Exchange Splitting of $^3T_{2g}$ Band in Antiferromagnetic $KNiF_3$

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Abstract

The absorption spectra of the $^3T_{2g}$ band in pure $KNiF_3$, $KMgF_3$: 0.015 Ni and layered K_2NiF_4 crystals are measured. The stress effect of the $^3T_{2g}$ band in $KNiF_3$ is also measured. The stress effect shows that the 6790 and 6951 cm^{-1} lines both split into two lines. This splitting can be explained qualitatively by the exchange effect in the $^3T_{2g}$ state.

1. Introduction

The crystal, $KNiF_3$ has many absorption bands in the region of photon energy ranging from 6000 to 50000 cm^{-1}. The gross features of these absorption bands are now well understood as transitions between levels of a Ni^{2+} ion which split by octahedral crystal-field.[1,2] This crystal is antiferromagnet. Below the Néel temperature, energy levels of a Ni^{2+} ion are modified by exchange interaction.[3] In the $^1E_g{}^a$ band located at 16000 cm^{-1}, new absorption bands such as exciton-magnon and exciton-magnon-phonon transitions which are not observed above the Néel temperature, appear in the antiferromagnetic phase.[4] These new absorption bands follow from the splitting of the ground state, $^3A_{2g}$ by the exchange interaction. Excited states should also split by the exchange interaction. This effect, however, has not been reported.

The purpose of this paper is to study the exchange effect in excited states. $KNiF_3$ has three spin-triplet bands, such as $^3T_{2g}$, $^3T_{1g}{}^a$ and $^3T_{1g}{}^b$ bands. The $^3T_{2g}$ band is mainly a pure electronic transition, *i.e.* a magnetic dipole transition, while the other bands are complicated by phonons.[2] We study the absorption spectrum of the $^3T_{2g}$ band in pure $KNiF_3$ and $KMgF_3$: 0.015 Ni crystals to see the exchange effect. The stress effect of $KNiF_3$ is studied to exmaine the fine structures of the $^3T_{2g}$ band. We also study the polarization dependence of absorption spectra of the layered K_2NiF_4 to clarify the mechanism of the transition.

2. Crystal Structure

Figure 1-(a) shows the crystal structure of the cubic perovskite $KNiF_3$. A Ni^{2+} ion locates at the body centered position of the cubic cell. Six F^- ions which locate at the face centered positions, form a regular octahedron around the Ni^{2+} ion.[5] The Néel temperature is 246K.[6] Below this temperature, Ni^{2+} ions couple antiferromagnetically through F^- ions, with spins parallel to the crystallographic axis.[7]

Figure 1-(b) shows the structure of the layered K_2NiF_4. An octahedron, formed by six F^- ions around the Ni^{2+} ion is compressed (1.5%) along the c-axis. The Néel temperature is 97.1 K.[8] The perovskitelike layers of $KNiF_3$ are separated by planes of K^+F^-. K_2NiF_4

Received September 26, 1977

behaves like a two-dimensional antiferromagnet.

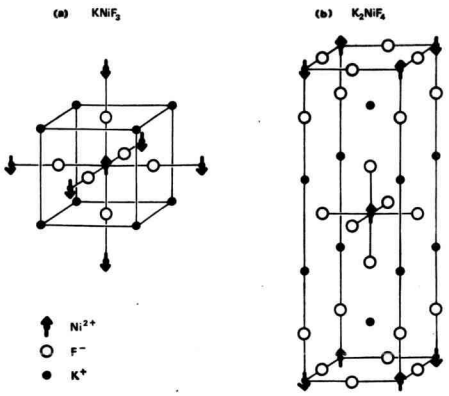

Fig. 1 Crystal structures of (a) $KNiF_3$ and (b) K_2NiF_4, in the antiferromagnetic phase.

3. Experimental

The crystals, $KMgF_3$: 0.015Ni and K_2NiF_4 were grown by the flux method.[9'10] The absorption spectra were measured with a Cary Model 14 spectrophotometer. The stress was applied to a sample by weight through a rod. A Glan-Thompson prism was used as a polarizer.

4. Experimental Results

Figure 2 shows the absorption spectra of the $^3T_{2g}$ band in $KNiF_3$ (a solid curve) and $KMgF_3$: 0.015 Ni (a dashed curve) at 77K. There are many structures in both spectra. These peaks are listed in Table I. The separation from the lowest frequency line is also shown in Table I. With shift of $KMgF_3$: 0.015Ni spectrum to higher frequency by 100cm^{-1}, the frequencies of the lines of both spectra agree well. This suggests that the exchange effect in the $^3T_{2g}$ state is not so large as to change throughly the spectrum.

Figure 3 shows the absorption spectra of $KNiF_3$ under the ⟨001⟩ stress at 77K. The stress

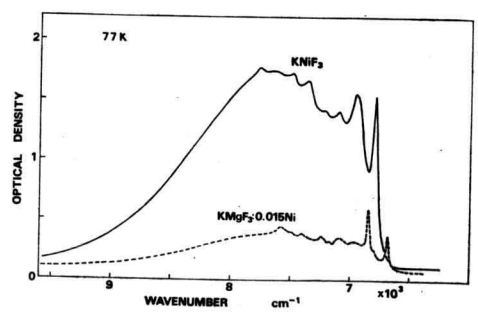

Fig. 2 Absorption spectra of the $^3T_{2g}$ band in $KNiF_3$ (thickness = 0.58 mm) and $KMgF_3$: 0.015 Ni (thickness = 5.8 mm) at 77K.

Table I. The peaks of the $^3T_{2g}$ band in $KNiF_3$ and $KMgF_3$: 0.015 Ni at 77K.

$KNiF_3$		$KMgF_3$: 0.015Ni		assignment by Ferguson[2]
peak position	separation from 6790 cm^{-1} line	peak position	separation from 6687 cm^{-1} line	
6790± 2	0	6687±3	0	Γ_3
6951± 3	161	6852±3	165	Γ_4
7100± 7	310	6960±5	273	
7228± 6	438	7083±8	376	
		7167±5	480	
7353± 8	563	7240±5	553	Γ_5
7496± 9	706	7401±5	714	Γ_2
7634±10	844	7499±8	812	
7755±10	965	7579±6	892	

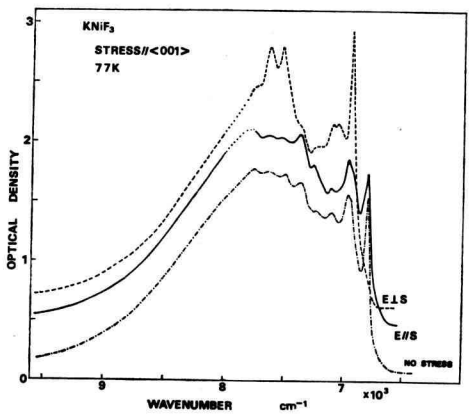

Fig. 3 Absorption spectra of the $^3T_{2g}$ band in $KNiF_3$ (thickness=0.58 mm) under the ⟨001⟩ stress at 77K. Stress is 20MPa.

Table II. The peaks of the $^3T_{2g}$ band in $KNiF_3$ under the ⟨001⟩ and ⟨111⟩ stress at 77K.

no stress	stress//<001>		stress//<111>	
	E//S	$E_\perp S$	E//S	$E_\perp S$
6790± 2	6791± 3		6793± 2	6810± 2
6951± 3	6957± 4	6928± 4	6951± 3	6953± 4
7100± 7	7105±10	7054± 7 7087± 7	7104± 6	7117±10
7228± 6	7250± 5	7220±15	7234± 5	7240± 5
7353± 8	7366±10		7366±10	7359± 5
7496± 9	7515±15	7491± 7	7526±14	7505±14
7634±10	7634±15	7619±14	7634±15	7622± 8

is 20MPa. A solid curve is the spectrum for light polarized parallel to the stress (abbreviated as E//S), and a dashed curve is the spectrum for light polarized perpendicular to the stress ($E_{\perp}S$). A chained curve is the spectrum with no stress. The characteristic properties of these spectra are as follows. The 6790 cm^{-1} line is not observed for $E_{\perp}S$. The 6951 cm^{-1} line consists of two lines located at 6928 and 6957 cm^{-1}. The 6928 cm^{-1} line becomes strong for $E_{\perp}S$. The lines at 7100, 7491 and 7619 cm^{-1} become strong for $E_{\perp}S$. These peaks are summarized in Table II.

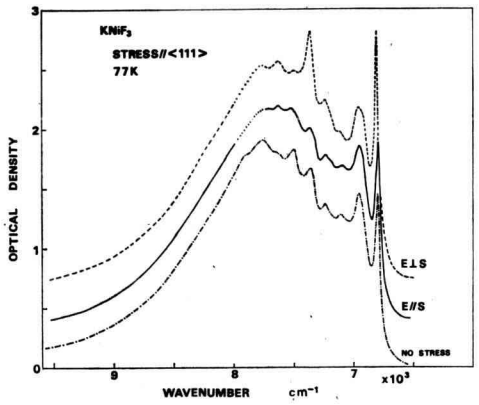

Fig. 4 Absorption spectra of the $^3T_{2g}$ band in $KNiF_3$ (thickness=0.62 mm) under the ⟨111⟩ stress at 77K. Stress is 15MPa.

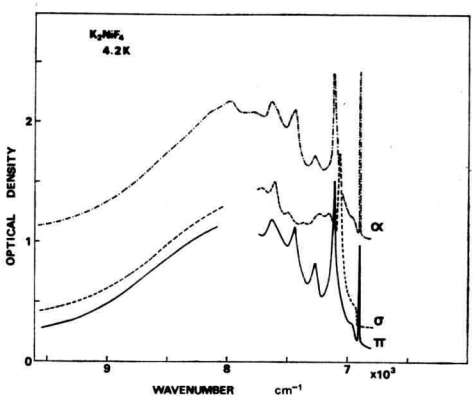

Fig. 5 Absorption spectra of the $^3T_{2g}$ band in K_2NiF_4 at 4.2K.

Table III. The peaks of the $^3T_{2g}$ band in K_2NiF_4 at 4.2K, and the mechanism of the transition assigned from the polarization dependence of the line. M1 represents a magnetic dipole transition and E1 an electric dipole transition.

α and π spectrum	σ spectrum	separation from 6895 cm^{-1} line	mechanism of transition
6895± 3		0	M1
	7066± 3	171	M1
7110± 3		215	M1
	7156± 8	261	M1
	7230±10	335	M1+E1
7270± 6		375	
	7367± 6	472	M1
7435± 6		540	M1
	7491±10	596	M1
	7605± 4	710	M1+E1
7635± 6		740	M1
7800±10	—	905	
7980± 8	—	1085	

Figure 4 shows the absorption spectra of $KNiF_3$ under the $\langle 111 \rangle$ stress at 77K. The stress is 15MPa. A solid curve is the spectrum for E//S, a dashed curve is for $E_\perp S$ and a chained curve is with no stress. These spectra show following results. The 6790 cm^{-1} line consists of two lines located at 6793 and 6810 cm^{-1}. The 6793 cm^{-1} line is observed for E//S, and the 6810 cm^{-1} line becomes strong for $E_\perp S$. The 7364 cm^{-1} line also becomes strong for $E_\perp S$. These peaks are listed in Table II. The effect of the $\langle 001 \rangle$ and $\langle 111 \rangle$ stress shows that the 6790 and 6951 cm^{-1} lines both consist of two lines.

Figure 5 shows the absorption spectra of K_2NiF_4 at 4.2K. The α spectrum (a chained curve) is for light propagated parallel to the c-axis of the crystal. The π (a solid curve) and σ (a dashed curve) spectra are for light polarized parallel and perpendicular to the c-axis. The frequencies of the peaks and the mechanism of the transition assigned from the polarization dependence are listed in Table III. In the Table, M1 represents a mangetic dipole transition and E1 an electric dipole transition.

5. Discussion

In this section, we try to assign the observed lines of the $^3T_{2g}$ band. The $^3T_{2g}$ state splits into four states such as Γ_2, Γ_3, Γ_4 and Γ_5 states by spin-orbit interaction. Liehr *et al.* calculated levels of a Ni^{2+} ion, using a four-parameter crystal-field approach.[11] Ferguson *et al.* decided the four parameters by fitting to lines in $KMgF_3$:Ni spectrum.[2] They assigned for the $^3T_{2g}$ band, 6790 cm^{-1} line as Γ_3, 6951 cm^{-1} line as Γ_4, 7353 cm^{-1} line as Γ_5 and 7496 cm^{-1} line as Γ_2, as shown in Table I. Hereafter we analyze these lines following their assignment.

Comparison of the spectrum of $KNiF_3$ with those of K_2NiF_4 shows that 6790 cm^{-1} line in $KNiF_3$ corresponds to 6895 cm^{-1} line in K_2NiF_4, 6951 cm^{-1} line to 7110 cm^{-1} line, 7353 cm^{-1} line to 7435 cm^{-1} line and 7496 cm^{-1} line to 7635 cm^{-1} line. These lines in K_2NiF_4 are magnetic dipole transitions. This shows that the corresponding lines of $KNiF_3$ are also magnetic dipole transitions.

We consider the stress effect of $KNiF_3$. These extremely anisotropic absorption spectra are caused by change of magnetic domains under stress, as described in the previous paper.[4] In the absence of stress, $KNiF_3$ has antiferromagnetic domains and the direction of and collinear spins distributes randomly among $\langle 001 \rangle$, $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. When the stress is applied, the crystal turns to a single domain, with spins parallel to the stress. The critical stress is 3MPa for the $\langle 001 \rangle$ direction, and 6MPa for the $\langle 111 \rangle$ direction. The ground state, $^3A_{2g}$ splits by exchange interaction into three levels apart by about 330 cm^{-1},[2] and at the low temperature the transitions occur from the lowest level. These transitions are anisotropic for the direction of spins.

The stress effect further shows that 6790 and 6951 cm^{-1} lines both consist of two lines. In the following, we discuss the effect of this splitting. The X-ray measurement shows that the crystal structure of $KNiF_3$ is cubic, even in the antiferromagnetic phase.[9] There is, however, the possibility that the lattice is slightly deformed along the direction of spins. We assume that this is the case. Under the $\langle 001 \rangle$ stress, a Ni^{2+} ion is affected by the tetragonal

crystal-field. The Γ_3 and Γ_4 states both split into two levels. Under the $\langle 111 \rangle$ stress, a Ni^{2+} ion is affected by the trigonal crystal-field. The Γ_3 state does not split in this case. This does not agree with the observed result. Even if a Ni^{2+} ion is assumed to be affected by the trigonal crystal-field in addition to the tetragonal crystal-field, the split components of the Γ_3 state have equal intensities for E//S and $E_\perp S$ polarizations. This result is contrary to the fact that the 6793 cm^{-1} line is observed for E//S and the 6810 cm^{-1} line is for $E_\perp S$. We consider whether the 6790 cm^{-1} line is really the Γ_3 state. The 6790 cm^{-1} line is observed for E//S, and not observed for $E_\perp S$ under the $\langle 001 \rangle$ stress. Among the levels, Γ_2 and Γ_3 states have this polarization dependence. The Γ_2 state is singlet and splits no further. Thus the 6790 cm^{-1} line is confirmed as the Γ_3 state. The other possibility is that the ground state splits into levels apart by about 20 to 30 cm^{-1}, under the crystal-field of low symmetry.[12] This effect, however, does not occur in $KNiF_3$, as the exchange interaction is dominant in the ground state. The observed splitting cannot be explained by the effect of crystal-field of low symmetry.

With respect to the effect of the lattice vibrations, the normal modes of $KNiF_3$ are $4T_{1u}+T_{2u}$. They are all odd parity modes. The Jahn-Teller effect does not occur.

We consider the exchange interaction in the exicted state, $^3T_{2g}$. The Hamiltonian for the exchange interaction in the $^3T_{2g}$ state, $\mathcal{H}_{ex}'$ is represented by the molecular field approximation as,

$$\mathcal{H}_{ex}' = g\beta H_{ex} S_z \qquad (1)$$

where g is Landé g-factor, β is Bohr magneton, H_{ex} is the exchange field applied to the $^3T_{2g}$ state and S_z is the z component of spin. Ferguson *et al.* decided the four parameters as $Dq=$ 698 cm^{-1}, $F_2=1520$ cm^{-1}, $F_4=114$ cm^{-1} and $\lambda=-310$ cm^{-1} by fitting to the levels of the $KMgF_3$: Ni spectrum. Their calculated values of the $^3T_{2g}$ band are as follows, Γ_3:6713 cm^{-1}, Γ_4: 6863 cm^{-1}, Γ_5: 7265 cm^{-1} and Γ_2: 7412 cm^{-1}. These values shift to lower frequency by about 80 cm^{-1}, compared with the observed frequencies of $KNiF_3$. For the moment, we use these values and calculate the energy levels including the exchange interaction of eq. (1).

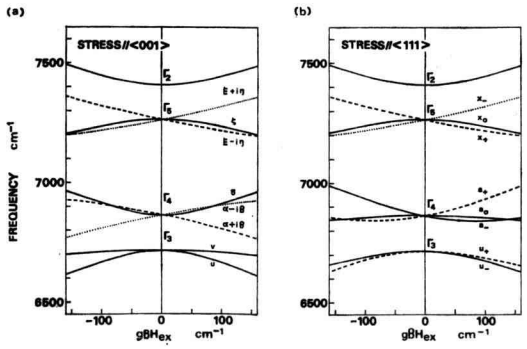

Fig. 6 The calculated result of the energy levels of the $^3T_{2g}$ state versus $g\beta H_{ex}$, under (a) the $\langle 001 \rangle$ stress, (b) the $\langle 111 \rangle$ stress. A solid curve is allowed for E//S, a dashed curve for $E_\perp S$, and a dotted curve is forbidden.

Table IV. The calculated result of transition intensities, $I_{E//S}$ for E//S and $I_{E\perp S}$ for $E_\perp S$, under the ⟨001⟩ and ⟨111⟩ stress. I_{NS} is intensity with no stress.

level	I_{NS}	⟨001⟩ stress					⟨111⟩ stress				
		state	$I_{E//S}$	$I_{E\perp S}$	$\frac{I_{E//S}}{I_{NS}}$	$\frac{I_{E\perp S}}{I_{NS}}$	state	$I_{E//S}$	$I_{E\perp S}$	$\frac{I_{E//S}}{I_{NS}}$	$\frac{I_{E\perp S}}{I_{NS}}$
Γ_3	2/9	u	1/4	0	3/2	0	u-	1/6	0	3/4	0
		v	1/12	0			u+	0	1/3	0	3/2
Γ_4	1/3	$\alpha+i\beta$	0	1/2	0	3/2	a-	1/3	0	5/4	0
		γ	1/4	0	3/4	0	a_0	1/12	0		
		$\alpha-i\beta$	0	0	0	0	a+	0	1/6	0	1/2
Γ_5	1/3	$\xi-i\eta$	0	1/2	0	3/2	x_+	0	1/2	0	3/2
		ζ	1/4	0	3/4	0	x_0	1/4	0	3/4	0
		$\xi+i\eta$	0	0	0	0	x_-	0	0	0	0
Γ_2	1/9	e_2	1/6	0	3/2	0	e_2	1/6	0	3/2	0

Figure 6-(a), (b) show the eigenvalues of the $^3T_{2g}$ state versus $g\beta H_{ex}$ under the ⟨001⟩ and ⟨111⟩ stress. A solid curve shows that the transition to this level is allowed for E//S, and a dashed curve for $E_\perp S$. A dotted curve shows that the transition to this level is forbidden. Their relative intensities are listed in Table IV. In this calculation, we consider the transition from the $S_z=-1$ site of the ground state. For the transition from the $S_z=1$ site, the sign of $g\beta H_{ex}$ is changed and Table IV is rewritten as follows: $\alpha+i\beta$ state is exchanged with $\alpha-i\beta$ state, $\xi+i\eta$ state with $\xi-i\eta$ state, u_+ state with u_- state, a_+ state with a_- state and x_+ state with x_- state. In Table IV, I_{NS} is the intensity with no stress, where spins are oriented randomly among the three equivalent directions, ⟨001⟩, ⟨100⟩ and ⟨010⟩. $I_{E//S}$ and $I_{E\perp S}$ are intensities for E//S and $E_\perp S$.

We compare them with the observed results. The sign of $g\beta H_{ex}$ is positive to fit to the observed result. Under the ⟨001⟩ stress, the Γ_3 state becomes strong (by factor of 3/2) for E//S, and is forbidden for $E_\perp S$. Under the ⟨111⟩ stress, the u_- state becomes weak (3/4) for E//S, and the u_+ state becomes strong (3/2) for $E_\perp S$. This result agrees with the 6790 cm^{-1} line. For the Γ_4 state under the ⟨001⟩ stress, the γ state becomes weak (3/4) for E//S, the $\alpha+i\beta$ state becomes strong (3/2) for $E_\perp S$. Under the ⟨111⟩ stress, the a_0 and a_- states become strong (5/4) for E//S, and the a_+ state becomes weak (1/2) for $E_\perp S$. For the ⟨001⟩ stress, this result agrees with the 6951 cm^{-1} line. For the ⟨111⟩ stress, however, the 6951 cm^{-1} line does not show structure. For the Γ_5 state, the calculated result agrees with the 7353 cm^{-1} line, except that this line is not so strong for $E_\perp S$ under the ⟨001⟩ stress. The 7496 cm^{-1} line does not agree with the calculated result of the Γ_2 state. The exchange interaction in the $^3T_{2g}$ state can explain the gross feature of the structures, especially the splitting and polarization dependence of the 6790 and 6951 cm^{-1} lines. There remains the problem to analyze quantitatively the levels and to obtain the amplitude of the exchange interaction in the $^3T_{2g}$ state.

6. Conclusion

The absorption spectra of the $^3T_{2g}$ band in pure $KNiF_3$ and $KMgF_3$:0.015 Ni crystals are measured to see the exchange effect in the excited $^3T_{2g}$ state. The exchange effect in the $^3T_{2g}$ state is not so large as to change throughly the spectrum. The polarization dependence of the absorption spectra of layered K_2NiF_4 is measured to clarify the mechanism of the transition. The stress effect of $KNiF_3$ is studied to exmaine the structures of the $^3T_{2g}$ band. The stress effect shows that the 6790 and 6951 cm^{-1} lines both split into two lines. This splitting can be explained qualitatively by the exchange effect in the $^3T_{2g}$ state.

Acknowledgements

The author would like to express his sincere thanks to Professor G. Kuwabara for allowing him to use the experimental facilities at the university of Tokyo. He also thanks to Dr. A. Tsuchida for providing him the $KNiF_3$ samples.

References

1) K. Knox, R.G. Shulman and S. Sugano: Phys. Rev. **130** (1963) 512.
2) J. Ferguson, H.J. Guggenheim and D.L. Wood: J. Chem. Phys. **40** (1964) 822.
3) J. Ferguson and H.J. Guggenheim: J. Chem. Phys. **44** (1966) 1095.
4) T. Bandai, H. Fukutani and G. Kuwabara: J. Phys. Soc. Japan **41** (1976) 137.
5) A. Okazaki and Y. Suemune: J. Phys. Soc. Japan **16** (1961) 671.
6) J. Nouet, A. Zarembovitch, R.V. Pisarev, J. Ferré and M. Lecomte: Appl. Phys. Letters **21** (1972) 161.
7) K. Hirakawa, T. Hashimoto and K. Hirakawa: J. Phys. Soc. Japan **16** (1961) 1934.
8) R.J. Birgeneau, H.J. Guggenheim and G. Shirane: Phys. Rev. Letters **22** (1969) 720.
9) K. Hirakawa, K. Hirakawa and T. Hashimoto: J. Phys. Soc. Japan **15** (1960) 2063.
10) T. Nagata, Y. Tomono and M. Kajiura: J. Phys. Soc. Japan **30** (1971) 1209.
11) A.D. Liehr and C.J. Ballhausen: Ann. Phys. **2** (1959) 134.
12) J. Ferguson, H.J. Guggenheim, H. Kamimura and Y. Tanabe: J. Chem. Phys. **42** (1965) 775.