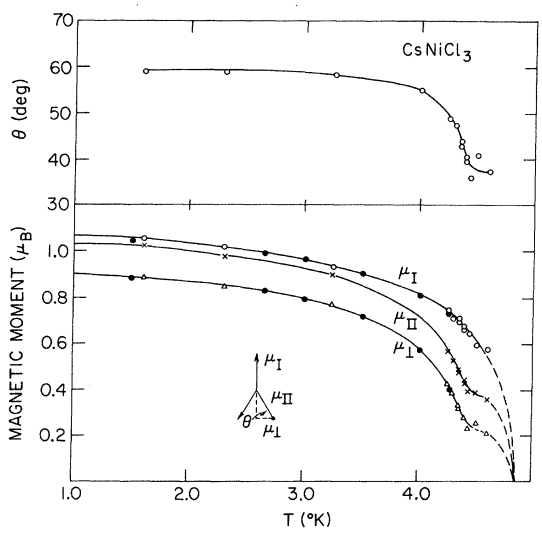

FIG. 3. Results of the structure refinement using model I. (a) The total moments on the Ni^{2+} ions (μ_I and μ_{II}) and the basal plane component on site II($\mu_\perp$). (b) The angle with the z axis made by the moments on site II as a function of temperature. In both parts of the figure the statistical errors are of the order of the size of the data points but increase as the temperature is raised and the total moments decrease.

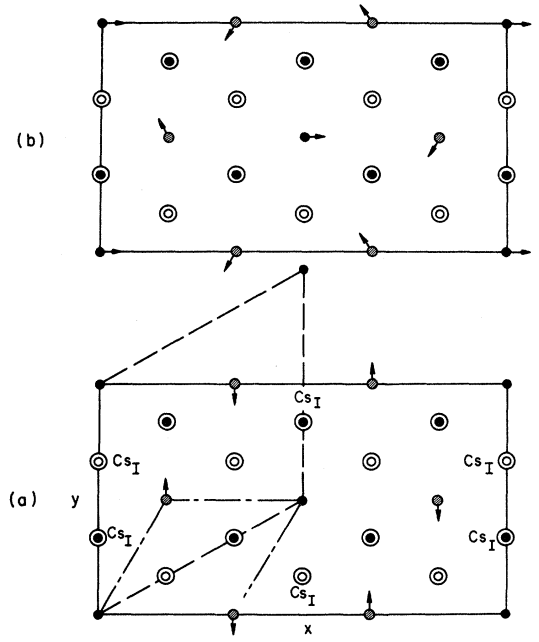

FIG. 4. (a) Unit cells for $CsNiCl_3$ (basal-plane projection). Closed and shaded circles represent Ni atoms at $z=0$ on sites I and II, respectively; doubled circles are Cs atoms, at heights along the z axis of $\frac{1}{4}$ (open centers) and $\frac{3}{4}$ (solid centers). The smallest cell (containing one Ni atom per layer) is the primitive paramagnetic cell, space group $P6_3/mmc$. The enlarged hexagonal cell containing three Ni atoms per layer, yields the observed magnetic reflections. The C-centered cell, derived from this enlarged cell, describes the magnetic symmetry of the ordered phase. Between T_N and 4.4 °K, the basal-plane component of the Ni moments are as shown, and as such produce no hyperfine field parallel to the c axis ($H_{\parallel}$) on the sites labeled Cs_I. Below 4.4 °K this component is believed to rotate by 90°. (b) An alternative model above 4.4 °K which also produces no $H_{\parallel}$ on the same Cs_I sites, but is not favored due to its monoclinic symmetry.

instead formed a triangular array, exactly the same fit to the data would be obtained, although the angles between the moments and the magnitudes of the moments would differ. Furthermore, if these moments were directed as in Fig. 4(b), then the hyperfine field along the c axis, $H_{\parallel}$, would again be zero on one-third of the Cs atoms. This model, however, has monoclinic symmetry and does not have any obvious physical origin. Likewise, model II (Fig. 2) gives an identical fit to the neutron data but once again is of rather dubious physical significance because of the particular orientation of moment required.

III. CONCLUSIONS

The improved resolution afforded by the use of long-wavelength neutrons has enabled us to confirm the existence of a second magnetic phase transition in $CsNiCl_3$ at about 4.4 °K. Above this temperature, the Ni^{2+} moments on one-third of the sites (I) lie along the c axis, while the moments on the remaining two-thirds of the sites (II) appear to be directed approximately toward a Cl ion in the surrounding octahedra in the yz plane. Below 4.4 °K the moments on the latter sites are oriented in the xz plane. The magnetic structure is a modified triangular arrangement which is consistent with a simple picture of competition between single-ion anisotropy and weak basal-plane exchange interactions as discussed previously in connection with $RbNiCl_3$.[6] The mechanism responsible for the reorientation of moments above 4.4 °K is not clear, but presumably has its origin in the local crystal fields associated with the chlorine octahedra. As was noted in the earlier work on $CsNiCl_3$[3] and $RbNiCl_3$,[6] the saturation Ni^{2+} moment is quite small, the observed value of $1.05\mu_B$ agreeing with the previously determined value of $(1.0\pm0.1)\mu_B$. This substantial deviation from the free-ion value is thought to be due to zero-point effects and a recent theoretical study[7] predicts a value very close to that actually observed. Another notable feature of the system is the difference in the moments on the two different Ni^{2+} sites in the vicinity of the second transition. These sites are chemically equivalent in the paramagnetic phase and there is no evidence of any crystallographic deformations associated with the magnetic ordering. Thus the environments of the two sets of nickel sites remain equivalent but the magnetic moments are nevertheless strikingly different.

†Work performed under the asupices of the U.S. Atomic Energy Commission.

[1] V. J. Minkiewicz, D. E. Cox, and G. Shirane, J. Phys. C **1**, 892 (1971).

[2] N. Mekata, K. Adachi, H. Takai, and N. Achiwa, Twelfth International Conference on Low Temperature Physics, Kyoto, 1970 (unpublished).

[3] D. E. Cox and V. J. Minkiewicz, Phys. Rev. B **4**, 2209 (1971).

[4] R. H. Clark and W. G. Moulton, Phys. Rev. B **5**, 788 (1972).

[5] K. Carter and R. Kromhout (private communication).

[6] W. B. Yelon and D. E. Cox, Phys. Rev. B **6**, 204 (1972).

[7] P. A. Montano, E. Cohen, and H. Shechter, Phys. Rev. B **6**, 1053 (1972).