Ferroelectrics, 2001, Vol. 258, pp. 177–182
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ONE- AND TWO-MAGNON CONTRIBUTIONS IN OPTICAL SPECTRA OF $KNiF_3$ SINGLE CRYSTAL

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(Received in final form April 15, 2001)

The one-magnon (1M) and two-magnon (2M) contributions were studied in optical absorption spectra of $KNiF_3$ single crystal, measured in the temperature range from 5 K to 300 K. The three absorption bands were considered in details. The first band is due to the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, centred at 7700 cm^{-1}, and contains the Brillouin zone-centre one-magnon contribution with the energy $\omega_{1M} = 25 \pm 5$ cm^{-1}. The other two bands are due to the electric-dipole transitions $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ and $^3A_{2g}(F) \rightarrow {}^1E_g(G)$, centred at 16000 cm^{-1} and 31200 cm^{-1}, respectively. Both bands contain the Brillouin zone-boundary two-magnon contribution with the energy $\omega_{2M} = 813 \pm 10$ cm^{-1}.

Keywords $KNiF_3$; magnons; optical absorption.

INTRODUCTION

Potassium nickel fluoride, $KNiF_3$, is a cubic perovskite with the lattice parameter $a = 4.014$ Å at $T = 298$ K. It orders antiferromagnetically below the Néel temperature $T_N = 253$ K [1] (246 K [2], 275 K [3]). The superexchange interactions couple nearest-neighbour (NN) Ni^{2+} ions ($S = 1$), located at opposite magnetic sublattices, by the exchange energy

$J_{NN} \approx 70$ cm^{-1} [1,4]. In the antiferromagnetic phase, the spins at nickel ions are aligned parallel to <111>, and their excitation spectrum has been studied in the past by electron spin resonance (ESR) measurements [5], far-infrared [5,6], optical [1,3] and Raman [4,7] spectroscopies and Brillouin scattering measurements [8]. However, the question on the one-magnon excitations in $KNiF_3$ remains open. In the past, they were identified with the far-infrared peak at 48.7 cm^{-1} [6]. But it was shown recently that the mode at 48.7 cm^{-1} is not magnetic in origin, and the far-infrared and ESR absorption mode at 2.54 cm^{-1} was related to the one-magnon processes [5]. The attempts to identify the magnon contributions in optical absorption spectra were unsatisfactory [1,3].

In our previous low-temperature studies [9], a comparative analysis of the magnetic-dipole band $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ in $KNiF_3$ and NiO allowed us to conclude that a zero-phonon line splitting can be attributed to the one-magnon absorption. In this work, we present temperature dependent optical absorption studies of $KNiF_3$ single crystal and extend our previous results on the magnetic-dipole band to two electric-dipole bands, containing contributions from two-magnon processes.

EXPERIMENTAL

Temperature dependent optical absorption measurements were performed on a transparent bright-green single crystal sample of $KNiF_3$ having the size 6×6×1 mm^3. The spectra were recorded in the energy range from 2500 nm to 190 nm with the spectral resolution 0.1 nm using the split-beam Jasco spectrophotometer (Model V-570). Deuterium discharge tube and tungsten iodine lamp were used as a source in the ranges from 190 nm to 350 nm and from 330 nm to 2500 nm, respectively. A photomultiplier tube and PbS photoconductive cell were used as a detector in the ranges from 190 nm to 900 nm and from 800 nm to 2500 nm, respectively. The temperature of the samples was varied in the temperature range from 5 K to 300 K (±1 K) using a liquid helium cryostat.

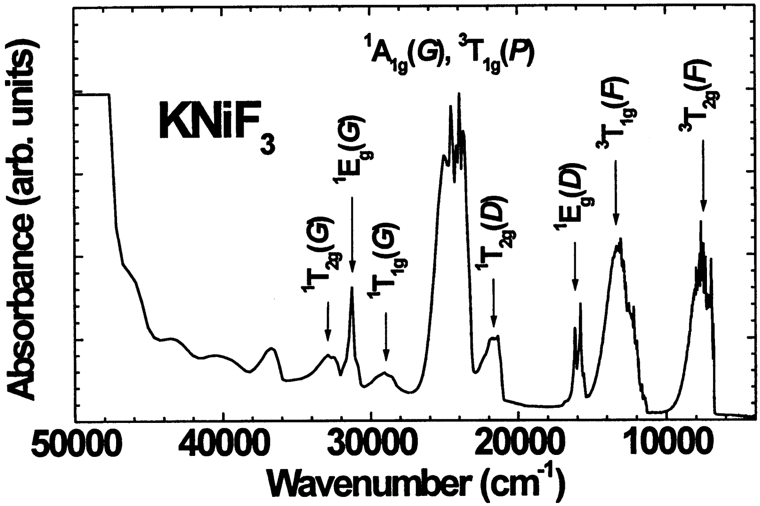

FIGURE 1 The absorption spectrum of KNiF$_3$ single crystal at 5 K. The electronic transitions are indicated by arrows.

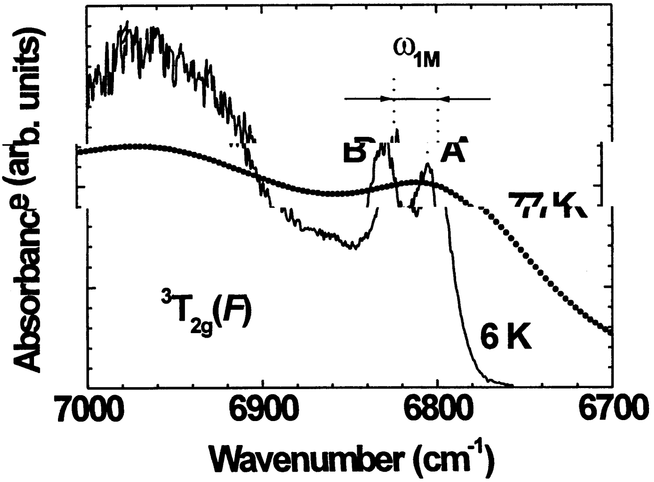

FIGURE 2 The low-energy side of the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ band in KNiF$_3$ at 6 K (line) and 77 K (circles). The pure exciton and exciton-magnon transitions are labelled by A and B, respectively.

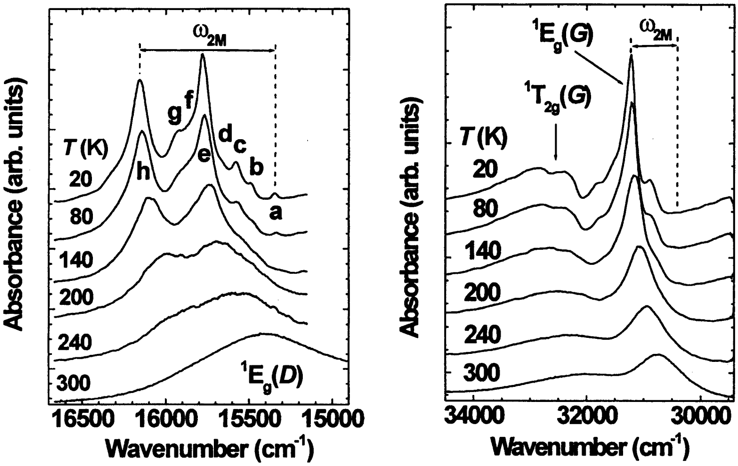

FIGURE 3 Temperature dependence of the optical absorption bands in the range of the electric-dipole transitions ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$ (left panel) and ${}^3A_{2g}(F) \rightarrow {}^1E_g(G)$ (right panel). The intervals between pure exciton and exciton—two-magnon transitions are indicated.

RESULTS AND DISCUSSION

Optical absorption spectrum of $KNiF_3$ single crystal at 5 K is shown in Fig. 1. The absorption bands are assigned following the energy levels diagram for $Ni^{2+}(3d^8)$ ion in a cubic crystal field with $Dq = 766$ cm^{-1} [9]. The first band, centred at 7700 cm^{-1}, has the magnetic-dipole nature and is due to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition. All other bands arise from vibrationally induced electric-dipole transitions. Further we will discuss two of them, corresponding to the transitions ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$, centred at 16000 cm^{-1}, and ${}^3A_{2g}(F) \rightarrow {}^1E_g(G)$, centred at 31200 cm^{-1}.

The magnetic-dipole band has a broad shape with fine vibrational structure and two sharp peaks, denoted by A and B and located at the low energy side of the band (Fig. 2). These peaks are the so-called zero-phonon lines, corresponding to the pure exciton transition (peak A) and the exciton-magnon excitation (peak B) [9]. The peak B is not visible already at 77 K because of a decrease of long-range magnetic correlations [10]. The energy difference of about 25 cm^{-1} between the two peaks is related to the zone-centre one-magnon energy ω_{1M} and can be used to estimate the J_{NN} value. We take the effective anisotropy field $H_A = 0.75$ cm^{-1} as in NiO [11] and $(\omega_{1M})^2 = 2\, J_{NN}\, S\, z\, H_A + (H_A)^2$ ($z = 6$ is the number of magnetic NN), then $J_{NN} = 69.4$ cm^{-1}.

The band at 16000 cm^{-1}, due to the electric-dipole transition transitions $^3A_{2g}(F) \rightarrow {}^1E_g(D)$, has several peaks, labeled from a to h in Fig. 3 (left panel). Note that the intense peak h has not been identified for many years [1,3], and very weak peaks d and f are observed for the first time in the present work. The pure exciton transition is forbidden and thus is attributed to the small peak a. The set of peaks from b to g is due to the phonon assisted absorption [10]: their energies are in good agreement with infrared active optical modes [12,13]. The strong peak h is related to the exciton—two-magnon excitation. Upon temperature increase, the peak position shifts to lower energies and the intensity decreases (Fig. 3): it completely disappears at about the Néel temperature. The energy $\omega_{2M} = 813$ cm^{-1} of the zone-boundary two-magnon excitation is determined by the difference between the peaks h and a.

Similar two-magnon contribution is observed in the electric-dipole transition $^3A_{2g}(F) \rightarrow {}^1E_g(G)$ at about 31200 cm^{-1} (right panel in Fig. 3). The peak shows close behavior with temperature increase and also disappears at about the Néel temperature. Note that the estimated two-magnons energy ω_{2M} is equal to about $11.7J_{NN}$.

CONCLUSIONS

In the present work we report on the temperature dependent optical absorption measurements of $KNiF_3$ single crystal. Three absorption bands, due to the magnetic-dipole $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition and two electric-dipole $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ and $^3A_{2g}(F) \rightarrow {}^1E_g(G)$ transitions are considered in details. Particular attention was devoted to the magnon contributions. The Brillouin zone-centre one-magnon assisted absorption with the magnon energy $\omega_{1M} = 25 \pm 5$ cm^{-1} was found in the magnetic-dipole band, whereas two electric-dipole bands contain the Brillouin zone-boundary two-magnon contribution with the energy $\omega_{2M} = 813 \pm 10$ cm^{-1}.

Acknowledgements

This work was partially supported by the grants of the Latvian Government (No. 96.0412 and 96.0670) and the Estonian Science Foundation (No. 3453).

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