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Cs^{133} and Cl^{35} NMR in Antiferromagnetic CsNiCl$_3$[†]

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The nuclear magnetic resonances of Cl^{35} and Cs^{133} in magnetically ordered CsNiCl$_3$ have been investigated to determine the magnetic structure and magnetic properties of this compound. Both the Cs and Cl resonances have been observed in single crystals over a temperature range 300 to 1.3 °K. These data show that CsNiCl$_3$ undergoes two magnetic transitions, one at (4.84 ±0.03) °K and the other at (4.40 ±0.03) °K. The higher-temperature transition corresponds to antiferromagnetic alignment of the Ni spin along the *c* axis, while the perpendicular part of the moment is probably paramagnetic. At 4.40 °K, the perpendicular component of the moment becomes ordered. The magnetization curves for the perpendicular and parallel components of the Ni moment have been obtained. When normalized to the appropriate Néel temperature, the reduced magnetization curves represented by components of the internal field parallel and perpendicular to the *c* axis have the same dependence upon temperature, as evidenced by the Cs and Cl resonances. Near the corresponding T_N, the critical exponent β is 0.32 ±0.03 for both the parallel and perpendicular components.

I. INTRODUCTION

There has been considerable recent interest in compounds of the ABCl$_3$ type. The magnetic properties of several of these compounds in which A is represented by Cs or Rb, and B by Cu, Ni, Co, or Fe, have been investigated by Achiwa.[1] His susceptibility data for CsNiCl$_3$ are characteristic of a linear antiferromagnetic chain with a broad peak at about 35 °K in the susceptibility-vs-temperature curve. Achiwa also inferred from the susceptibility data that a paramagnetic-to-antiferromagnetic transition occurs at 4.5 °K.

Several neutron diffraction experiments have been performed on[2-5] CsNiCl$_3$ and the isomorphic compound RbNiCl$_3$,[2,6] and conflicting results have been reported. Achiwa[1] found no antiferromagnetic peak in CsNiCl$_3$ at 1.9 °K. Smith *et al.*[5] saw no evidence of three-dimensional magnetic ordering at 4.6 °K. From powder neutron diffraction data Minkiewicz *et al.*[3] found the Néel temperatures of CsNiCl$_3$ and RbNiCl$_3$ to be 4.5 and 11 °K, respectively, and that the two compounds had the same magnetic structure, which was an antiferromagnetic alignment of spins along the *c* axis with a screw spiral in the basal plane. Single-crystal data by Mekata *et al.*[2] gave

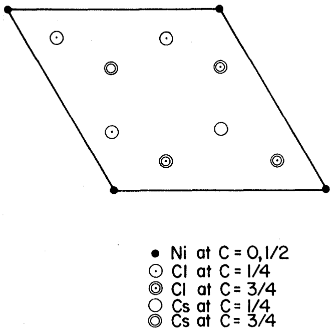

FIG. 1. Projection of crystal structure of $CsNiCl_3$ in the (001) plane. The $NiCl_6$ octahedra share faces along the c axis, [001].

results in agreement with Ref. 3. Cox and Minkiewicz[4] have recently reexamined $CsNiCl_3$ using one of our single crystals and found only one transition at (4.3 ± 0.1)°K. They confirmed the triangular arrangement of moments deduced in their previous study.[3] Epstein *et al.*[6] performed a neutron diffraction experiment on $RbNiCl_3$ powder and reported that the magnetic structure is a collinear antiferromagnetic alignment with the spin direction along the c axis. This is in contradiction to the results of Minkiewicz *et al.*[3] However, they do agree on the dimensions of the magnetic unit cell: $a^* = \sqrt{3}a$ and $c^* = c$.

Previous nuclear quadrupole resonance work has been performed on Cl^{35} in the paramagnetic state by Rinneberg *et al.*[7] They determined the quadrupole coupling constant (e^2qQ) and magnetic shift tensors at the chlorine sites. They also found the axes of the field gradient tensor (FGT) with V_{xx} parallel to the c axis, along $\langle 001\rangle$, V_{yy} perpendicular to the c axis and pointing toward the Ni chain axis, along $\langle 120\rangle$, and V_{zz} perpendicular to the Ni-Cl-Ni plane, along $\langle 100\rangle$. In this work, the Cs^{133} and Cl^{35} nuclear magnetic resonances have been investigated in the magnetically ordered temperature region.

II. EXPERIMENTAL

The single crystals of $CsNiCl_3$ used in this work were grown by Peirce of this laboratory. The method is described in detail elsewhere.[8] An equimolar mixture of CsCl, previously purified by distillation, and $NiCl_2$, purified by sublimation, were fused in an evacuated silica tube. The resulting $CsNiCl_3$ was sealed under 200 Torr of helium and converted to a single crystal by the vertical Bridgman method. Elemental analysis showed that to within 0.1% the constituents were combined in stoichiometric ratios. X-ray analysis gave $a = 7.16$ Å and $c = 5.92$ Å, which is in agreement with the published values.

The crystal structure of $CsNiCl_3$ is shown in Fig. 1. The $(NiCl_6)$ octahedra share faces and form linear chains along the hexagonal c axis. The Cl ions form equilateral triangles centered about the chain and are all chemically equivalent. Each Cl ion has two nearest-neighbor Ni ions along a chain and two second-nearest neighbors, also along the same chain. The Cs ions lie in the center of a triangle formed by three Ni chains and each Cs has six nearest-neighbor Ni ions.

The frequency-swept pulsed spectrometer used for much of this work has been described elsewhere.[9] However, owing to the closely spaced Cs quadrupole resonances, magnetic modulation could not be used in the Cs resonance work and therefore the spectrometer was modified to use coherent detection and a boxcar integrator for the output. When operated in this mode, it was necessary to sweep the magnetic field. No modulation was used. The magnetic field was measured by using the H nuclear resonance in a water solution of copper sulfate.

Temperature measurements were made with a four-wire germanium-resistance thermometer with an absolute calibration of ±0.01 °K. The emf developed across the thermometer was measured by a differential voltmeter and the computed resistance compared with a polynomial least-squares interpolation of the calibration points. The calibration is magnetic field dependent, and owing to difficulties encountered in calibration of the thermometer in an external field, the absolute accuracy for data taken in an external field is ±0.03 °K. Temperature control was achieved by converting the error voltage from the differential voltmeter to a current which was passed through a 10-Ω resistor in the helium bath. The thermometer, sample, and heating resistor were closely spaced in the 1.25-in.-diam tail section of a glass Dewar which was filled with liquid helium. Temperatures below 4.2 °K were obtained by pumping on the helium bath. In order to obtain temperatures between 4.2 and 5 °K the helium chamber was pressurized up to 11 psi. By regulating the pressure above the liquid helium, the above feedback network could maintain temperature equilibrium to within 1 mdeg from 1.3 to 5 °K.

The sample was mounted in a probe which allowed rotation of the crystal to within an accuracy of ± 2° about a horizontal axis while immersed in the helium bath. Complete rotation data were obtained by a combination of this horizontal rotation and a rotation of the magnet about the vertical axis.

III. Cl DATA AND INTERPRETATION

The results of our experiments at 300 °K gave Cl parameters which are in agreement with those reported by Rinneberg *et al.*[7] The parameters determined by our Zeeman rotation experiments at 300, 77, and 1.4 °K are shown in Table I. The Cl^{37} parameters were in agreement with those for Cl^{35} in both the paramagnetic and ordered state. Only the Cl^{35} results will be discussed. The Cl resonance

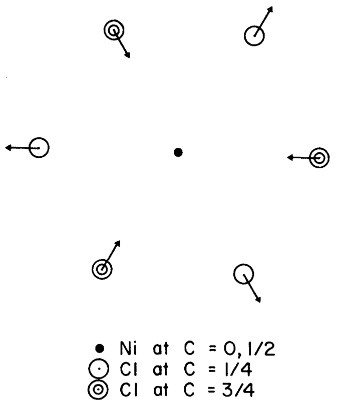

FIG. 2. Directions of $\vec{H}_{\text{int}}$ at Cl sites associated with the antiferromagnetic chains having Ni moments ∥ [001].

increased in intensity as the temperature was lowered from 300 °K, reaching a maximum at 4.93 °K where the resonance was very strong. The intensity decreased rapidly as T was lowered below 4.93 °K and the resonance could not be observed below 4.86 °K.

The Cl resonances in the magnetically ordered state were first observed at 1.4 °K. Five transitions were observed in zero external field, three of them corresponding to Cl^{35}. The Cl energy levels were determined by solving the following Hamiltonian exactly using a direct diagonalization procedure:

$$\mathcal{H} = -\gamma\hbar\vec{H}\cdot\vec{I} + [e^2qQ/4I(2I-1)] \times [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \ .$$

The program uses a variable metric minimizer to optimize the parameters e^2qQ, η, θ, ϕ, and $\vec{H}_{\text{int}}$, where θ and ϕ are the usual polar coordinates of $\vec{H}_{\text{int}}$ with respect to the FGT axes. The fields were found to be parallel or antiparallel to V_{yy} within ± 2°, and of magnitude 22.493 ± 0.005 kG at 1.4 °K. The other parameters at 1.4 °K are listed in Table I. The parameters determined for a 10-kG external field were the same as for a 500-G field to within 0.4%.

The hexagonal symmetry is reflected in the rotation data and implies that all the observed Cl sites are magnetically equivalent with respect to each chlorine's FGT axis. Maximum splitting of the transiting frequencies was observed for $\vec{H}_0$ parallel to V_{yy} and zero splitting for $\vec{H}_0$ perpendicular to V_{yy}. The crossing points allowed determination of the V_{yy} direction to ± 0.3°. The direction of $\vec{H}_{\text{int}}$ at the Cl sites, shown in Fig. 2, is in the plane of the Cl triangle and is directed toward or away from the Ni chain.

The frequencies of the transitions were followed as a function of temperature from 1.3 to 3.9 °K. At each temperature the magnitude of the internal field was calculated and these values were used to compute the magnetization curve discussed in Sec. V. The ordered state Cl resonances were not sufficiently intense above 3.90 °K to be observable.

From the above analysis, the magnitude and direction of the internal magnetic field at the Cl sites has been established. As will be shown in Sec. IV, the Cs NMR requires that there must be at least two distinct types of alignment of the Ni moments along different chains. In order to determine the types of alignment, a point dipole summation was performed over the magnetic ions of the lattice and the resulting direction of the field at the Cl sites compared with the experimentally determined directions. The results showed that the Cl sites which we observed are positioned on a chain for which the Ni ions are aligned antiferromagnetically with their moments parallel or antiparallel to the c axis. These chains will be referred to as type A, and chains for which the moment has a perpendicular component will be referred to as type B. Only the type-A configuration gives fields in the (001) plane with $H_{\text{int}} \parallel V_{yy}$ at the associated Cl sites. Also, the summation reveals that the Cl ions' four nearest-neighbor Ni ions contribute at least 97% of the field at the Cl site. If the type-B chains are antiferromagnetic, the contribution of the nearest-neighbor type-B chains can only introduce a ± 2° variation in the direction of the field at the Cl sites on chain A.

Thus, from the Cl data alone, it can only be concluded that there exists one type of Ni chain for which the Ni moments are aligned antiferromagnetically with their direction parallel or antiparallel to the c axis ($\vec{m} \parallel c$). There may be other chains with different types of alignment, but, within experimental error, the Cl data do not indicate or deny their existance. If there are chains with different alignments, and as will be shown from the Cs data there must be such chains, then only resonances from Cl nuclei in the chain with $\vec{m} \parallel c$ are observed. At present we have no explanation why Cl atoms associated with the other chains are not observed.

It should be noted that the Cl rotation data require that either Ni ions on the antiferromagnetic collinear chain described above are not ferromagnetic in

TABLE I. Experimental values for ν_0 (pure quadrupole frequency) and η (asymmetry parameter) for Cl^{35} in $CsNiCl_3$.

Temp (°K)	ν_0 (MHz)	η
300	8.349 ± 0.005	0.387 ± 0.0015
77	8.486 ± 0.005	0.414 ± 0.002
1.4	8.588 ± 0.006	0.472 ± 0.004

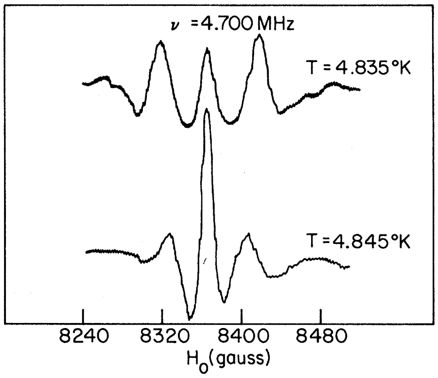

FIG. 3. Recorder trace of Cs^{133} NMR spectra near the 4.84 °K transition for $\nu = 4.700$ MHz and $\vec{H}_0$ rotated 54.7° from the c axis ($\theta = 54.7°$).

a plane perpendicular to c, or that antiferromagnetic domains exist. Otherwise, the resonances would only be shifted and not split by an external field. When an external magnetic field was applied parallel to V_{yy} at 1.3 °K the Cl resonances split into two resonances of unequal intensity. Rotating $\vec{H}_0$ through 180° caused the relative intensities to be interchanged, indicating the existence of antiferromagnetic domains in $CsNiCl_3$.

IV. Cs DATA AND INTERPRETATION

The Cl analysis was near completion before the Cs NMR was attempted in hope of resolving the discrepancy between the Cl NMR data and the structure deduced by neutron diffraction experiments. The site symmetry at the Cs site requires that the FGT be axially symmetric. Hence, $\eta = 0$ and V_{zz} is parallel to the c axis, as was verified by experiment. The energy levels for a nucleus for which the magnetic contribution is much larger than the quadrupole contribution are approximated, to first order, by

$$E_m = -\gamma\hbar H_0 m + \frac{e^2qQ}{4I(2I-1)}\left(\frac{3\cos^2\theta - 1}{2}\right) \times [3m^2 - I(I+1)] ,$$

where θ is the angle which $\vec{H}$ makes with the V_{zz} direction. As is expected for Cs, spin $\frac{7}{2}$, seven equally spaced resonances are observed. At $\theta = 54.7°$, the value of $3\cos^2\theta - 1$ is equal to 0 and the quadrupole contribution to E_m vanishes so that the seven resonances coalesce to form a single line. This phenomenon was quite useful in the confirmation of the V_{zz} direction and in the alignment of the crystal. The Cs parameters are shown in Table II. For the Cs data reported here, the operating frequency ν was held constant at 4.700 MHz and the external field was varied.

In an external field of 8.4 kG, with $\theta = 54.7°$, the single paramagnetic Cs resonance suddenly split into two resonances as the temperature was lowered below 4.84 °K, as shown in Fig. 3. With $T = 4.46$ °K and $\theta = 0°$, only one set of seven Cs resonances was observed. At $\theta = 54.7°$ two single resonances could be seen and at $\theta = 90.0°$ two sets of seven resonances were evident. The spectra at 4.46 °K are shown in Fig. 4. These data in the temperature region between 4.84 and 4.40 °K imply that the Ni moments on the separate chains are ordered both along the chain and between the chains in a manner that creates an internal field at the Cs site which is in the (001) plane. This requires that the component of the Ni moments parallel to the c axis be long range correlated and that the components perpendicular to c are either correlated in a manner such that the dipole fields at the Cs site cancel, or that these components are uncorrelated (paramagnetic) so that their contribution time averages to zero. The intensity of the resonances is a strong function of ϕ, the polar angle in the hexagonal plane. Maxi-

TABLE II. Experimental values of $\Delta H/H_0 \equiv (\omega/\gamma_N - H_0)/H_0$ and $e^2qQ/\hbar$ (quadrupole coupling constant) for Cs^{133}.

Temp (°K)	$\Delta H/H_0$ (%)	$e^2qQ/\hbar$ (MHz)
300	0.42 ±0.02	0.293 ±0.003
77	1.08 ±0.02	0.312 ±0.003
5.0	0.73 ±0.02	0.318 ±0.003

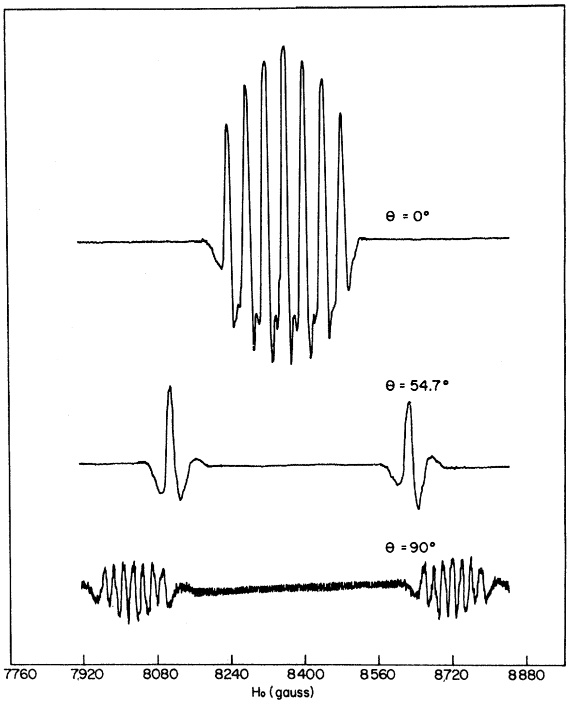

FIG. 4. Cs NMR spectra at $T = 4.46$ °K (0.060 °K above the lower transition) for $\theta = 0°$, 54.7°, and 90° with $\phi = 60°$.

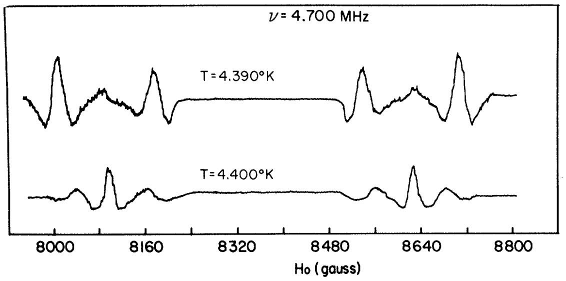

FIG. 5. Cs NMR spectra near the 4.40 °K transition with $\vec{H}_0$ at $\theta = 54.7°$, $\phi = 60°$.

mum intensity was observed with $\vec{H}_0$ parallel to the Ni-Cs plane, which we define as $\phi = 60°$, and the intensity is a minimum when $\phi = 30°$ or $90°$. The intensity variation had 60° symmetry. In this temperature region the intensity data imply that the direction of $\vec{H}_{\text{int}}$ in (001) is parallel to the Ni-Cs plane at the Cs sites, i.e., along $\phi = 60°$.

As the temperature was lowered below 4.40 °K, with $\theta = 54.7°$, each of the two single Cs resonances suddenly split into two lines, as shown in Fig. 5. At 4.27 °K, for $\theta = 0°$, two sets of seven resonances were observed; for $\theta = 54.7°$, four single lines were seen; for $\theta = 90°$, again there were two sets of seven lines. This sequence is shown in Fig. 6. These data for temperatures below 4.40 °K show the existence of a component of the internal field at the Cs site which is parallel to the c axis. This implies that, at 4.40 °K, the perpendicular component of the Ni moment becomes ordered, or the spin configuration changes so as to create a component of the internal field at the Cs site parallel to c. Again, there is a large variation of intensity with ϕ; maximum intensity was obtained for $\phi = 60°$ and minimum intensity for $\phi = 30°$ and $90°$. The hexagonal symmetry was still evident from the rotation data. As ϕ was varied, no change in the magnitude of $\vec{H}_{\text{int}}$ was detected within the experimental accuracy of ± 13 G. In the temperature region below 4.40 °K, the fields lie on the surface of a cone, which has a half-angle of 44.5°, and spaced at 60° intervals at 1.4 °K. The internal field at all the Cs sites which were observed had the same magnitude.

All the above spectra were also taken with $\nu = 2.700$ MHz; however, the intensities were quite low and only the data at 4.700 MHz are reported. No variation of $\vec{H}_{\text{int}}$ with the magnitude of $\vec{H}_0$ was observed. Other resonances than the ones described above were observed, but some could not be resolved from the strong resonances, and all were weaker by at least a factor of 100 than the resonances reported here. The origin of these resonances will be explained in Sec. V. The Cs resonances at 4.27 °K were easily saturated and required repetition rates on the order of 30 msec.

As with the Cl resonances, the existence of a domain structure was inferred from a relative intensity change as the temperature was lowered to 1.4 °K.

Because the maximum internal field at the Cs site was approximately 0.8 kG and $\vec{H}_0$ was about 8.4 kG, a particular direction of $\vec{H}_0$ measured the component of $\vec{H}_{\text{int}}$ along $\vec{H}_0$ within 1%. The magnitude of the components of the internal magnetic field at the Cs site parallel to the c axis and perpendicular to c were measured as a function of temperature from 1.3 to 4.84 °K. The results are shown in Fig. 7. Because the magnitude of the perpendicular component of the internal field ($\vec{H}^{\perp}_{\text{int}}$) varies continuously with temperature from 1.3 to 4.84 °K, the projection of each Ni moment on the c axis must remain constant from 4.84 to 1.30 °K. Since the Cl data determine the existence of one chain for which the Ni moment is along the c axis for $T \leq 3.9$ °K, this chain must still exist for temperatures up to 4.84 °K if $\vec{H}_{\text{int}}$ is continuous.

The above data provide direct evidence of two magnetic transitions in CsNiCl_3, which occur at (4.84 ± 0.04) and (4.40 ± 0.04) °K in an 8-kG external field. This requires that there should be two specific-heat "spikes." At our suggestion Carter and Kromhout[10] have measured the specific heat in this temperature range and found two sharp spikes which occur at (4.750 ± 0.02) and (4.315 ± 0.015) °K in zero external field.[10] The specific-heat data confirm our NMR results and show that the neutron diffraction experiments[4] must only see the three-dimensional order below the second transition.

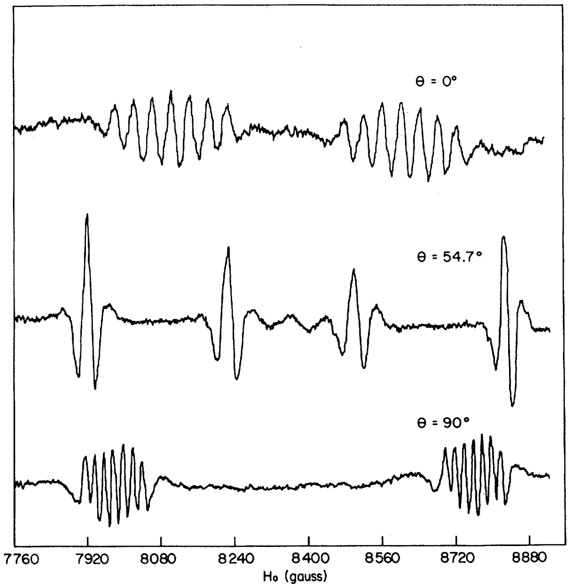

FIG. 6. Cs NMR spectrum at $T = 4.27$ °K with $\theta = 0°$, 54.7°, 90°, and $\phi = 60°$.

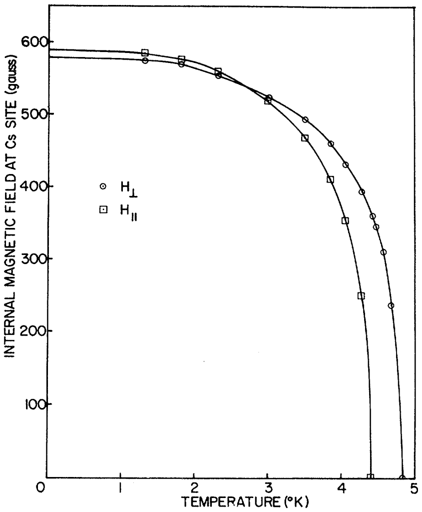

FIG. 7. Magnitude of $\mathrm{H}_{\mathrm{int}}^{\perp}$ and $H_{\mathrm{int}}^{\parallel}$ at the Cs site as a function of temperature, with $\nu = 4.700$ MHz and $\vec{\mathrm{H}}_0 \approx 8.4$ KG.

V. ANALYSIS AND MODELS

In this section several possible spin configurations will be considered and compared with the experimental data. The model proposed by Cox and Minkiewicz[4] from their neutron diffraction data consists of three separate types of Ni chains with moments assumed to lie in a plane containing the c axis. On one chain the moments are aligned in an antiferromagnetic manner, parallel or antiparallel to the c axis. The moments on the next two chains are rotated 120° and 240°, respectively, from the c axis. This model is consistent with their magnetic cell dimensions, which are $a^* = \sqrt{3}a$, $c^* = c$. They were not able to determine the direction of the moments within the spin plane and were also unable to choose between a multidomain and a single domain structure. From the intensity of the $(\frac{1}{3}, \frac{1}{3}, 1)$ reflection as a function of temperature, they reported $T_N = (4.29 \pm 0.1)$ °K and the critical exponent β equal to 0.27 ± 0.03. This measurement, extrapolated to 0 °K, gave them the value of the Ni^{2+} moment as $(1.05 \pm 0.1)\ \mu_B$.

A point dipole summation over the Ni moments using various spin configurations was performed in order to calculate the internal field at the Cs nuclei, which was then compared with the experimentally observed directions and magnitude. Owing to the antiferromagnetic chains and the site symmetry at the Cs ion, the component of the dipolar field perpendicular to the c axis ($H_D^{\perp}$) at the Cs site is due only to the component of the Ni moment parallel to the c axis ($m^{\parallel}$). Similarly, $H_D^{\parallel}$ is due to the component of the Ni moment perpendicular to the c axis ($m^{\perp}$). The maximum $H_D^{\perp}$ is obtained when $m^{\parallel} = |\vec{m}|$, that is, with the moments parallel or antiparallel to the c axis; however, using $\vec{m} = 1.05\mu_B$ gives $H_D^{\perp} = 235$ G, whereas the experimental value is 578 G. Using the neutron diffraction model[4] for the spin structure, the dipole sum gives $H_D^{\perp} = 176$ G, which is a factor of 3.3 too low. The discrepancy could result from several causes. One possibility is that the value of m is too small by a factor of 3.3. This would give $\vec{m} = 3.5\mu_B$ which would be unusally high. A part of the internal field at the Cs ion could result from a hyperfine interaction; however, it appears that the predominant superexchange path would be through two Cl ions, leaving a negligible hyperfine interaction at the Cs ion. Calculations by Mohrmann and Garrett[11] show that each Cl ion has 18% of an unpaired d electron on it which is transferred from the two nearest Ni ions. It is conceivable that this unpaired spin could contribute to the dipolar field at Cs; however, a crude calculation putting 18% of the spin on the chlorine leads to a smaller field due to cancellation. Another possibility is that the point dipole calculation is inaccurate for this case owing to the large cancellation from adjacent sets of neighbors. With $m = 1.05\mu_B$, a sum over the six nearest-neighbor Ni ions gives $H_D^{\perp} = 341$ G, including the six next-nearest neighbors, reduced $H_D^{\perp}$ to 137 G. Another possibility is the existence of a "shielding" of the Ni spins by the electron cloud of the Cl ions. The chlorine atoms could preferentially "shield" the Ni ions which contribute to the "negative" terms in the dipolar summation.

The above data show that at 4.84 °K the parallel component of the Ni moments order antiferromagnetically along the chain with at least two different magnitudes of $m^{\parallel}$. From the Cl data, one of these chains has $m^{\parallel} = \pm |\vec{m}|$. The neutron diffraction data show that below 4.3 °K, two-thirds of the chains have $m^{\parallel} = \pm \frac{1}{2} |\vec{m}|$. Our data show that $m^{\parallel}$ varies continuously up to 4.84 °K, so that in the temperature region between 4.40 and 4.84 °K the magnetic alignment is as shown in Fig. 8, except that $m^{\perp}$ is either uncorrelated or has a configuration such that $H_{\mathrm{int}}^{\parallel}$ is zero. The only way $m^{\perp}$ can order so as to produce $H_{\mathrm{int}}^{\parallel} = 0$ at all Cs sites is if $m^{\perp}$ is ferromagnetic along the chain. However, this arrangement would cause each of the Cs sites to have unequal values of $H_{\mathrm{int}}^{\perp}$ and would not allow $H_{\mathrm{int}}^{\perp}$ to be continuous across the lower transition. We therefore believe that the perpendicular components of the spins do not have long-range correlations between the two transitions. The sequence of moments along an $\vec{a}$ direction in the lattice is 1, $-\frac{1}{2}$, $-\frac{1}{2}$, 1, ..., where the spacing is $|\vec{a}|$ and the moments are all parallel or antiparallel to the c axis. This arrangement results in a field at the Cs site in the (001) plane directed toward or away from the neighboring Ni chain which has $\vec{m} \parallel c$. These chains are labeled type A in Fig. 8. For this magnetic

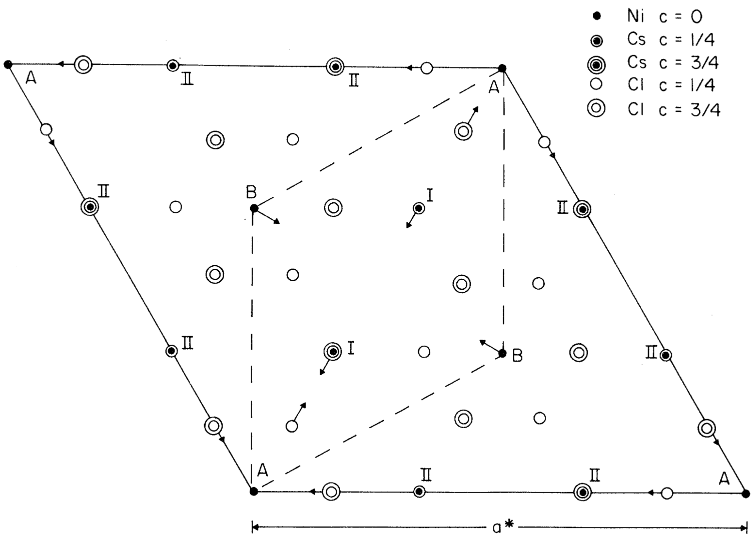

FIG. 8. Magnetic cell for $CsNiCl_3$ below $T = 4.40$ °K. The Ni chains labeled A have $\vec{m} \parallel$ [001]. For the chains labeled B, $\vec{m}$ is rotated 120° from [001] with the direction of $m^\perp$ shown for Ni ions at $c = 0$. The Cs ions labeled I are the ones having observable resonances. The arrows at the type-I Cs sites show the direction of the [001] component of $\vec{H}_{\text{int}}$. Type-II Cs ions do not have resolvable resonances. The arrows at the Cs and Cl sites show the directions of H_{int}.

structure, the ordered-state Cl NMR results are due to the Cl atoms around type-A chains. Below 4.40 °K there exists a static component of the internal field along the c axis at the Cs site. For an antiferromagnetic alignment of the Ni moments along the chain, $H_D^{\parallel}$ results from $m^\perp$, indicating that $m^\perp$ becomes long range correlated at 4.40 °K. The chains labeled type B are those for which the Ni moments have a perpendicular component. Several spin configurations were considered in an attempt to explain the Cl and Cs NMR data. A least-squares minimization routine was used in conjunction with the point dipole summation to fit the magnitude and direction of the observed internal fields in both temperature regions. The direction of $m^\perp$ cannot be uniquely determined; however, the best agreement with the data is obtained if $m^\perp$ is along the directions shown in Fig. 8. The analysis of the Cs data indicates that the observed Cs NMR transitions are from sites labeled type I. The arrows on the Cs and Cl sites show the directions of $H_{\text{int}}^\perp$ at these sites. This interpretation yields only 360° symmetry for a rotation of $\vec{H}_0$ in the (001) plane for the Cs NMR. The hexagonal symmetry is presumed to be a result of the multidomain structure. The Cs sites labeled type II are the origins of the weak resonances mentioned previously. The low intensity and the unresolvability of those resonances is probably the result of a small canting of the Ni spins by the external field.

The normalized parallel and perpendicular interna fields as a function of the reduced temperature are shown in Fig. 9. The transition temperatures are 4.40 and 4.84 °K, respectively. We have assumed $\vec{H}_{\text{int}}(T) \propto \vec{m}(T)$, which is valid if the hyperfine cou-

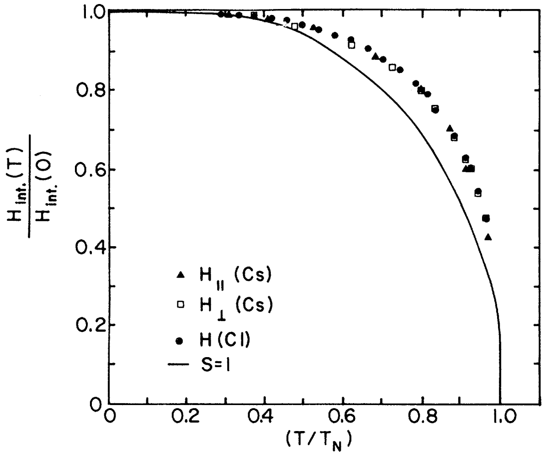

FIG. 9. Normalized internal magnetic field as a function of reduced temperature for $H_{\text{int}}^\perp$ and $H_{\text{int}}^{\parallel}$ at the Cs site and $\vec{H}_{\text{int}}$ at the Cl site. The associated transition temperatures are 4.84 and 4.40 °K, respectively. The solid curve represents the magnetization according to molecular field theory for $S = 1$.

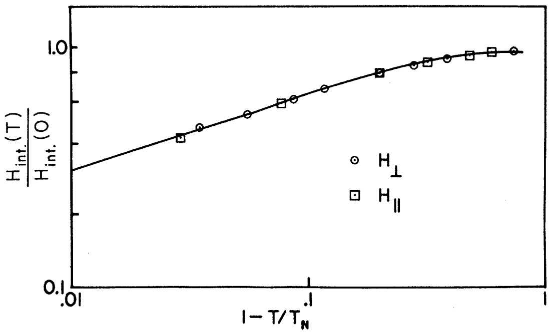

FIG. 10. Log-log plot of $H_{\text{int}}(T)/H_{\text{int}}(0) = A[1-(T/T_N)]^\beta$, where $T_N = 4.84$ °K (4.40 °K) for $H_{\text{int}}^\perp(H_{\text{int}}^{\parallel})$. The value of the critical exponent β is 0.32 ± 0.03.

pling is independent of temperature. Also shown is the normalized field at the Cl sites. Since the field at the Cl ion is primarily due to type-A chains, the Néel temperature is taken as 4.84 °K. Normalized to this temperature, the field and thus the magnetization, as measured by the Cl NMR, have the same temperature dependence as $H^{\perp}_{\text{int}}$ and $H^{\parallel}_{\text{int}}$ at the Cs site. These three magnetization curves also agree with the reduced neutron diffraction magnetization curve.[4] The reduced magnetization obtained from the Brillouin function for $S = 1$ is represented by the solid line in Fig. 9. Figure 10 shows a graph of $H^{\parallel}_{\text{int}}$ and $H^{\perp}_{\text{int}}$ vs $(1 - T/T_N)$, which gives the critical exponent β as 0.32 ± 0.03 for both $m^{\perp}$ and $m^{\parallel}$.

The Cl NMR in RbNiCl$_3$ gave essentially the same results, except that the magnitude of $\vec{H}_{\text{int}}$ was different. Work is underway on the Rb NMR investigation in the RbNiCl$_3$.

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Interference and Intermediate-Level-Width Corrections to the Orbach Relaxation Rate*

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A modification of the Orbach relaxation process arising from the phonon-induced intermediate level width is developed. It is shown from a numerical integration, including all two-phonon terms (resonant, interference, nonresonant), that the temperature dependence of the two-phonon spin-lattice relaxation process at temperatures intermediate between the Orbach and Raman regimes can be substantially altered. Thus, determination of excited-state splittings using the temperature dependence of the Orbach relaxation rate can be misleading, should experimental considerations limit the range over which T measurements are made. In general, the effect of the intermediate level width is to diminish the slope of $1/T_1$ vs $1/T$, yielding an apparent reduction in the excited splitting as compared to optical determinations. An apparent concentration dependence of the exponent in the Orbach relaxation process can also obtain from the same source, by virtue of a change in the sound velocity changing the intermediate level width.

I. INTRODUCTION

A well-known spin-lattice relaxation process in both iron-group and rare-earth paramagnetic salts was first proposed by Finn, Orbach, and Wolf[1] in terms of a two-step direct process. Later, Orbach,[2] and independently Aminov,[3] recast the process in terms of a two-phonon process analogous to resonance fluorescence in gases. These two approaches each have their appropriate regime, having to do with the origin of the linewidth of the intermediate level. In all treatments to date, the two-phonon contribution to the relaxation rate has been divided into two parts: resonant