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Optical absorption spectra of the one-dimensional antiferromagnets: Exciton-magnon transition and double excitation in $CsNiBr_3$

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The polarized absorption spectra of the one-dimensional (1D) antiferromagnet $CsNiBr_3$ are investigated in the infrared and visible regions at 15–300 K. The temperature dependence of the magnon sideband due to the exciton-magnon transition is observed for the first time for a 1D antiferromagnet other than the Mn^{2+}-compound antiferromagnets. The intensity of the magnon sideband associated with the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition of Ni^{2+} is observed to increase with increasing temperature at low temperatures, but to decrease slowly from about 90 K, which does not agree with the temperature dependence calculated using the Ebara and Tanabe classical spin method. The discrepancy between the observation and calculation indicates that the classical spin approximation gives a reliable result for high-spin magnetic ions such as Mn^{2+} ($S=\frac{5}{2}$) but not for low-spin ions such as Ni^{2+} ($S=1$). Except for two bands the observed absorption bands can be satisfactorily interpreted using the ligand-field model for a Ni^{2+} ion in an octahedral environment; one of the two bands without ligand-field correspondence is a weak band at 712 nm (14 045 cm^{-1}) and the other is a broad and strong band at 16 500–18 500 cm^{-1}. From the temperature dependence, location, and comparison with other magnets, the former band is attributable to the double excitation band, whereas the latter band is suggested to be attributable to the charge-transfer band.

I. INTRODUCTION

Two kinds of parity-forbidden absorption bands are observed in the infrared through visible absorption spectra of magnetic insulators: one is due to the spin-allowed transition in magnetic ions, and the other is due to the spin-forbidden transition. The former band is stronger in intensity than the latter band. In the spin-allowed, but parity-forbidden, band, the odd-parity lattice vibration plays an important role in relaxing the parity selection rule, giving rise to a vibration-induced absorption band. On the other hand, the exchange dipole mechanism of two magnetic ions is responsible for the spin-forbidden band, giving rise to the electric-dipole-allowed exciton-magnon transition (so-called exciton-magnon combination band or magnon sideband).[1]

A number of experimental and theoretical studies have been done on the magnon sidebands in various magnetic insulators, especially in the three- and two-dimensional (3D and 2D) magnetic materials. Regarding the 1D materials, there is only one theoretical work, in which Ebara and Tanabe calculated the temperature dependence of magnon sidebands using the classical approximation for spins.[2] Their results have been used to explain the experimental results of not only 1D antiferromagnets but also 1D ferromagnets.[3–6] In Fig. 1 we show the temperature dependence of the magnon-sideband intensity in 1D antiferromagnets $N(CH_3)_4MnCl_3$ (i.e., TMMC) and $CsMnCl_3 \cdot 2H_2O$ (CMC), which was derived using the Ebara and Tanabe theory, and compare it with the experimental results obtained by Day and Dubicki[3] and Yamamoto *et al.*[7] The theory is seen to be successful in explaining the experiments qualitatively, especially the existence of a broad maximum in the (30–50)-K region.

In Fig. 2 we show the temperature dependence of magnon-sideband intensity in various transition-metal ions (with the ground-state spin $S=1,\ldots,3$), which were derived using the Ebara and Tanabe theory. It is noted that a different temperature dependence is derived between the high- and low-spin magnetic ions. Unlike the cases of 1D, 2D, and 3D Mn^{2+} ($S=\frac{5}{2}$) compounds,[8–10]

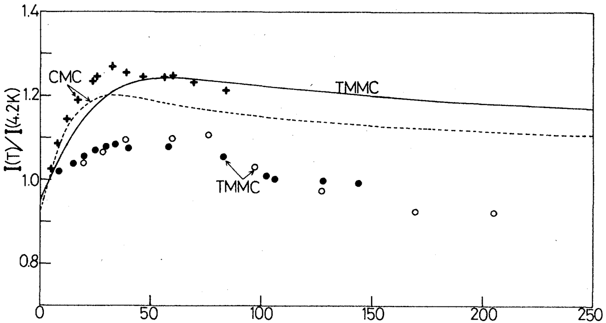

FIG. 1. Theoretical and experimental temperature dependence of the intensity of magnon sideband in TMMC and CMC. The open and solid circles indicate the experimental values of the $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) band intensity in TMMC obtained by Day and Dubicki (Ref. 3) and Yamamoto *et al.* (Ref. 7), respectively, whereas the pluses indicate the experimental values of the $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) band intensity in CMC obtained by Day and Dubicki (Ref. 3).

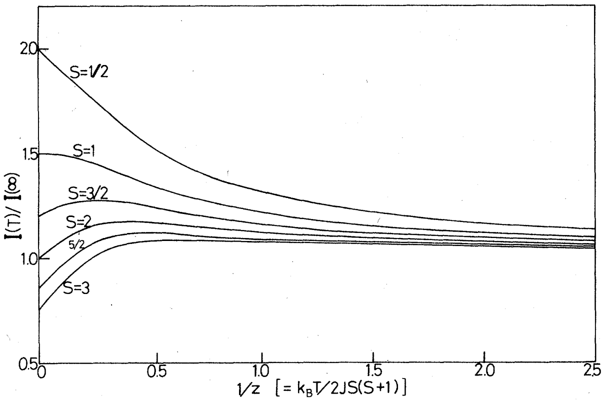

FIG. 2. Calculated temperature dependence of magnon-sideband intensity in various magnetic ions with the ground-state spin S. The calculation was done using the method of Ebara and Tanabe (Ref. 2).

no broad maximum exists for the low spins of $S=\frac{1}{2}$ and 1. Is this true?

So far, the experimental work on 1D antiferromagnets has been done predominantly for Mn^{2+} compounds such as TMMC, CMC, and $CsMnBr_3 \cdot 2H_2O$ (CMB).[3,7,11] On the other hand, a detailed investigation has not been carried out for the magnon sideband associated with other transition-metal ions such as Ni^{2+}. The present work was undertaken to answer the above question. Here we investigate the magnon sideband of the 1D antiferromagnet $CsNiBr_3$.

$CsNiBr_3$ ($T_N = 11.75$ and 14.25 K) is an isotropic Heisenberg system with $S=1$ spin.[12] Above $T_N = 14.25$ K it can be described as a 1D antiferromagnet with intrachain exchange interaction $J/k_B = -17.0$ K along the c axis and single-ion anisotropy constant $D/k_B = -1.5$ K. The absorption spectra have been investigated so far by McPherson and Stucky[13] and Ackerman *et al.*[14] at 5, 77, and 300 K. They suggested the existence of an absorption band due to double excitation in paired Ni^{2+} ions (i.e., double-exciton band[1]) in addition to the spin-allowed and spin-forbidden bands. The assignment for all the observed Ni^{2+} absorption bands, however, has not been established completely since the detailed temperature dependence of the absorption bands is necessary to the band assignment. In this paper we first show the absorption spectra, after which we make band assignments by comparison with the result of ligand-field calculation. Then we confirm the assignment taking into account the temperature dependence of absorption bands, and lastly we discuss the magnon sidebands which appear in the spin-forbidden bands.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Polarized absorption spectra in the visible through infrared region were measured with a Shimadzu MPS-50L spectrophotometer. A Glan prism was used as a polarizer. The crystal used had dimensions of about $8 \times 5 \times 0.5$ mm^3, which was cut along the crystal c axis. Single crystals of $CsNiBr_3$ were supplied by K. Iio. The crystal was cooled in an Osaka Sanso Crio-Mini cryostat which allows cooling down to 15 K.

Figure 3 shows the polarized absorption spectra of $CsNiBr_3$ at 15 K, which are consistent with the previous measurements.[13-15] Two broadbands are observed in the infrared region, which show the enhancement of the intensity with increasing temperature at high temperatures above 50 K. This indicates that they are due to the electric-dipole-allowed transition which is induced by lattice vibrations.[15] A weak band is observed in the

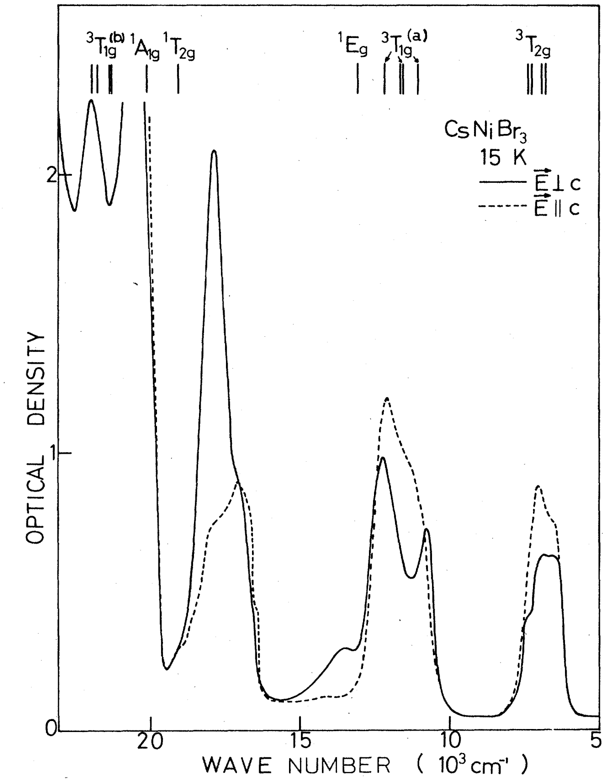

FIG. 3. Polarized absorption spectra of $CsNiBr_3$ at 15 K. The calculated energy levels of Ni^{2+} ions in octahedral crystal symmetry are shown in the upper part.

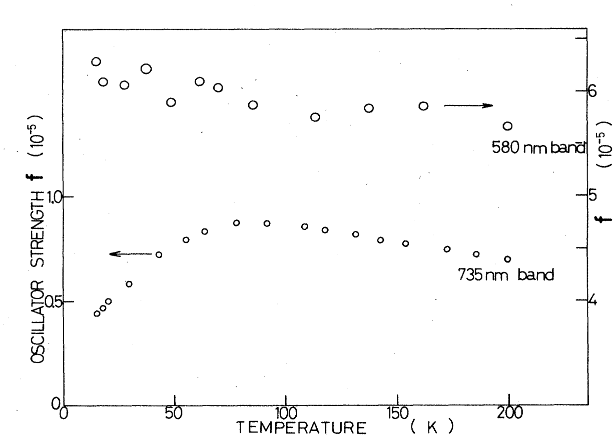

FIG. 4. Temperature dependence of oscillator strength f of the broad 580-nm band measured with **E**$||c$ polarization and of the 735-nm band measured with **E**$\perp c$ polarization.

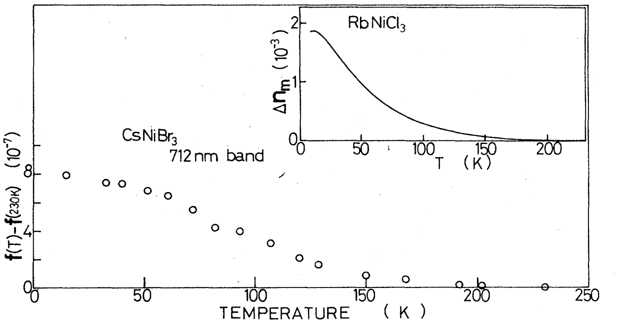

FIG. 5. Temperature dependence of oscillator strength f of the weak 712-nm band measured with $\mathbf{E}||c$ polarization. Inset shows the temperature dependence of magnetic linear birefringence Δn_m of RbNiCl$_3$ obtained by Iio, Hyodo, and Nagata (Ref. 24).

(13 000—15 000)-cm^{-1} region. Its peak position, however, is different between the $\mathbf{E}\perp c$ and $\mathbf{E}||c$ polarizations: A band peaking at 735 nm (13 605 cm^{-1}) is observed in the $\mathbf{E}\perp c$ spectrum, whereas a considerably weak band peaking at 712 nm (14 045 cm^{-1}) is observed in the $\mathbf{E}||c$ spectrum. The 735-nm band is observed to shift toward the low-energy side with increasing temperature. The temperature dependence of the 735-nm band intensity is shown in Fig. 4, where a broad maximum is observed near 80—90 K. This is consistent with the previous measurement by Ackerman *et al.*,[14] who found that the intensity is greater at 80 K than at 4 or 300 K. On the other hand, a different temperature dependence is observed for the 712-nm band (Fig. 5). The intensity of the 712-nm band decreases monotonically with increasing temperature and no maximum appears in measurements between 15 and 270 K.

A relatively strong band with structure is observed in the (16 500—18 500)-cm^{-1} region. The broadband with a high peak at 580 nm (17 241 cm^{-1}) observed by the $\mathbf{E}||c$ polarization shows a tendency of slowly decreasing in intensity with increasing temperature, as seen in the upper part of Fig. 4. The same behavior is observed for another strong band with a peak at 559 nm (17 889 cm^{-1}) observed by the $\mathbf{E}\perp c$ polarization.

III. DISCUSSION

A. Band assignment

Ligand-field calculations were carried out in order to make a band assignment. We derived the transition energies from the ground state $^3A_{2g}$ of the Ni^{2+} ion using the matrices of Liehr and Ballhausen[16] for the d^8-electron configuration system in an octahedral environment under both the strong- and weak-field approximations. Their matrix elements are functions of four quantities, F_2, F_4, λ, and Dq. We calculated the energy-level diagrams as a function of crystal-field strength Dq using various values for the spin-orbit coupling constant λ. In this calculation, we used values of $F_2=1260$ cm^{-1} and $F_4=90$ cm^{-1} as the electron correlation constants since these values are known to give a good agreement between calculated and observed transition energies for various Ni^{2+} compounds.[16] We also tried to carry out the diagonalization of the ligand-field matrices using other F_2 and F_4 $(=F_2/14)$ values. A good fit to the observed spectrum, however, was obtained in the case of $F_2=1260$ cm^{-1} and $F_4=90$ cm^{-1}, $Dq=-700$ cm^{-1} and $\lambda=-275$ cm^{-1}, which was calculated using the strong-field approximation. The calculated transition energies and band assignments are given in Table I and the upper part of Fig. 3.

The fit between the calculated transition energies and absorption-band positions is quite acceptable considering, for example, the width and structure of two infrared bands: The structure of the broad 7000- and 12 000-cm^{-1} bands is suggested to arise from the spin-orbit splitting. Thus, these bands are attributable to the spin-allowed transitions $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^3T_{1g}^{(a)}$, respectively, in agreement with the previous assignments.[13,14] This is consistent with the temperature dependence of these bands in that they grow with increasing temperature.[15] Our assignment of the strongest band appearing near 20 500 cm^{-1} to the spin-allowed $^3A_{2g}\rightarrow{}^3T_{1g}^{(b)}$ transition is in agreement with the assignment in the cases of various Ni^{2+} fluorides, chlorides, and bromides.[17–22] From comparison between the calculated transition energies and absorption spectrum, the weak 735-nm band is suggested to be attributable to the spin-forbidden $^3A_{2g}\rightarrow{}^1E_g$ transition. The same assignment has been done for such a weak band in many Ni^{2+} compounds, which is located in the (13 000—15 000)-cm^{-1} region at the high-energy tail of the $^3A_{2g}\rightarrow{}^3T_{1g}$ band.[18–22] We discuss the 735-nm band in Sec. III B.

Unlike the cases of the infrared and 735-nm bands, there is no ligand-field energy level corresponding to another weak 712-nm band (see Fig. 3). The temperature dependence of the 712-nm band is different from that of the 735-nm band, indicating that the former band is not attributable to a component of the latter band. The 712-nm band shows a monotonical decrease in intensity with increasing temperature as seen in Fig. 5. Such a behavior is quite similar to that of the double-exciton band, which is observed in various magnetic insulators, including the 1D ferromagnet CsNiF$_3$.[1,6,8,10,19] The double-exciton band is expected to show a similar temperature dependence as the magnetic linear birefrigence (MLB) since the magnetic short-range order is predominantly responsible for both the double-exciton band and MLB.[23] The MLB datum of CsNiBr$_3$ in the (15—300)-K region is unfortunately not available, but we found the MLB datum of RbNiCl$_3$.[24] RbNiCl$_3$ has the same crystal structure as CsNiBr$_3$, and its transition temperature ($T_N=11$ K) and exchange energy ($J/k_B=-21$ K) are quite close to those of CsNiBr$_3$. Therefore, the temperature dependence of the MLB of RbNiCl$_3$ can be expected to be similar to that of CsNiBr$_3$. In Fig. 5 we insert the MLB datum of RbNiCl$_3$, which was measured by Iio, Hyodo, and Nagata.[24] As seen in Fig. 5, the MLB is similar to the temperature dependence of the 712-nm band. Therefore, taking into account that the energy of the $(\mathbf{E}||c)$-polarized 712-nm (14 045-cm^{-1}) band is close to twice as much as the energy of peak position (at 7017 cm^{-1}) of the $(\mathbf{E}||c)$-polarized $^3A_{2g}\rightarrow{}^3T_{2g}$ band, we can suggest strongly that

TABLE I. Peak positions of absorption bands of $CsNiBr_3$ at 15 K and their level assignments. The Ni^{2+} ligand-field energy calculation was done under the strong-field approximation (see text).

Observed energies of peak positions (cm^{-1})		Calculated energy levels relative to the Ni^{2+} ground level $^3A_{2g}$ (cm^{-1})	
$\mathbf{E}\perp c$ polarization	$\mathbf{E}\parallel c$ polarization		
6 689	~6 690	$^3T_{2g}$ Γ_2	6 751
6 897		Γ_4	6 892
	7 017	Γ_5	7 230
7 300	~7 300	Γ_2	7 373
10 753		$^3T_{1g}^{(a)}$ Γ_1	11 055
	~11 100	Γ_4	11 502
	12 121	Γ_3	11 610
12 225		Γ_5	12 145
13 605		^1E_g Γ_3	13 050
	14 045	double-exciton band	
~17 123	17 123	charge-transfer band	
17 889	17 889		
	18 939	$^1T_{2g}$ Γ_5	19 065
		$^1A_{1g}$ Γ_1	20 081
20 492		$^3T_{1g}^{(b)}$ Γ_5	21 280
		Γ_3	21 356
22 026		Γ_4	21 742
		Γ_1	21 928

the 712-nm band is attributable to the double-exciton band.

There is no ligand-field energy level corresponding to the strong band located in the (16 500—18 500)-cm^{-1} region (Fig. 3). It is difficult to assign this band to the spin-forbidden $^3A_{2g}\rightarrow{}^1T_{2g}$ transition since (a) the $^1T_{2g}$ energy level deviates from the band position considerably, and (b) the band is stronger in intensity than the spin-allowed bands. [It is reasonable to attribute the $^3A_{2g}\rightarrow{}^1T_{2g}$ band to a weak-absorption band which appears at about 528 nm (18 939 cm^{-1}) as a shoulder on the high-energy tail of the broad (16 500—18 500)-cm^{-1} band.] Krausz *et al.* have suggested that a broad polarized band with strong intensity is possible to be assigned to a charge-transfer band.[4] Unlike the other band, the broadband of $CsNiBr_3$ exhibits no prominent change in intensity against temperature. The charge-transfer band is expected to have an intensity which is almost independent of temperature since it arises from the electric-dipole-allowed transition. The slight intensity decrease is observed with increasing temperature for the 580-nm band (see Fig. 4). This is understood as follows. The odd-parity lattice vibrations mix the T_{1u}-type excited state of the charge-transfer band into the $^3T_{2g}$ and $^3T_{1g}$ excited states of the spin-allowed bands, resulting in the increase of the spin-allowed band intensity with increasing temperature but resulting in the decrease of the charge-transfer band intensity; the decreased intensity of the charge-transfer band is understood to be used to grow the spin-allowed bands. On the other hand, since the covalency between metal and halide ions is stronger in Ni^{2+} bromides than in Ni^{2+} chlorides and Ni^{2+} fluorides, the charge-transfer transitions are expected to appear at lower energy in the bromides than in the fluorides.[13] A strong band corresponding to the (16 500—18 500)-cm^{-1} band of $CsNiBr_3$ has not been observed in Ni^{2+} fluorides at the low-energy side of the stronger $^3A_{2g}\rightarrow{}^3T_{1g}^{(b)}$ band.[19,20,22] Therefore, it is possible to attribute the (16 500—18 500)cm^{-1} band to the charge-transfer band.

B. Magnon sideband

The 735-nm band is attributable to the spin-forbidden $^3A_{2g}\rightarrow{}^1E_g$ transition as mentioned above. In the magnetic insulators such a spin-forbidden and parity-forbidden transition gains electric dipole intensity by exciton-magnon coupling, giving rise to magnon sidebands. The magnon sidebands of 1D antiferromagnetic Ni^{2+} compounds will be expected to follow the theoretical temperature dependence of the $S=1$ case shown in Fig. 2. The temperature dependence of the 735-nm band, however, is different from the expected one. The 735-nm band grows with increasing temperature from 15 K and starts to decrease from about 90 K (Fig. 4), whereas no maximum exists at a finite temperature in the theoretical curve. The experimental curve is similar to the theoretical one in the high-spin cases such as Mn^{2+} ($S=\frac{5}{2}$), since the rate of growth observed below 80 K is considerably higher than the rate of decrease observed above 90 K.

The theoretical curve of Fig. 2 was derived using the classical approximation for the spin-correlation functions. Ebara and Tanabe have pointed out that the classical approximation may give a better result for the high-spin case than for the low-spin case, and it is more reliable at high temperatures than at low temperatures. Therefore we cannot compare our experimental result with the $S=1$

theoretical curve in the low-temperature region, but we will be allowed to do it in the high-temperature region. In fact, the 735-nm band intensity decreases slowly with increasing temperature above 100 K and shows a tendency to approach a constant value at high temperatures; both situations are consistent with the theoretical curve. This indicates that the classical spin method of Ebara and Tanabe is certainly reliable at high temperatures for the low-spin magnetic ions but it is not reliable at low temperatures although it gives a good result for the high-spin magnetic ion such as Mn^{2+} even at low temperatures. We expect that an exact calculation of magnon sideband intensity for the $S=1$ case would give a temperature dependence similar to that of the 735-nm band. Thus, with regard to the temperature dependence of 1D antiferromagnets, there is believed to be no difference, qualitatively, between the Ni^{2+} and Mn^{2+} cases.

IV. CONCLUSIONS

We note the following conclusions.

(1) Contrary to the prediction which was done using the classical approximation for spins in 1D antiferromagnets, the magnon sideband of $CsNiBr_3$ is observed to increase the intensity with increasing temperature at low temperatures and slowly decrease from about 90 K. Such a temperature dependence is quite similar to the case of 1D antiferromagnets TMMC and CMC. From the discrepancy between prediction and observation, it is concluded that the classical spin approximation is not reliable for the low-spin ions such as Ni^{2+} ($S=1$).

(2) A weak band observed at 712 nm is attributable to the double-exciton band since (a) the energy is close to twice of the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition energy, and (b) the temperature dependence is similar to the case of the double-exciton band observed in various magnetic insulators including $CsNiF_3$.

(3) A strongly polarized band appearing in the (16 500–18 500)-cm^{-1} region is suggested to be attributable to the charge-transfer band, from the strong intensity, the temperature dependence, and the comparison with the spectra of Ni^{2+} fluorides.

ACKNOWLEDGMENT

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[1] See, e.g., a review article by Y. Tanabe and K. Aoyagi, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 604.

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