PHYSICAL REVIEW B VOLUME 17, NUMBER 1 1 JANUARY 1978

# $^1E_g$ spin-forbidden transition in $NiBr_2$: temperature dependence and magnetoabsorption

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(Received 19 November 1976; revised manuscript received 1 June 1977)

A detailed study of the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition at low temperatures in antiferromagnetic $NiBr_2$ is presented. The spectrum consists of a number of peaks, some of them rather narrow, three of which are of extrinsic origin. In the intrinsic part of the absorption, two peaks (at 8 and 38 $cm^{-1}$ from the lowest-energy sharp peak at 5 °K) have an interesting temperature dependence around 20 °K. At this temperature, in fact, the 8-$cm^{-1}$ displaced sideband merges with the lowest-energy sharp peak, whereas the other peak grows much stronger above 20 °K. A magnetic field in the $c$-axis direction affects only the 8-$cm^{-1}$ displaced sideband with an asymmetric splitting. These features are discussed in terms of spin waves of the magnetic structure of $NiBr_2$, which has two phases, one collinear above 20 °K and one probably noncollinear and with the spins canted out of the basal plane, at low temperatures. It is suggested that the canting of the spins is due to competition between anisotropy and zero-point motion of the spins and the noncollinear order is due to temperature renormalization of competing exchange interactions.

## I. INTRODUCTION

The crystal-field spectrum of $Ni^{2+}$ ion has been extensively studied in various materials both magnetic and nonmagnetic; the $Ni^{2+}$ ion was in them both as an impurity or as a basic stoichiometric component.

The energy position of the various bands has been satisfactorily accounted for by the diagonalization of the $d^8$ matrices prepared by Liehr and Ballhausen.[1] Some of the spin-orbit and vibronic structures have also been studied in detail on some specific materials. The $^1E_g$ spin-forbidden band, however, has certainly given the argument for most of the discussion on the crystal-field spectrum. In $KNiF_3$, $K_3Ni_2F_7$, and $RbNiF_3$ (Refs. 2–6) there is a "satellite" peak at an energy of about 800–900 $cm^{-1}$ greater than the zero-phonon line. The "satellite" is absent when $Ni^{2+}$ is diluted in $KMgF_3$ (Refs. 2 and 3) and is not clearly evident in $NiF_2$.[7] In a former work of ours on $NiCl_2$ and $NiBr_2$,[8] the structures of the $^1E_g$ band were rather narrow and well defined, "satellite" included, in $NiBr_2$; in $NiCl_2$ no band or group of peaks that could be reasonably attributed to the $^1E_g$ has been found.

Here we want to report on our recent effort to clarify the "puzzle" of the $^1E_g$ band in $NiBr_2$. We present in Sec. II a study of the temperature dependence and of the magnetic effects on the lowest-energy sharp peaks of the $^1E_g$. A discussion of these features in terms of the magnetic structures existing in $NiBr_2$ above and below 20 °K will also be given.

After the submission of this paper, optical and neutron-scattering measurements[9] have been published on the same compound. There is agreement in the experimental data, but our theoretical discussion has been revised to take into account the new data.

## II. EXPERIMENTAL RESULTS AND DISCUSSION

Crystal of $NiBr_2$ were prepared in our laboratories with the flow system.[8] More will be said below.

Absorption data were taken with the sample in a home-made stainless-steel liquid-helium cryostat and by a Cary 14 spectrophotometer.

The temperature was allowed to increase spontaneously and checked by a Cryogenic Linear Temperature Sensor by Oxford Instruments. The reading uncertainty plus the delay between sample holder and sample produced an error of the order ±2 °K.

For magnetoabsorption measurements we used a Bruker Physik AG magnet with a continuous regulation up to 21 kG and a Monospek 1000 monochromator supplied with a 1200-lines/mm grating.

After the publication of our paper[8] on nickel halides, it was realized that in the $^1E_g$ (Ref. 10) region of the absorption spectrum a few peaks and particularly those at 16 883, 17 064, and 17 129 $cm^{-1}$ were sensitive to the conditions of growth and annealing of the samples.[11] The "series" appeared in crystals grown in defect of halogen and cooled in nitrogen and was practically absent in crystals grown in excess of bromine and cooled in a flux of bromine. Samples prepared in the first way (always with the flow system) and subsequently kept for 10 h at 400 or 500 °C in bromine atmosphere showed an absorption spectrum in which the intensity of the series was greatly reduced and the reduction was dependent on the temperature of the treatment.

In Fig. 1, one can see how the $^1E_g$ absorption looks like in samples prepared in the two different ways.

The three extrinsic peaks form a series produced by the presence of a defect whose ionic model we do not know as yet. An unusual detail of the strongest peak of the series is that the width at half-height is concentration dependent. The sequence of the oscillator strengths and spacings among the lines of the series are essentially hydrogenlike. This result obviously suggests reconsideration of certain interpretations given to the "satellite" peak in $KNiF_3$ and $RbNiF_3$.[2–6] We were, however, more interested in the study of the "intrinsic" spectrum and left this topic aside for future work.

The intrinsic spectrum deserves few comments. It has been observed[12] that at the lowest energies there is a sharp and strong peak at 16 434 $cm^{-1}$ followed by a smaller one at 16 442 $cm^{-1}$ and a weak shoulder extending up to 16 500 $cm^{-1}$; we will show below the temperature and magnetic field dependence of these structures. Most of the oscillator strength of the $^1E_g$ transition is concentrated in the part of the spectrum which extends from 16.500 to 16.800 $cm^{-1}$. One noticeable feature in this region is the sharp edge due to the presence of a narrow peak with maximum at 16 616 $cm^{-1}$ which overlaps the 16 500–16 800 broad band. Other absorption bands are located at $\simeq$16 800 and $\simeq$17 040 $cm^{-1}$. The mechanism responsible for each of these peaks is not known. The main absorption is probably due to phonon-assisted electric-dipole transition.

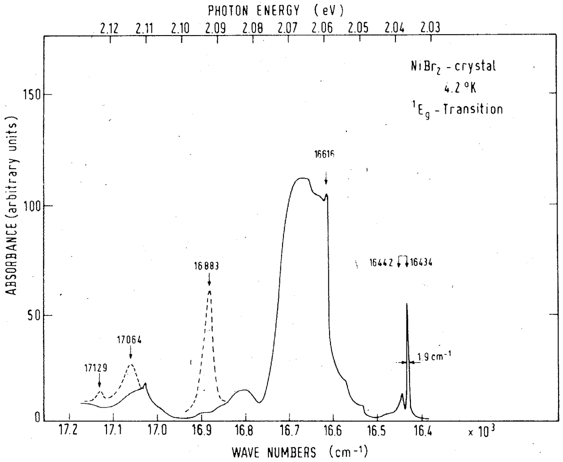

FIG. 1. Absorption spectrum of $NiBr_2$ in the $^1E_g$ region at 4.2 °K. Dotted bands only appear in samples annealed in nitrogen atmosphere.

In Fig. 2 the temperature dependence of the absorptions in the 16 400–16 500-$cm^{-1}$ region is shown. The subsidiary peak at 16 442 $cm^{-1}$ shows a strong temperature dependence: it decreases in energy and coalesces at $T \simeq 20$ °K with the main peak whose position is only slightly temperature dependent [Fig. 2(b)].

At the same time the shoulder at 16 472 $cm^{-1}$, which is weak at $T = 5$ °K, increases and above $\simeq$20 °K becomes the main feature of this part of the spectrum [Fig. 2(a)].

We have also studied the magnetic field dependence of the sharp peaks at 16 434 and 16 442 $cm^{-1}$. When the magnetic field is in the $c$ direction the strongest peak shows no change whereas the weaker peak at 16 442 $cm^{-1}$ splits asymmetrically [Fig. 3(a)], one of the components remaining almost at its $H = 0$ position and the other shifting to lower energy. We are not able to determine reliably the functional $H$ dependence of the splitting [Fig. 3(b)] but $\Delta E$ is appreciably smaller than the Zeeman splitting, $2g\mu_B H$ ($\simeq$4.4 $cm^{-1}$ at 20 kG). The same peaks show no magnetic field dependence up to 20 kG, when the direction of $H$ is in the $c$ plane.

The most noticeable feature of the $^1E_g$ absorption is the presence of the two peaks at 16 434 and 16 442 $cm^{-1}$ which are extremely sharp, the half-width being $\simeq$1 $cm^{-1}$. At first one may think that this couple of peaks is due to a splitting of the $^1E_g$ electronic level caused by a distortion of the basic cubic crystal field. For instance, in $K_3Ni_2F_7$ the first structures of the $^1E_g$ absorption have been attributed to zero-phonon lines of electric dipole character,[4] the distance between these two ($\simeq$75 $cm^{-1}$) being due to tetragonal splitting. In the case of $NiBr_2$ there is no such kind of splitting in the zero phonon line of the $^3T_{2g}$ absorption (unpublished results and Ref. 8) and so there are no lower symmetry perturbing fields. We further observe a clear inequivalency among the two peaks both respect to the temperature and magnetic field dependence and this is in contrast with the hypothesis that they are coming from the splitting of a level. The two sharp lines cannot be due to a splitting of the exciton level due to a static exchange field because both lines disappear by increasing the temperature or by applying a strong magnetic field in the basal plane[9] when the system changes to a higher-symmetry magnetic phase (see below).

The presence of the two sharp peaks as well as of the peak at 16 472 $cm^{-1}$ only at low temperatures where $NiBr_2$ is magnetically ordered and the electric-dipole nature[9] of these peaks suggests that they are magnon sidebands of the purely excitonic $^1E_g$ transition, which is not seen. We discuss this interpretation on the basis of what is known[9, 13–15] on the magnetic structure of this compound. The magnetic structure

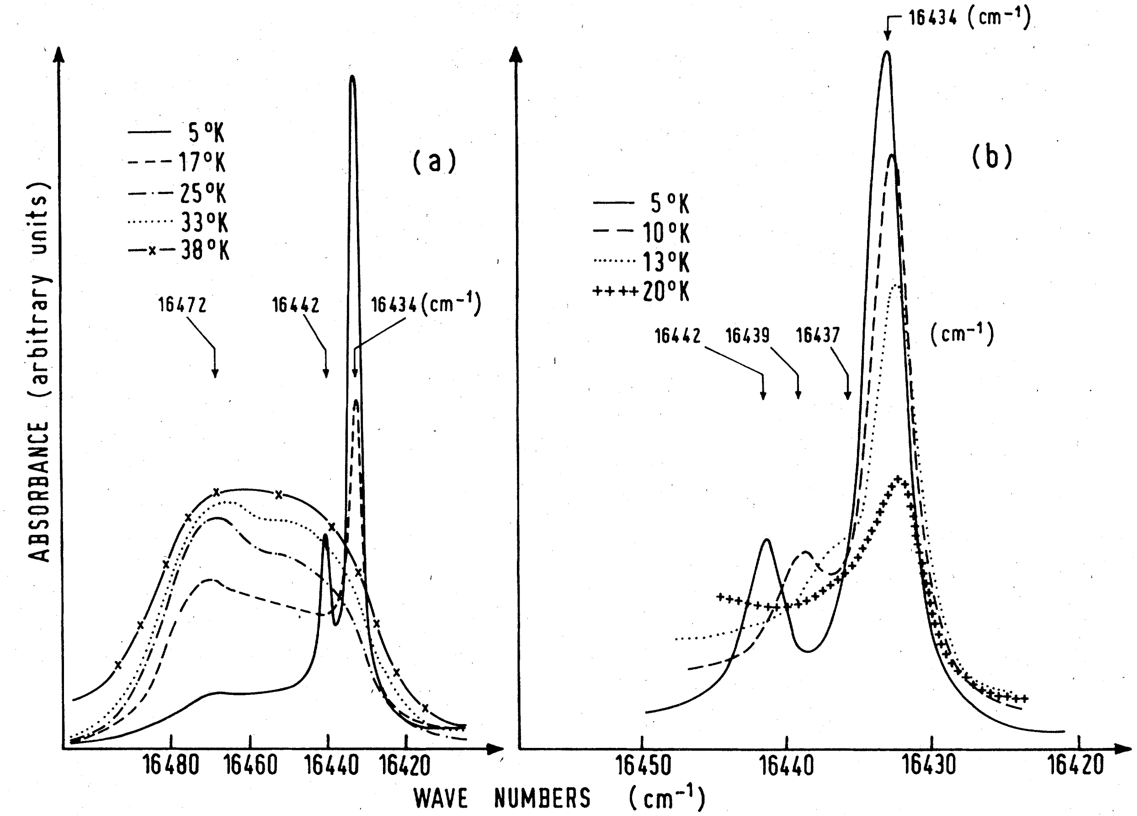

FIG. 2. Absorption spectrum of the lowest energy peaks of the $^1E_g$ transition at various temperatures, (a). Detailed temperature-dependence of the sharp peaks is given in (b).

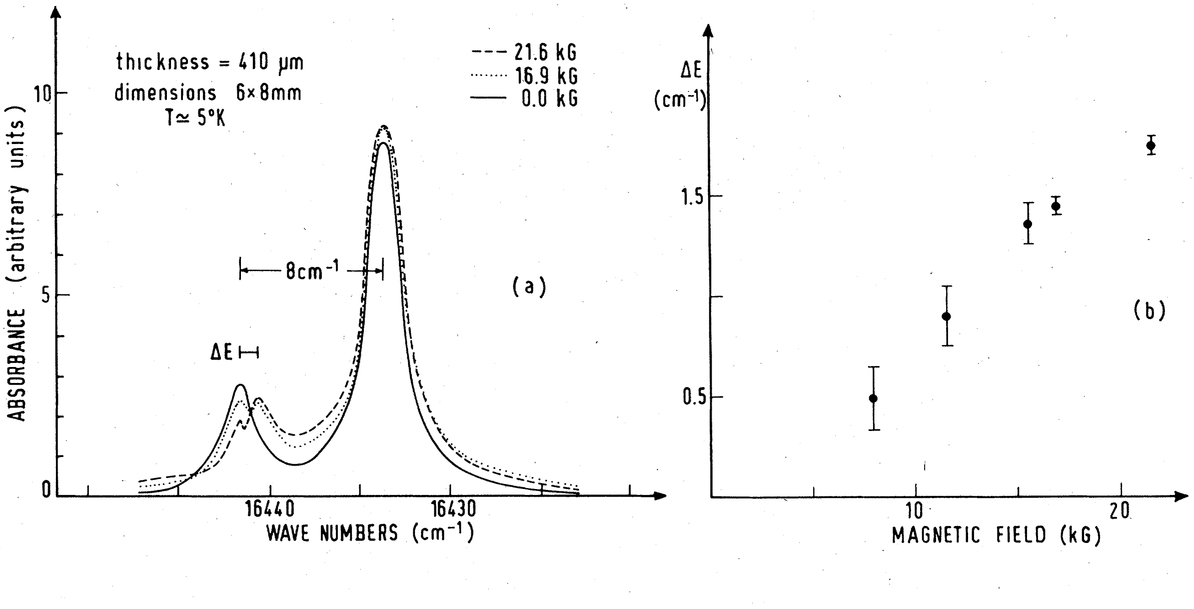

FIG. 3. Magnetic field dependence of the absorption of the $^1E_g$ sharp peaks for $\vec{H} \parallel \vec{c}$, (a). Splitting of the 16442-cm$^{-1}$ line vs external magnetic field, (b).

and the exchange parameters have not yet been elucidated so that we can present only conjectures which suggest further experimental and theoretical work.

$NiBr_2$ has the $CdCl_2$ structure, the magnetic $Ni^{2+}$ ions forming hexagonal layers which are intercalated by two layers of the halide ions. As in all isostructural magnetic compounds the intralayer magnetic interactions are expected to dominate over the interlayer interactions due to this lattice anisotropy. $NiBr_2$ is an antiferromagnet with the Néel temperature $T_N = 52$ °K. From 20 °K to $T_N$ the magnetic structure is collinear, with the spins of each hexagonal $Ni^{2+}$ layer ferromagnetically ordered and with an antiferromagnetic stacking of the layers. The $c$ axis is the hard direction so that the spins lie in the $c$ plane. In the $c$ plane there is a very small anisotropy so that the system has essentially the $X$-$Y$ symmetry. Thus $NiBr_2$ in this phase has the same magnetic structure as $NiCl_2$.[16] Taking into account the common pattern of the magnetic interactions in the isostructural compounds, the intraplane magnetic interactions in $NiBr_2$ are expected to consist of a dominant ferromagnetic nearest-neighbor interaction and of a weaker antiferromagnetic second-neighbor interaction. In addition the interplane interaction is antiferromagnetic. The main difference between $NiBr_2$ and $NiCl_2$ is due to the fact that in $NiBr_2$ the interlayer and intralayer antiferromagnetic couplings must be relatively more important than in $NiCl_2$ because of the negative asymptotic Curie temperature[13] ($\theta = -20$ °K) of $NiBr_2$ compared with $\theta = 67$ °K of $NiCl_2$.

Below 22 °K the magnetic structure of $NiBr_2$ changes but it is not yet known in detail. The neutron-scattering data have been interpreted in terms of a canted structure, the average angle $\theta$ between the spin direction and the $c$ axis being temperature dependent with the value $\theta \simeq 36$ ° at low temperature. The spins are probably noncollinear and some kind of helical[9] or triangular[15] structure has been suggested.

Above 22 °K the sharp lines are not present and only the 16 472-$cm^{-1}$ broad peak is present in this region of the spectrum. This peak appears as a "hot band," i.e. it gains intensity only at finite temperature, and it has been interpreted[17] as an in-plane magnon sideband in which the exciton transition takes place together with the annihilation of a thermally excited magnon. This interpretation presents some problems if we interpret the two sharp lines present at low temperature as magnon sidebands. In fact a "hot band" occurs at a lower energy than the pure exciton transition but the sharp lines are "cold bands," i.e., their intensity increases with decreasing temperature, and they should occur at higher energy than the exciton transition. We note moreover that above 20 °K the intensity of the broad peak increases with increasing temperature but much less than with the $T^2$ law valid below 20 °K.[17] On the other hand, below 20 °K the optical transition must be discussed in terms of the low-temperature magnetic order and not of the one prevailing at higher temperature.

We turn now to the magnetic phase below 22 °K. The explanation of the presence of a canting angle presents some difficulties. In fact the mechanisms responsible for noncollinear order in other magnetic substances are not effective in this case. Antisymmetric exchange cannot be present for symmetry reasons[18] nor a competing effect between nonequivalent magnetic sites as in garnets. Neither competing effect between exchange interaction and different anisotropy terms is expected to give rise, as in the rare earths,[19] to canted structure at least in the mean-field theory. In fact $Ni^{2+}$ is described by an effective spin $S = 1$ so that the crystal field can give rise to only one anisotropy term: the quadratic one.

Then the Hamiltonian reads

$$\mathcal{H} = -\sum_{ij} [J(i-j) + J'(i-j)]\vec{S}_i \cdot \vec{S}_j + D \sum_i (S_i^z)^2 \quad , \tag{1}$$

where $J(i-j)$ indicates the intraplane interaction, $J'(i-j)$ is the interplane interaction, assumed antiferromagnetic, and $D$ is the anisotropy coefficient. Let us consider an antiferromagnetic cone structure

$$\langle S_i^z \rangle = S \cos\theta \cos\left( \pi \frac{c}{z_i} \right) \quad , \tag{2}$$

$$\langle S_i^x \rangle = S \sin\theta \cos\vec{Q} \cdot \vec{r}_i \quad , \tag{3}$$

$$\langle S_i^y \rangle = S \sin\theta \sin\vec{Q} \cdot \vec{r}_i \quad , \tag{4}$$

where $\theta$ is the spin angle with respect to the $c$ axis, $c$ is the interplane distance, and $\vec{Q}$ describes the periodicity of the spin order. In the mean-field approximation the energy reads

$$E = -S^2(J(\vec{Q}) + J'(\vec{Q})) + [D + J(\vec{Q}) + J'(Q) - J(0) - J'(\pi/c)]S^2 \cos^2\theta \quad , \tag{5}$$

where $J(\vec{Q})$ and $J'(\vec{Q})$ are the Fourier coefficients of $J(i-j)$ and of $J'(i-j)$, respectively, and $J'(\pi/c)$ is the Fourier coefficient of $J'(i-j)$ when the wave vector is in the $z$ direction with $Q_z = \pi/c$. Minimization of (5) with respect to $\vec{Q}$ and $\theta$ gives the equilibrium state. The periodicity vector $\vec{Q}$ is determined by maximization of $J(\vec{Q}) + J'(\vec{Q})$ and from (5) we obtain $\theta = 0$ (uniaxial case) or $\theta = \frac{1}{2}\pi$ (planar case) depending whether the coefficient of $\cos^2\theta$ is negative or positive. We conclude that there is no possibility for a canted structure. Anisotropic exchange does not alter this conclusion nor dipolar anisotropy which favors the spins laying in the plane.

The previous calculation is altered if one considers the quantum theory, i.e., one takes into account the effect of zero-point motion of the spins. When $\theta = 0$

and $J'=0$ there is no zero-point motion and the energy is correctly given by (5) because $S^z$ commutes with the Hamiltonian (1). But zero-point motion is present when $\theta \neq 0$ or $J' \neq 0$ and the quantum energy is lower than the classical value (5), due to the possibility of spin flop of couples of antiparallel spins. When noncollinear order ($\vec{Q} \neq 0$) is present the spin-flop probability decreases as $\theta$ increases because not all nearest neighbor spins on adjacent planes are antiparallel as when $\theta = 0$. Therefore, the energy (5) should be corrected by a term $\delta E(\theta)$ which is minimum for $\theta = 0$ and is maximum for $\theta = \frac{1}{2}\pi$ and its value depends on the value of the periodicity vector $\vec{Q}$ as indicated by the results for a ferromagnetic cone structure.[19] $\delta E(\theta)$ does not depend simply on $\cos^2\theta$ and the possibility arises that the energy is minimized by a value of $\theta$ intermediate between 0 and $\frac{1}{2}\pi$: even if the classical expression (5) favors the planar structure, $\theta = \frac{1}{2}\pi$, the zero-point energy is maximum in such a situation and an angle $\theta < \frac{1}{2}\pi$ would lower the energy if the $\theta$ dependence of $\delta E(\theta)$ is stronger than the one of the anisotropy energy. Such mechanism can play a role if the anisotropy is very small, as in $NiBr_2$, and if the zero-point motion is appreciable as in the case of periodic, $\vec{Q} \neq 0$, spin configurations.

We consider now the possible origin of a periodic spin configuration in $NiBr_2$. The layer structure of this compound permits to exclude the possibility of interlayer interaction farther than nearest neighbor. Thus $J'(\vec{Q})$ is minimum when $Q_z = \pi/c$, corresponding to the antiferromagnetic ordering between planes. Competition is present between the intraplane interactions. In all the other compounds of this family the nearest-neighbor intraplane interaction $J_1$ is ferromagnetic but the second-neighbor interaction $J_2$ is antiferromagnetic.[16,20] $J(\vec{Q})$ depends only on $Q_x$ and $Q_y$ and if we take $Q_y = 0$ (we choose the axis as in Ref. 16) it reads

$$J(Q) = 2J_1(1 + 2\cos\tfrac{1}{2}\sqrt{3}aQ_x) + 2J_2(\cos\sqrt{3}aQ_x + 2\cos\tfrac{1}{2}\sqrt{3}aQ_x) \ , \qquad (6)$$

where $a$ is the lattice parameter in the basal plane. $J(Q)$ is maximum for $Q_x = 0$, corresponding to a collinear structure, only if $J_1 + 3J_2 > 0$. Otherwise the maximum is displaced from the origin at

$$\cos\tfrac{1}{2}\sqrt{3}aQ_x = -(J_1 + J_2)/2J_2 \ , \qquad (7)$$

corresponding to a helical order in which the spins along the (0,1) direction in the basal plane are parallel[20] and there is a rotation angle $\gamma$ between adjacent rows with $\cos\gamma = -(J_1 + J_2)/2J_2$. The presence of interlayer interaction changes only slightly this result because the stability condition for the collinear structure becomes

$$J_1 + 3J_2 + \tfrac{1}{3}J' > 0 \ , \qquad (8)$$

if we take into account nearest-neighbor interplane interaction only.

The possibility of a transition from a collinear to a noncollinear structure as the temperature changes, arises because of the different renormalization of the interaction parameters with temperature. At not too high temperatures the system can be described on the basis of self-consistently renormalized spin waves[16,21,22] and from the expression for the renormalized interaction parameters,[16,22] one finds that $|J_2(T)|$ decreases with increasing temperature more rapidly than $J_1(T)$. Therefore there is the possibility that $J_1(T) + 3J_2(T) + \frac{1}{3}J'(T)$ changes sign at a certain temperature if the zero-temperature value of this quantity is slightly negative: at low temperature the system would have noncollinear order, but at higher temperature it would change to a collinear one. The required interaction parameters for this to happen are reasonable if we take into account that $|J_2|/J_1 = 0.22$ in $NiCl_2$ and that the antiferromagnetic coupling increases in going from the chlorides to the bromides.[20] In conclusion we suggest that in $NiBr_2$ the magnetic phase transition takes place because of renormalization of the interaction parameters and below 22 °K there is an antiferromagnetic cone structure in which the spins in the basal plane are noncollinear. Moreover in the ground state the spins form a canting angle out of the basal plane because of competition between the anisotropy energy favoring the basal plane and the zero-point motion favoring the $c$ axis direction.

The two sharp lines present in the low-temperature phase can be reasonably assigned to magnon sidebands. Spin waves in the hypothesized structure of $NiBr_2$ have not been studied in the literature, but we can get some information from the spin-wave spectrum $\epsilon_q$ in the cone structure.[23] In this structure $\epsilon_q$ is very flat with two low-energy minima at $\vec{q} = \pm 2\vec{Q}$, one of the minima being at zero energy if there is no anisotropy. The mechanism responsible for the minima are present also in an antiferromagnetic cone structure so that we expect a roughly similar behavior of the spin-wave spectrum. At these two minima of $\epsilon_q$ the density of states has two sharp maxima and these could be associated with the two sharp peaks at 16 434 and 16 442 $cm^{-1}$. These peaks, being related to the periodicity vector $\vec{Q}$, which in our picture is temperature dependent, could well have a temperature-dependent energy as it happens in some rare earths[23] and this would explain the behavior of the 16 442-$cm^{-1}$ peak.

A small magnetic field is expected to play only a minor role on the spin-wave spectrum when the field is applied in the basal plane because there is no preferential action on the different spins. On the contrary a magnetic field in the $c$ axis direction affects differently spins in adjacent planes by raising the energy spins in one plane and lowering the energy of the spins in the adjacent planes. A spin wave which involves the motion of spins on two planes is expected to depend only weakly on $H_z$ because of compensation but, on the contrary, a spin wave which involves predominantly spins in one plane is expected to split under the effect of $H_z$. Thus, the experimental data can be interpreted if the peak at 16 434 $\mathrm{cm}^{-1}$ corresponds to an interplane magnon and the peak at 16 442 $\mathrm{cm}^{-1}$ to an intraplane magnon.

In conclusion, the present data call for further experiments on the magnetic properties of $\mathrm{NiBr}_2$, in particular precise measurements of high-temperature susceptibility and NMR in the 20–30 °K temperature region and further measurements of neutron scattering, both elastic and inelastic. Also calorimetric measurements should be useful.

On the theoretical side the spin waves in layer compounds with noncollinear order in the plane should be studied as well as spin waves in antiferromagnetic cone structures together with the related calculation of the ground-state energy.

## ACKNOWLEDGMENTS

It is our pleasure to thank D. L. Spini for helpful cooperation in the experimental work. We also acknowledge interesting correspondence with Dr. P. Day.

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