PHYSICAL REVIEW B VOLUME 39, NUMBER 13 1 MAY 1989

# Basal-plane birefringence and magnetic ordering in hexagonal antiferromagnets $CsNiX_3$ ($X$ = Cl, Br)

Motoaki Sano
*Department of Applied Electronics, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan*

Katsunori Iio and Kazukiyo Nagata
*Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo 152, Japan*

(Received 8 July 1988; revised manuscript received 12 October 1988)

The basal-plane birefringence (for light propagating along the $c$ axis) was measured in the hexagonal antiferromagnets $CsNiCl_3$ and $CsNiBr_3$. The results confirmed the sequence of magnetic ordering suggested in NMR and neutron-diffraction studies, that is, the basal-plane components of the magnetic moments were ordered in the low-temperature phase ($T < T_{N2}$), but not in the intermediate phase ($T_{N2} < T < T_{N1}$). It was newly found that a multidomain structure with respect to the direction of the spin plane is established in the low-temperature phase in the absence of external field, and that a single-domain structure is stabilized for the field perpendicular to the $c$ axis above about 0.3 T. The magnetic ordering process of the $z(\parallel c)$ component is discussed with respect to the temperature dependence of the birefringence in the $ac$ plane.

The magnetic-ordering processes in hexagonal $ABX_3$-type antiferromagnets are of special interest because successive phase transitions are often exhibited owing to the spin frustration of an antiferromagnetic triangular lattice. $CsNiCl_3$ and $CsCoCl_3$ have been extensively studied in order to elucidate the magnetic structures of the two ordered phases.[1-16] In this paper, the results of the birefringence measurements on the basal plane in $CsNiCl_3$ and $CsNiBr_3$ are reported and the magnetic-ordering processes of these systems are discussed.

The crystal structure of $CsNiCl_3$ belongs to the space group $P6_3/mmc$. Magnetic $Ni^{2+}$ ions, surrounded octahedrally by six $Cl^-$ ions, form linear $-Ni^{2+}\text{-}3Cl^--$ chains along the $c$ axis. The chains are combined in a triangular array so that the $Ni^{2+}$ ions are located on the basal triangular lattice. As Achiwa has shown, this system is a good one-dimensional antiferromagnet.[1] In the temperature region where the weak interchain exchange interaction is relevant to magnetic ordering, each antiferromagnetic chain may be regarded as one classical spin.[2] The magnetic lattice can be divided into six sublattices (i.e., the antiferromagnetic chain into two sublattices and the antiferromagnetic triangular lattice into three sublattices). In an antiferromagnetic Heisenberg system, a 120° structure is stabilized at the ground state. A feature of this structure is that a "spin plane" is established on which the triangle of moments lies. Whether the spin plane is parallel or perpendicular to the basal plane depends on the magnetic anisotropy of the system. In $CsNiCl_3$, the spin plane is perpendicular to the basal plane because of its weak Ising-type anisotropy.[3] This structure will be named the *ac*-plane triangular structure.

For the structure of the intermediate phase[4] of $CsNiCl_3$, three possible models have been proposed so far:[5] (a) a sinusoidal-cosine model, (b) a sinusoidal-sine model, and (c) a spin-reorientation model. Both (a) and (b) are the models in which only the $z(\parallel c)$ component of the moment is ordered. On the contrary, (c) is the *ac*-plane triangular structure whose spin plane is rotated around the $c$ axis by an angle of 90° from that of the ground state. The former two disagree with the latter about whether or not the basal-plane components of the moments are disordered in the intermediate phase. Some NMR studies[4,6] and a recent neutron-scattering study[7] have suggested that the basal-plane components are disordered in the intermediate phase. However, a previous birefringence measurement seemed to be in favor of the ordering of the basal-plane components in the intermediate phase because the temperature dependence of the *ac*-plane birefringence $\Delta n^{ca}(T)$ $(=n^c-n^a)$ in this system exhibits sharp bends at the upper Néel point $T_{N1}$ as well as at the lower $T_{N2}$.[8]

Figure 1 shows the previously published $\Delta n^{ca}(T)$ (Ref. 8) of $CsNiBr_3$ (Ref. 9) isomorphic to $CsNiCl_3$. Since a singularity below $T_{N1}$ is much stronger than that of magnetic energy, it was attributed to the broken axial symmetry around the $c$ axis due to the onset of the *ac*-plane triangular structure. This conjecture seemed to be supported by $\Delta n^{ca}(T)$ of $CsCoCl_3$ (Ref. 8) and $CsMnBr_3$ (Ref. 10) which exhibit no anomalies at their Néel points. Since $CsCoCl_3$ is a good Ising system, and $CsMnBr_3$ (Ref. 11) is a Heisenberg system with *XY*-like anisotropy, their magnetic symmetries in the ordered phases are not lowered but remain hexagonal. Therefore, it is reasonable that these systems exhibit no anomalies, in contrast with $CsNiCl_3$ or $CsNiBr_3$.

However, a recent birefringence measurement[10] in $CsMnI_3$,[12] which is a Heisenberg system with weak Ising anisotropy, showed that the basal-plane components are ordered in the low-temperature phase. Moreover, several theoretical studies have also pointed out that the basal-plane components are not ordered in the intermediate phase.[13-15] Therefore, in order to determine whether or not the basal-plane components are ordered in the intermediate phase, it is important to examine the magnetic symmetry in the basal plane for the two ordered phases of the $CsNiCl_3$ family.

For observing a symmetry change in the basal plane directly, we measured the birefringence for light propagating along the $c$ axis ($\Delta n^{xy}=n^x-n^y$) in $CsNiCl_3$ and $CsNiBr_3$, where $x$ and $y$ refer to the axes parallel and perpendicular to the cleavage $(11\bar{2}0)$ plane in the basal plane, respectively. Through the development of the formalism of the dielectric constant of magnetic systems in terms of the spin-dependent electronic polarizability,[17] the birefringence measurement has been recognized as a useful method for studying magnetic properties, especially the temperature dependence of the spin-correlation function, of transparent substances. A number of measurements showed that the birefringence is proportional to the magnetic energy, provided the magnetic point symmetry of the system is not changed at the critical point.[18] However, when the symmetry of the system is lowered in the ordered phase, additional birefringence is produced. In uniaxial crystals, the $ac$-plane birefringence is described as

$$\Delta n^{zx}=\sum_{\langle ij\rangle}[A_{ij}\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle+B_{ij}(\langle S_i^zS_j^z\rangle-\langle S_i^xS_j^x\rangle)+B_{ij}(\langle S_i^zS_j^z\rangle-\langle S_i^yS_j^y\rangle)+C_{ij}(\langle S_i^xS_j^x\rangle-\langle S_i^yS_j^y\rangle)] \quad (1)$$

where the $A$ terms correspond to magnetic energy, the $B$ terms to a uniaxial anisotropy, and the $C$ terms to the anisotropy in the basal plane which appears when the magnetic symmetry in the basal plane is broken. On the other hand, $\Delta n^{xy}$ consists of only the $C$ terms:

$$\Delta n^{xy}=-\sum_{\langle ij\rangle}2C_{ij}(\langle S_i^xS_j^x\rangle-\langle S_i^yS_j^y\rangle)\,. \quad (2)$$

Therefore, $\Delta n^{xy}$ appears only when the symmetry in the basal plane is lowered, e.g., owing to the onset of the $ac$-plane triangular structure.

The single crystals of the $CsNiCl_3$ family were grown by the Bridgman method. Specimens were single-crystal plates cut parallel to the basal plane with about 1-mm thickness. The surfaces were polished by rouge with ethanol on a pitch plate. A 632.8-nm He-Ne laser was employed as a light source and the diameter of the beam was 0.3 mm. The birefringence was measured by the rotating analyzer method and the data were assembled automatically by a minicomputer.

The temperature dependence of $\Delta n^{xy}$ in $CsNiBr_3$ is shown in Fig. 2. The measurements were carried out under the magnetic field of 0.4 T parallel to the $x$ axis [Fig. 2(a)] and parallel to the $y$ axis and zero field [Fig. 2(b)]. Similar behavior has been observed in $CsNiCl_3$, as shown in Fig. 3. A notable point is that no additional variations in $\Delta n^{xy}(T)$ appear under zero field. A temperature variation of $\Delta n^{xy}$ under a zero field can be attributed to inevitable misalignment of the specimen. However, when a magnetic field is applied parallel to the basal plane, additional variation in $\Delta n^{xy}$ appears in the low-temperature phase ($T<T_{N2}$). The direction of the additional variation below $T_{N2}$ is negative for the field parallel to the $x$ axis. The magnitudes of about $10^{-7}$ in $\Delta n^{xy}$ are close to the precision of the present method ($10^{-8}$) and much smaller than those in the $ac$-plane birefringence whose magnitude is approximately in the order of $10^{-5}$. The extra birefringence under the field above $T_{N2}$, whose direction of variation is opposite to the additional variations below $T_{N2}$, is assigned to the birefringence due to a

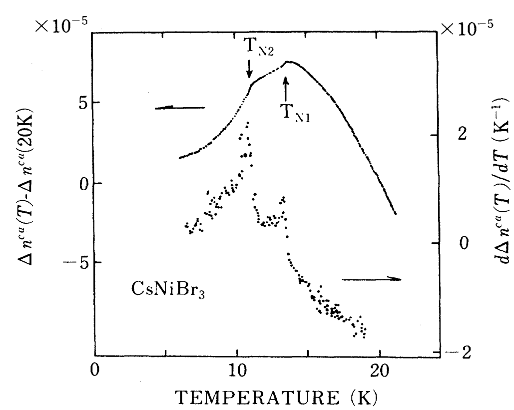


FIG. 1. Temperature dependence of $\Delta n^{ca}$ in $CsNiBr_3$ isomorphic to $CsNiCl_3$, which takes the $ac$-plane triangular structure at the ground state. Sharp bends appear at both $T_{N1}$ (=13.46 K) and $T_{N2}$ (=11.07 K) (from Ref. 8).

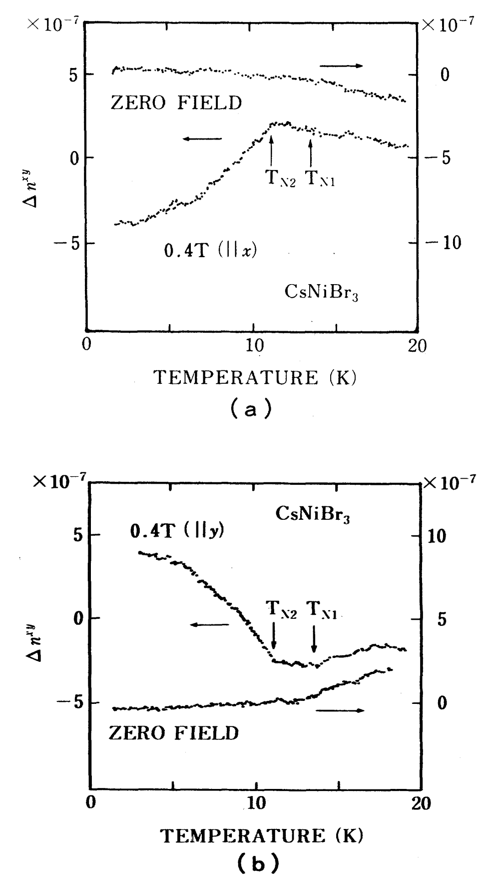


FIG. 2. Temperature dependence of $\Delta n^{xy}$ in $CsNiBr_3$ under the magnetic field of 0.4 T (a) parallel to the $x$ axis, (b) parallel to the $y$ axis and zero field.

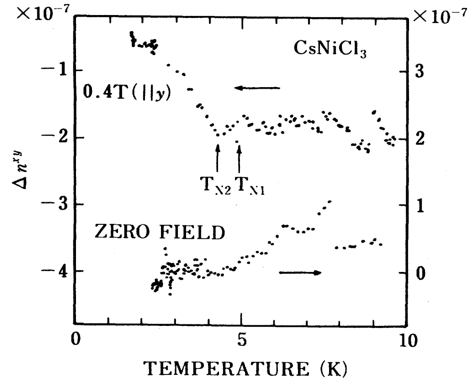


FIG. 3. Temperature dependence of $\Delta n^{xy}$ in $CsNiCl_3$ under the magnetic field of 0.4 T parallel to the $y$ axis and zero field. $T_{N1}$ and $T_{N2}$ are 4.85 and 4.27 K, respectively (Ref. 8).

Cotton-Mouton effect irrespective of the onset of long-range order, because its field dependence is proportional to the square of the magnetic field. From these results, the following has been pointed out for the magnetic ordering process in the $CsNiCl_3$ and $CsNiBr_3$. First, the basal-plane components are disordered in the intermediate phase. Therefore, the possibility of the spin-reorientation model should be eliminated. Second, they are ordered in the low-temperature phase so that the $ac$-plane triangular structure is established macroscopically. These two conclusions are consistent with the results of the NMR studies[4,6] and the recent neutron-diffraction study.[7]

Figure 4 shows the field dependence of $\Delta n^{xy}$ in $CsNiBr_3$ below $T_{N2}$ with the correction of the Cotton-Mouton effect. One can see that the field dependence of $\Delta n^{xy}$ is saturated by a field above about 0.3 T in the basal plane and that the saturated magnitudes of $\Delta n^{xy}$ are almost equal under the following two directions of magnetic field: parallel to the $x$ axis and parallel to the $y$ axis. Another notable fact is that the magnitude of $\Delta n^{xy}$ returns to zero with the decrease in the applied field even after the saturation. These characteristics of the field dependence of $\Delta n^{xy}$ suggest that a triply degenerated domain structure with respect to the direction of the spin plane is stabilized without an applied field, and that one can make the spin plane almost perpendicular to the applied field above about 0.3 T in the basal plane through the spin-flop mechanism. Such a domain rearrangement in $CsNiCl_3$ has already been found by the forced magnetostriction experiment.[19] However, at which temperature it occurs was not determined. Similar behavior has been observed in $CsMnI_3$.[10,12]

Incidentally, the types of behavior of the spin plane under the field in the basal plane are roughly explained by a modified spin-flop theory which was developed by Zandbergen.[12] In the present $ac$-plane 120° structure with six sublattices, the magnetic susceptibility perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) to the spin plane differ from each other owing to the antiferromagnetic chain (note that $\chi_\perp = \chi_\parallel$ in a 120° structure with three sublattices). Therefore, the total free energy at the ground state is given by

$$F = -\tfrac{1}{2}(\chi_\perp \sin^2\theta + \chi_\parallel \cos^2\theta)H^2 + K\sin^3 3(\theta - \phi)\,, \qquad (3)$$

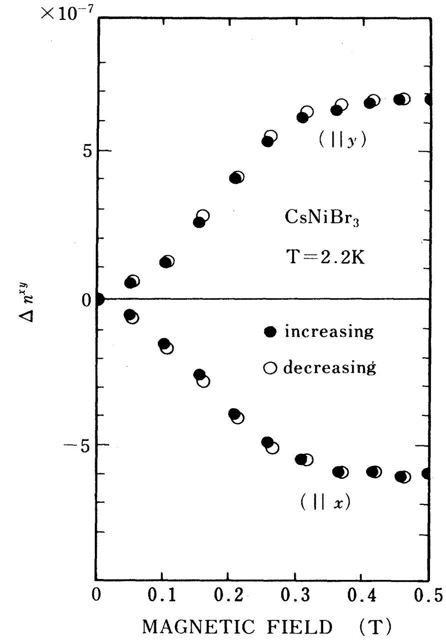


FIG. 4. Magnetic field dependence of $\Delta n^{xy}$ in $CsNiBr_3$. They saturate above about 0.3 T and the absolute values of saturation are almost equal under the following two directions of magnetic field: parallel to the $x$ axis and parallel to the $y$ axis.

where $\theta$ is the angle between the spin plane (perpendicular to the basal plane) and the applied field $H$ in the basal plane; $\phi$ is the angle between the spin plane and one of the six easy axes of the hexagonal anisotropy. The hexagonal anisotropy constant $K$ can be estimated from the spin-flop field $H_F$ parallel to the basal plane

$$K = \tfrac{1}{6}\Delta\chi H_F^2\,, \qquad (4)$$

where $\Delta\chi = \chi_\perp - \chi_\parallel$. From the present experimental result of $H_F \sim 3$ kOe (0.3 T) and $\Delta\chi \sim 5\times10^{-3}$ erg/Oe$^2$mol estimated by magnetic torque measurements,[20] the anisotropy constant $K/k_B$ is evaluated as $1\times10^{-4}$ K per magnetic ion under Zandbergen's formulation. As above, the measurement of $\Delta n^{xy}$ has clearly revealed the ordering process of the basal-plane moments of the $ac$-plane triangular structure.

However, it is still difficult to explain the experimental results of $\Delta n^{ca}(T)$ because its two sharp bends exist even when $\Delta n^{xy} = 0$ or the $C$ terms are canceled out. In typical uniaxial magnetic systems, the singularity of the other terms of $\Delta n^{ca}$, except for the $C$ terms, at the critical point is thought to be vanishingly small because the Heisenberg-to-Ising crossover occurs gradually above $T_N$ so that the singularity at $T_N$ is masked by the "tail." Therefore, another mechanism for the sharp bends of $\Delta n^{ca}(T)$ should be taken into account.

It seems adequate that in order to understand the anomaly of $\Delta n^{ca}(T)$ the frustration effect must be taken into consideration. In $CsNiCl_3$, the magnetic moments cannot align parallel to the $c$ axis without competing with the exchange interactions which tend to make the moments order in a 120° array. As a result, the Heisenberg-to-Ising crossover will be suppressed so that the spin space remains almost isotropic even in the vicinity of $T_{N1}$. In this connection, a spin-wave theory shows that the effective anisotropy of this system is weakened to $(D/zJ)^3$, where $D$ denotes the magnitude of a single-ion anisotropy, $J$ denotes the exchange interaction constant in the basal plane, and $z$ denotes the number of the nearest-neighbor spins ($z=6$ in the present case).[21] Moreover, it has recently been pointed out by an NMR study that moments in the *ac* plane can rotate considerably freer in the *ac* plane.[6] Therefore it is possible that a crossover from quasi-isotropic to uniaxial magnetic behavior occurs abruptly below $T_{N1}$. As a result, the $B$ term in Eq. (1) must be essential to explain the sharp bend of the *ac*-plane birefringence $\Delta n^{ca}(T)$ at $T_{N1}$ in the present case. On the other hand, though $CsCoCl_3$ has complete frustration, the frustration is not effective as far as the change of the magnetic symmetry is concerned because the direction of the spin moment is restricted to the $c$ axis. Moreover, since the $CsMnBr_3$ system does not have such competitions and the crossover from a Heisenberg spin to an $XY$ spin occurs gradually, the singular behavior of the $B$ terms are trivial at $T_N$. Accordingly, only the $CsNiCl_3$ system has the possibility of showing the sharp bend in $\Delta n^{ca}(T)$.

However, the sharp bend of $\Delta n^{ca}(T)$ at $T_{N2}$ cannot be explained by the $B$ terms because the symmetry has already been broken at $T_{N1}$. Therefore, the first $A$ term in Eq. (1) will be essential to explain the bends of $\Delta n^{ca}(T)$ at $T_{N2}$. Because of the spin frustration, the evolution of the short-range order of the interchain spins can also be suppressed so that $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is believed to behave like $\langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle$ with respect to the interchain spins. Nevertheless, this does not agree with the results of the specific-heat experiments which exhibit rather dull peaks.[22] A new theoretical approach to confirm this picture is expected.

In summary, through the birefringence investigation in the $c$ plane, it is confirmed that the basal-plane components of the magnetic moments are not ordered in the intermediate phase of the $CsNiCl_3$ system, which was consistent with the result in NMR and neutron-scattering studies. Another result is that a multidomain structure with respect to the direction of the spin plane around the $c$ axis is stabilized in the low-temperature phase, and a single-domain structure is established for the field perpendicular to the $c$ axis above about 0.3 T. As for the strange behavior on $\Delta n^{ca}(T)$, it is believed that the frustration effect will play important role to sharpen the singularity at the Néel points.

The authors would like to thank Professor Y. Ueno and Professor S. Miyashita for their stimulating discussions. We also thank Dr. H. Tanaka for his help in preparing single crystals and his discussions.

[1] N. Achiwa, J. Phys. Soc. Jpn. **27**, 561 (1969).

[2] M. Mekata, J. Phys. Soc. Jpn. **42**, 76 (1977).

[3] V. J. Minkiewicz, D. E. Cox, and G. Shirane, Solid State Commun. **8**, 1001 (1970); M. Mekata, K. Adachi, H. Takaki, and N. Achiwa, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, 1970,* edited by E. Kanda (Academic, Tokyo, 1971), p. 801.

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

[5] W. B. Yelon and D. E. Cox, Phys. Rev. B **7**, 2024 (1973).

[6] S. Maegawa, T. Goto, and Y. Ajiro, in *Proceedings of the Eighteenth International Conference on Low Temperature Physics, Kyoto, 1987* [Jpn. J. Appl. Phys. **26**, Suppl. 26-3 (1987) ]; J. Phys. Soc. Jpn. **57**, 1402 (1988).

[7] H. Kadowaki, K. Ubukoshi, and K. Hirakawa, J. Phys. Soc. Jpn. **56**, 751 (1987).

[8] K. Iio and K. Nagata, J. Magn. Magn. Mater. **54-57**, 1393 (1986).

[9] R. Brener, D. Moses, H. Shechter, E. Ehrenfreund, J. Makovsky, and T. Wei, Phys. Status Solidi (a) **31**, K31 (1975); R. Brener, E. Ehrenfreund, H. Shechter, and J. Makovsky, J. Phys. Chem. Solids **38**, 1023 (1977).

[10] K. Iio, H. Hotta, M. Sano, H. Masuda, H. Tanaka, and K. Nagata, J. Phys. Soc. Jpn. **57**, 49 (1988).

[11] M. Eibschütz, R. C. Sherwood, F. S. L. Hsu, and D. E. Cox, in *Magnetism and Magnetic Materials—Chicago, 1971,* edited by D. C. Graham and J. Rhyne, AIP Conf. Proc. No. 5 (American Institute of Physics, New York, 1972), p. 684.

[12] H. W. Zandbergen, J. Solid State Chem. **35**, 367 (1980).

[13] F. Matsubara, J. Phys. Soc. Jpn. **51**, 2424 (1982).

[14] S. Miyashita and H. Kawamura, J. Phys. Soc. Jpn. **54**, 3385 (1985).

[15] Xiaodong Zhu and M. B. Walker, Phys. Rev. B **36**, 3830 (1987).

[16] M. L. Plumer, Kelvin Hood, and A. Caillé, Phys. Rev. Lett. **60**, 45 (1988).

[17] Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Lett. **15**, 1023 (1965); T. Moriya, J. Phys. Soc. Jpn. **23**, 490 (1967).

[18] J. Ferré and G. A. Gehring, Rep. Prog. Phys. **47**, 513 (1984).

[19] J. A. Rayne, J. G. Collins, and G. K. White, J. Appl. Phys. **55**, 2404 (1984).

[20] H. Tanaka (private communication).

[21] T. Suzuki and Y. Natsume, J. Phys. Soc. Jpn. **56**, 1577 (1987).

[22] K. Adachi and M. Mekata, J. Phys. Soc. Jpn. **34**, 269 (1973).