Magnetic resonance in the noncollinear hexagonal antiferromagnet $RbNiCl_3$

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The temperature evolution of the antiferromagnetic resonance in the quasi-one-dimensional noncollinear antiferromagnet $RbNiCl_3$ is studied. Measurements were carried out for frequencies between 42 and 78 GHz, in magnetic fields up to 40 kOe and in the temperature range of 1.55 to 20 K. Good agreement between experimental and theoretical results is obtained for the values $J' = (38 \pm 4)$ GHz and $D = (1 \pm 0.1)$ GHz, where J' is the exchange integral and D is the easy axis anisotropy constant.

INTRODUCTION

Recently, there has been much interest in the magnetic properties of compounds of the ABX_3 type, where A = Cs, Rb; B = Mn, Ni; and X = Cl, Br, I, because of two peculiarities of their magnetic structure: (1) quasi-one-dimensionality (the exchange interaction in the direction of the crystal axis is much greater than the exchange interaction in the basal plane) and (2) there is ordering of noncollinear spin configurations at temperatures lower than T_N (T_N is the temperature of three-dimensional magnetic ordering). At the transition, the system orders in a plane 120° configuration, whose magnetic properties are usually described by the following Hamiltonian:

$$\mathscr{H}=2J\sum_{i,j}{}' S_iS_j+2J'\sum_{i,j}{}'' S_iS_j+D\sum_i (S_i^z)^2-\gamma H\sum_i S_i, \qquad (1)$$

where S_i, S_j are spins on B type ions i and j, respectively, J is the exchange integral along the C_6 crystallographic axis, J' is the exchange integral in the basal plane (for $RbNiCl_3$ the exchange interaction is antiferromagnetic, i.e., J, $J' > 0$), and D is the anisotropy constant, whose sign determines the orientation of the plane where the spins lie with respect to the crystal axes. The first term in Eq. (1) describes the exchange energy along the chain, the second one gives the exchange energy in the basal plane and the third and forth terms give the anisotropy and Zeeman energies, respectively.

The existence of a noncollinear magnetic structure in $RbNiCl_3$ for $T < T_N$ was established by neutron diffraction studies.[1] These studies have been carried out mainly at $T = 4.5$ K. It was found that the plane in which the spins lie is perpendicular to the basal plane of the crystal, i.e. $D < 0$. Every third spin in the basal plane is aligned along the C_6 axis while the other two spins are canted with respect to it at a $\theta = 60°$ angle (see Fig. 1).

We have studied $RbNiCl_3$ single crystals using electron spin resonance; at temperatures below T_N, antiferromagnetic resonance (AFMR) is observed, whereas electron paramagnetic resonance (EPR) is observed for temperatures greater than T_N. Measurements of AFMR in antiferromagnetic materials with the magnetic structure described above were made for the first time in $CsNiCl_3$ crystals;[2] however, the fairly low temperature of the three-dimensional ordering ($T_N = 4.5$K) did not allow the authors of Ref. 2 to study variations of the AFMR spectra with temperature in detail. T_N is higher in $RbNiCl_3$, as follows from measurements of static magnetic properties:[3] $T_N = 11$ K. Therefore, it is possible to study in detail how AFMR spectra of $RbNiCl_3$ vary with temperature, to determine effective magnetic fields and constants, and to check the validity of the model proposed in Ref. 2. This is the aim of this paper.

MAGNETIC PROPERTIES OF $RbNiCl_3$

Studies of the magnetic properties of ABX_3 compounds were initiated by Achiva.[3] He determined how the magnetic susceptibility χ varies with temperature and performed EPR measurements for various orientations of the magnetic field with respect to the crystal axis in $RbNiCl_3$ single crystals. At $T = T_{\max} = 45$ K there is a soft maximum in the $\chi(T)$ curve which is characteristic of one-dimensional chains. A transition to three-dimensional ordering was observed at $T_N = 11$ K. From EPR measurements, the g-factor was determined: $g_\perp = 2.23$ and $g_{\parallel} = 2.21$. Values of 292 GHz and 333 GHz were obtained for the exchange integral J, from the values of $T_{\max}$ and $\chi_{\max}$, respectively. The value $J'/J \approx (0.1$–$0.01)$ was estimated.

Much later, Witteven and van Veen repeated the magnetic susceptibility and EPR experiments in polycrystalline $RbNiCl_3$. Their results agreed with the results of Ref. 3; however, they obtained different values of the exchange integral: J(from $T_{\max}$) = 333 GHz, J(from $\chi_{\max}$) = 387 GHz and J (determined from the fit to the spin-wave model in a wide temperature range for $T > T_N$) = 383 GHz.

Values of J and T_N have also been obtained from double refraction of light in experiments on single $RbNiCl_3$ crystals at temperatures of 6–300 K.[5] The values given therein are $J = (426 \pm 37)$ GHz and $T_N = 11.0$ K.

The effect of strong magnetic fields on the magnetic

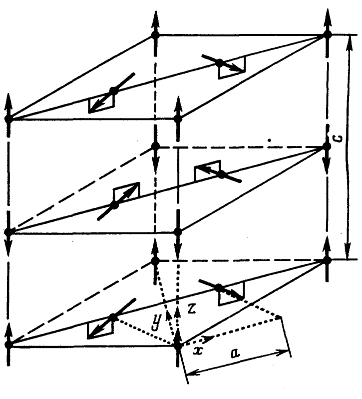

FIG. 1. Magnetic structure of ABX_3 compounds for $T < T_N$ for small anisotropy.

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structure was studied in Ref. 6. When a magnetic field is applied along the $\mathbf{C}_6$ axis, a phase transition (spin–flop of sublattices) occurs at a critical field H_C; the magnitude of H_C increases with increasing temperature from 20 to 25 kOe.

THEORETICAL CALCULATIONS OF AFMR SPECTRA

Microscopic calculations carried out in the framework of the six sublattices model,[7] for $T=0$ and the magnetic field $\mathbf{H}$ parallel to the $\mathbf{C}_6$ axis, yield the following equations for the resonance frequencies: for $H<H_C$,

$$\nu_1=\gamma(\eta_0 H_c^2+H^2)^{1/2},\quad \nu_2=\gamma\frac{H_c}{2\sqrt{3}}\frac{\tilde{D}}{J}\left[1-\left(\frac{H}{H_c}\right)^2\right]^{1/2},$$
$$\nu_3=0,\quad \nu_{4,5}=6\sqrt{2}(JJ')^{1/2},\quad \nu_6=12(JJ')^{1/2}, \tag{2a}$$

whereas for $H>H_C$,

$$\nu_{1,2}=\gamma\left\{\left[\left(\frac{1+\eta_0}{2}H\right)^2-\eta_0 H_c^2\right]^{1/2}\pm\frac{1-\eta_0}{2}H\right\}, \tag{2b}$$

where $\eta_0=(s1+9J'/4J)^{-1}$, $\tilde{D}=D(1-1/2S)=D/2$, and H_C is the critical field for a spin–flop to a state in which the plane containing the spins is perpendicular to the $\mathbf{C}_6$ axis. The AFMR spectrum consists of six modes: three exchange modes and three relativistic modes. We are interested in the $\nu_1(H)$ and $\nu_2(H)$ modes whose frequencies lie in the experimentally accessible range. A second (phenomenological) approach allows one to determine the AFMR spectrum taking into account finite-temperature effects. Macroscopic calculations in the exchange interaction approximation were carried out for an arbitrary angle φ between the external magnetic field and the $\mathbf{C}_6$ crystal axis.[2] According to these calculations, the resonance frequencies are the roots of the equation,

$$\left(\frac{\nu}{\gamma}\right)^4-\left(\frac{\nu}{\gamma}\right)^2[H^2+\eta^2H^2\cos^2(\alpha-\varphi)-\eta H_c^2(3\cos^2\alpha-1)]$$
$$+\eta[H_c^2\cos^2\alpha-H^2\cos^2(\alpha-\varphi)][\eta H_c^2\cos 2\alpha-\eta H^2\cos^2(\alpha-\varphi)$$
$$-H^2\sin^2(\alpha-\varphi)]=0. \tag{3}$$

where $\eta=(\chi_\perp-\chi_\parallel)/\chi_\parallel$, γ is the gyromagnetic ratio, and α is the angle between the normal to the spin plane and the $\mathbf{C}_6$ axis, given by,

$$\operatorname{tg} 2\alpha=H^2\sin 2\varphi/(H^2\cos 2\varphi-H_c^2).$$

When H is parallel to the $\mathbf{C}_6$ axis, we have

$$\frac{\nu_1}{\nu}=(\eta H_c^2+H^2)^{1/2},\quad \nu_2=\nu_3=0, \tag{4a}$$

for $H<H_C$, whereas,

$$\frac{\nu_{1,2}}{\gamma}=\left[\left(\frac{1+\eta}{2}H\right)^2-\eta H_c^2\right]^{1/2}\pm\frac{1-\eta}{2}H,\quad \nu_3=0. \tag{4b}$$

holds for $H>H_C$. Comparing the results of these two calculations at $T=0$, we can easily establish a relation between the constants in the Hamiltonian (1) and the macroscopic parameters. It follows that

$$\eta_0=\eta(T=0)=(1+{}^9/_4J'/J)^{-1},$$
$$H_c^2=16\tilde{D}JS^2(1+{}^9/_4J'/J)(1+{}^9/_8J'/J). \tag{5}$$

SAMPLES AND EXPERIMENTAL METHOD

The $\mathrm{RbNiCl_3}$ compound was synthesized in the form of a polycrystalline sediment by mixing hot solutions of RbCl and $\mathrm{NiCl_2}$ in concentrated HCl acid. The dry $\mathrm{RbNiCl_3}$ sediment was place in a quartz ampule under vacuum and was then slowly lowered through a furnace heated to 750°C. The single crystal obtained was annealed over 10 days at temperatures of 500–600°C. The correspondence between the crystalline structure of the material obtained and the $\mathrm{RbNiCl_3}$ structure was established by means of X-ray analysis ($a=6.953\pm0.004$ Å, $c=5.886\pm0.006$ Å). The crystals were transparent, red, and of parallelepiped shape with linear dimensions ~ (1–2) mm. The crystallographic axes were oriented by the x-ray method.

A direct-amplification spectrometer was used in the experiments. They were performed over the range of frequencies 42 GHz to 78 GHz in fields up to 40 kOe, and in the temperature range of 1.55 K to 20 K. The sample was placed in a short-circuit waveguide. Absorption of ultra high frequency (UHF) power was observed in the reflected signal. The temperature was measured by a semiconductor thermometer. The external magnetic field was provided by a superconducting solenoid. The measurements were carried out for various values of the angle φ between the magnetic field and the $\mathbf{C}_6$ axis of the crystal. The magnitude of φ was determined to within ± 1°.

RESULTS AND DISCUSSION

An EPR-absorption line, with a linewidth of $\Delta H\approx0.5$ kOe, is observed for temperatures higher than $T_N=11$K. Our results show that the resonant frequencies and magnetic fields obey the relation, $\nu=\gamma H$, where $\gamma(=3.1\,\mathrm{GHz/kOe})$ is a constant nearly independent of temperature. These results agree with the data of Ref. 3.

The resonance spectra are more complicated at temperatures below T_N. Figure 2 shows how ν depends on H for different directions of the magnetic field with respect to the principal crystal axis. The solid lines are calculated using the formulas given in Ref. 2; η and H_C are variable parameters which are chosen to give the best fit to the experimental results. As shown in Fig. 2, there is a good agreement between experimental and calculated results. Figure 3 shows the AFMR spectra of $\mathrm{RbNiCl_3}$ for $\mathbf{H}$ parallel to the $\mathbf{C}_6$ axis at three different temperatures. The variation of these spectra with temperature can be observed easily. The temperature dependence of η and of H_C in $\mathrm{RbNiCl_3}$, obtained from

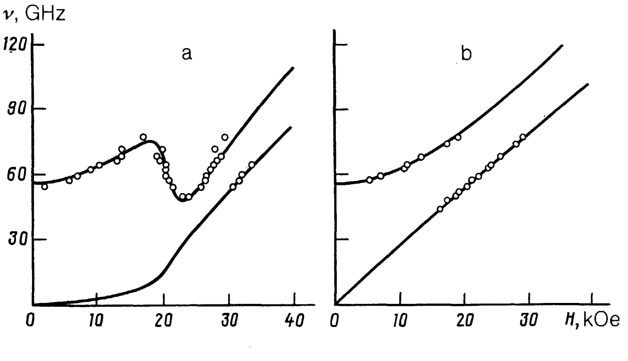

FIG. 2. AFMR spectra in $\mathrm{RbNiCl_3}$ at $T=2$ K: (a) $\varphi=5°$; (b) $\varphi=90°$.

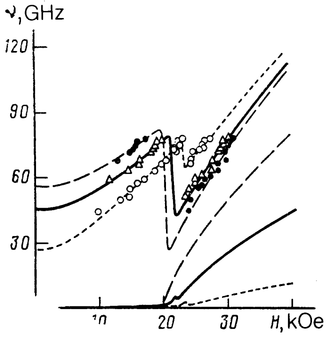

FIG. 3. AFMR spectra in $RbNiCl_3$ for **H** parallel to the C_6 axis at different temperatures: ●—$T = 3$ K; Δ—$T = 6$ K; O—$T = 9$ K.

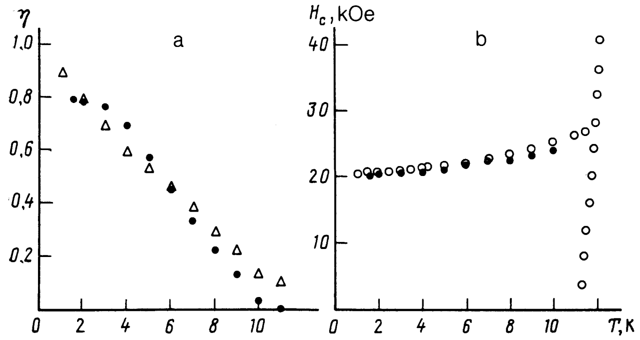

FIG. 4. Temperature variation of (a) $\eta = (\chi_\perp - \chi_\parallel)/\chi_\parallel$ and (b) the spin-flop transition field H_C; ●—AFMR data, Δ—results of Ref. 2, O—data from Ref. 6.

the comparison of the experimental data with theoretical calculations, is shown in Fig. 4. As the temperature is raised from 1.55 K to $T_N = 11$ K, the magnitude of η drops from its maximum value of 0.8 (for $T = 1.55$ K) to zero, while the critical field H_C increases smoothly from 20.1 kOe to 24 kOe. For comparison, values of η and H_C obtained from magnetic susceptibility measurements,[3] and from measurements of the induced magnetization[6] are shown in Fig. 4. the agreement between our results and data from static measurements is good.

From the values of η and of H_C at $T = 0$, obtained by extrapolations of η and H_C as functions of T, we can estimate the exchange integral J' and the anisotropy constant D, using the formulas of Ref. 5 and the value of J from other experiments. Taking $J = 383$ GHz (as the most reliable value), we get $J' = (38 \pm 4)$ GHz and $D = (-1 \pm 0.1)$ GHz. For a $CsNiCl_3$ crystal, which is isomorphic to $RbNiCl_3$ and very close to $RbNiCl_3$ with regard to magnetic properties, we have $J = 345$ GHz,[8] $J' = 8.2$ GHz and $D = -1.2$ GHz.[7] The value of the exchange interaction J' in $RbNiCl_3$ is almost five times greater than the value of J' for $CsNiCl_3$, while the values of the exchange integrals J along the principal crystal axis and the anisotropy constant are similar. We note that the transition temperature into the ordered state is proportional to the square root of the product of the exchange integrals, i.e. $T_N \propto (JJ')^{1/2}$. The proportionality coefficient is equal to 1.84 for $CsNiCl_3$ and 1.90 for $RbNiCl_3$.

For quite negative values of the anisotropy constant, the magnetic structure may deviate from the equilateral triangular structure. The effect of the anisotropy on the triangular configuration can be calculated from the following formula:[8]

$$\cos\theta = \frac{1}{2(1+D/12J')}.$$

Our data for $RbNiCl_3$ give $\varphi = 59.9°$, i.e., the spins of the magnetic atoms lie close to the edges of equilateral triangles, in agreement with neutron scattering results.[1]

Given the values of the exchange integral J' and of the anisotropy constant D, one can estimate the resonance frequency $\nu_2(H)$ for H parallel to C_6 and $H < H_C$. The value $\nu_2(H = 0) = 0.24$ GHz is in agreement with our data.

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