Magnetic properties of the noncollinear antiferromagnet $KNiCl_3$

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Neutron-scattering measurements are reported on the magnetic structure of the noncollinear quasi-one-dimensional antiferromagnet $KNiCl_3$. At 4.5 K there is a commensurate triangular structure. From the magnetization measurements a magnetic phase diagram for a field applied within the basal plane was determined. At low temperatures there is a phase transition at field (2.3 ± 0.1) T to a collinear magnetic structure. From measurements of the spin-wave dispersion along the chain direction the intrachain exchange coupling J=(0.310 ± 0.006) THz and the single-ion anisotropy D=(0.13 ± 0.01) THz were deduced after taking into account a correction for quantum fluctuations.

Recent interest in the $KNiCl_3$ family of crystals, such as $RbFeBr_3$,[1–3] $RbVBr_3$,[4,5] $RbMnBr_3$,[6–9] and $KNiCl_3$,[10,11] may be attributed to the experimental opportunity to investigate the magnetic properties of easy-plane triangular lattice antiferromagnets with partially released spin frustration. In contrast to the simpler case of $CsMnBr_3$, where the magnetic ions form a hexagonal lattice with the space group $P6_3/mmc$,[12] the presence of successive distortional phase transitions in the $KNiCl_3$ family leads to the generation of lower-symmetry phases with space groups such as $P6_3cm$, $P\bar{3}c1$. The crystal distortions break the symmetry and so change the exchange interaction between neighboring in-plane magnetic ions. This results in magnetic structures where the angle between neighboring moments is changed slightly from a 120° triangular configuration. Neutron-diffraction measurements have established that in $RbFeBr_3$ (Ref. 1) and in $RbVBr_3$ (Ref. 4) the magnetic ordering is commensurate [magnetic Bragg peaks at position $(h/3, h/3, l)$], while in $RbMnBr_3$ (Ref. 8) there is an incommensurate ordered structure with magnetic Bragg peaks at $(h/8 \pm \delta, h/8 \pm \delta, l)$ where $\delta = 0.0183$. The exact magnetic structure of $KNiCl_3$ has not been determined so far; however, from previous electron-spin-resonance (ESR) measurements[10,13] a triangular spin structure has been inferred with the angle between neighboring magnetic moments slightly different from 120°. For a better understanding of the physical processes that take place in this and similar systems it is necessary to know the exact magnetic structure and the magnitudes of the exchange couplings and magnetic anisotropy constant.

In this paper we report the results of neutron-scattering and magnetization measurements on a single crystal of $KNiCl_3$. A comparison of the results with a mean-field model of isolated one-dimensional chains allowed us to determine the parameters of the exchange interaction along the c direction, J, and the single-ion anisotropy D. Some conclusions can also be made about the nearest-neighbor in-plane exchange interaction between magnetic ions in equivalent (J_1) and nonequivalent (J_2) crystallographic sites.

The neutron-scattering measurements were carried out on the N5 triple-axis spectrometer at the NRU reactor at Chalk River Laboratories. Silicon (111) reflections were used to monochromatize and analyze the neutron beam; the scattered neutron energy was fixed at 3.52 THz. A pyrolytic graphite filter was installed in the scattered beam to remove higher-order contamination.

We work in terms of the reciprocal lattice of room-temperature $KNiCl_3$ (lattice parameters $a = 11.803$ Å, $c = 5.936$ Å). This structure is related to the $CsNiCl_3$ structure by enlarging the a axis by the factor of $\sqrt{3}$ and shifting the two inner face-sharing chains of octahedra along the c axis.[15] The single-crystal sample ($5 \times 7 \times 10$ mm^3) was aligned in a helium cryostat in two different ways, so that the horizontal scattering plane contained (hhl) reflections in the first case and $(h0l)$ reflections in the second case. Magnetic Bragg peaks at (101) and (201) [which correspond to $(1/3, 1/3, 1)$ and $(2/3, 2/3, 1)$ in the prototype $CsNiCl_3$-type lattice] were observed at low temperatures. This observation confirms the existence of a commensurate triangular spin structure in $KNiCl_3$.

Typical examples of spin-wave excitations along the c axis in $KNiCl_3$ at $T = 4.5$ K are shown in Fig. 1. Typical counting times were 30 min at each point. Figure 2 plots the energy of spin waves as a function of the reduced wave vector q, where the crosses and squares represent excitations around (111) and (101) reflections, respectively. The lines drawn in the figure are given by the formulas for noninteracting antiferromagnetic chains:

$$\hbar\omega_1(q) = 4JS \sin\frac{q}{2}\sqrt{4\cos^2\frac{q}{2} + \frac{D}{J}}, \qquad (1)$$

$$\hbar\omega_2(q) = 4JS \cos\frac{q}{2}\sqrt{4\sin^2\frac{q}{2} + \frac{D}{J}},$$

where $S = 1$ is the spin of the Ni ions, $J = (0.365 \pm 0.007)$ THz, and $D = (0.116 \pm 0.010)$ THz. These formulas were obtained in Ref. 14 for the classical one-dimensional antiferromagnet with a single-site anisotropy. The good agreement between observed and

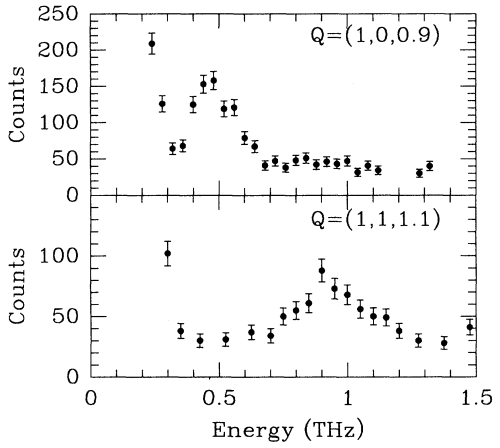

FIG. 1. Spin-wave excitations in $KNiCl_3$ at 4.5 K along the c axis at $Q = (1, 0, 0.9)$ and $Q = (1, 1, 1.1)$. Counting times are about 30 min per point.

calculated spin-wave frequencies provides confirmation of the magnetic quasi-one-dimensional nature of the $KNiCl_3$; that is, the interchain exchange interaction is much smaller than the intrachain exchange and the anisotropy. This is expected to be a common feature of the $KNiCl_3$ family of materials. It should be noted that quantum corrections to Eq. (1) are required.[16] For exchange along chains the correction is given by the formula

$$J_Q = J\left[1 + \frac{\pi - 2}{2\pi S} + \frac{\pi^2 - 10}{4\pi^2 S^2} + O\left(\frac{1}{S^3}\right)\right], \qquad (2)$$

while for the anisotropy

$$D_Q = D\left(1 - \frac{1}{2S}\right)\left(1 - \frac{2\ln(D_Q/J_Q)}{\pi S}\right), \qquad (3)$$

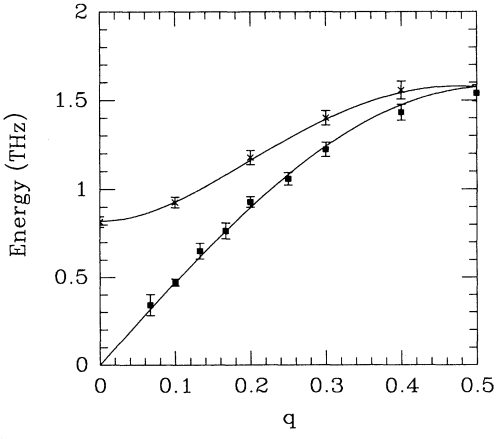

FIG. 2. Spin-wave dispersion relation in $KNiCl_3$ at 4.5 K along the hexagonal axis. The solid points give the observed spin-wave energies at $Q = (1, 0, 1-q)$ and the crosses give the spin-wave energies at $Q = (1, 1, 1+q)$. The lines are given by the formula (1) with $J = 0.365$ THz, $D = 0.115$ THz.

where the subscript Q refers to the theory with the addition of quantum renormalizations. Taking into account these corrections we obtained the value of the intrachain magnetic coupling constant in $KNiCl_3$, $J = (0.310 \pm 0.006)$ THz, and the value of the single-ion anisotropy $D = (0.13 \pm 0.01)$ THz. This value of J is in excellent agreement with that given by Tanaka *et al.*[10] from high-temperature susceptibility measurements, $J = 15.0$ K $= 0.312$ THz, but the value of D is much larger than $D = 0.86$ K $= 0.018$ THz reported in the same paper.

We should add a remark about the details of the determination of the Hamiltonian constants from the susceptibility measurements. While the value J might be determined relatively precisely [the accuracy seems to be of order (10–20)%] it is extremely difficult to determine the value of the single-ion anisotropy from the susceptibility measurements, because $\chi(T)$ is insensitive to changes in D; for example, substituting $10D$ for D into the expressions for $\chi(T)$ given in Ref. 10 leads to only a 2% change of χ at $T = 150$ K. For this reason the value of D calculated from the spin-wave excitations energy appears to be more reliable.

In addition to the neutron-scattering measurements, we performed a series of magnetization measurements using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The magnetic moment of the sample was determined for applied magnetic fields up to 5 T at temperatures of 2.1 and 4.5 K. The magnetization curves look very similar to those previously observed in the other easy-plane triangular antiferromagnets $CsMnBr_3$ (Ref. 17) and $RbMnBr_3$ (Ref. 7). A magnetic phase transition corresponding to the collapse of two of the three pairs of magnetic sublattices[16] was detected at $H_{\perp c} = (2.3 \pm 0.1)$ T for $T = 2.1$ K and at $H_{\perp c} = (2.2 \pm 0.1)$ T for $T = 4.5$ K. The only difference from the case of the 120° triangular spin structure is that the ratio $\chi_{\parallel}/\chi_{\perp}$ changes from 2 to about 1.5. In the classical limit, this susceptibility ratio determines the ratio of in-plane exchange constants:

$$\frac{\chi_{\parallel}}{\chi_{\perp}} = \frac{3}{1 + \frac{1}{2}\left(\frac{J_1}{J_2}\right)^2}, \qquad (4)$$

and so $J_1/J_2 \approx 1.41$. The phase transition field at zero temperature specifies the value of $(2J_2 - J_1)$:[10]

$$H_c^2 = 48J(2J_2 - J_1)S^2, \qquad (5)$$

where $H_c(T = 0) = 2.3$ T, and so $(2J_2 - J_1) = 2.78 \times 10^{-4}$ THz, $J_1 \approx 6.7 \times 10^{-4}$ THz, $J_2 \approx 4.7 \times 10^{-4}$ THz. The formula (4) was derived in a mean-field approximation, ignoring the large influence of the quantum fluctuations on the magnetization process.[18–20] As a result the experimentally measured magnetizations of quasi-one-dimensional antiferromagnets are considerably less than predicted by linear spin-wave theory—in our case the reduction of the magnetization is about 40%. In addition, Eq. (4) is valid only in the limit $D \ll 4J$. The latter condition is not strictly valid for $KNiCl_3$ where the anisotropy is about 40% of the exchange coupling. There-

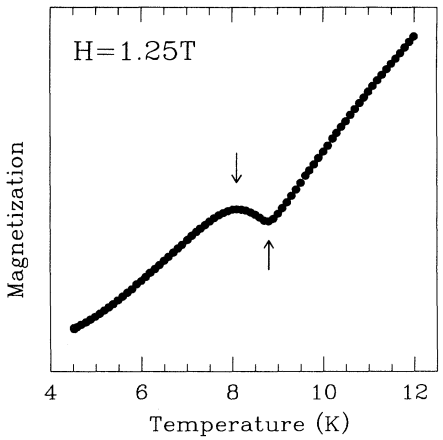

FIG. 3. The temperature dependence of the magnetization at $H = 1.25$ T in arbitrary units. The arrows at 8.1 and 8.8 K correspond to the temperatures of the phase transitions.

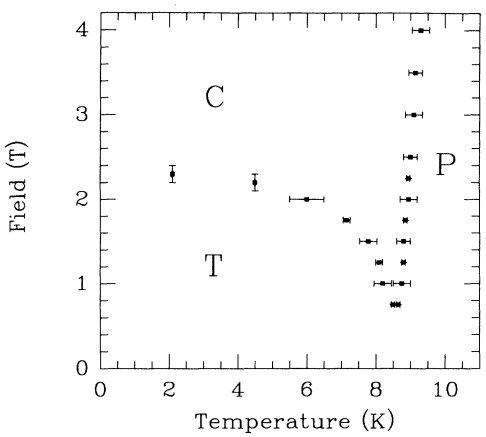

FIG. 4. The magnetic phase diagram of the $KNiCl_3$ for $H \perp c$ from the magnetization measurements. The first two points at low temperature correspond to the phase transition from the triangular (T) to the collinear (C) phase and are taken from $M(H)$ measurements. The other points are from $M(T)$ measurements.

fore values obtained for the interchain exchange constants should be considered as approximate.

In order to determine the phase diagram of $KNiCl_3$ a series of temperature scans was taken at constant magnetic field. The temperature was varied from 4.5 to 15 K in 0.1- or 0.5-K steps. An example of the temperature dependence of the magnetization at $H = 1.25$ T is shown in Fig. 3. In a field less than 2 T each magnetization curve shows two abrupt changes of slope, corresponding to transitions from the triangular to the collinear phase and from the collinear to paramagnetic phase. In higher fields only the latter transition was detected. Our measurements in low magnetic field do not indicate any signs of two successive transitions (splitting of T_N), although this is predicted to exist by the mean-field theory[21,22] and was observed in the isostructural compound $RbVBr_3$.[5] The minimum magnetic field at which we could resolve two phase transitions (at 8.50 and 8.65 K) was 0.75 T; at $H = 0.5$ T some anomaly in the slope of the magnetization curves still exists, but it is not possible to distinguish between the two transition temperatures. If this splitting exists, the difference between T_{N1} and T_{N2} is less than 0.15 K. Figure 4 shows the magnetic phase transition data. The overall picture is very similar to that observed for the undistorted easy-plane triangular antiferromagnet $CsMnBr_3$ (Ref. 23) with a tetracritical point at zero field and temperature 8.6 K.

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