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LOW TEMPERATURE OPTICAL ABSORPTION BY MAGNONS IN $KNiF_3$ AND NiO SINGLE-CRYSTALS

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Abstract. Optical absorption spectra of $KNiF_3$ and NiO stoichiometric single-crystals were measured at 5 K in the range from 4000 to 50000 cm^{-1}. The observed bands are interpreted based on the energy levels diagram for Ni^{2+} ($3d^8$) ion in a cubic crystal field. The crystal-field parameter Dq is equal to 766 cm^{-1} in $KNiF_3$ and 890 cm^{-1} in NiO. Particular attention is paid to the band due to the magnetic-dipole $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition, located at 7700 cm^{-1} in $KNiF_3$ and at 8900 cm^{-1} in NiO. We show that the energy difference between the two peaks, located at the low energy side of the band, is related to the zone-center ($k = 0$) one-magnon energy, so that the low-energy peak is attributed to the pure exciton transition, whereas the high-energy peak to the exciton-magnon excitation. The estimated one-magnon energies are 25 ± 5 cm^{-1} in $KNiF_3$ and 39 ± 3 cm^{-1} in NiO.

1. Introduction

$KNiF_3$ and NiO have cubic perovskite and rock-salt structures, respectively, in which Ni^{2+} ions are located at the centre of regular NiF_6 and NiO_6 octahedra. Both compounds exhibit antiferromagnetic (AF) ordering ($S = 1$) below the Néel temperature ($T_N = 246$ K [1] (253 K [2, 3, 4], 275 K [5]) for $KNiF_3$ and $T_N = 523$ K for NiO [6]). The AF structure is mainly determined by dominating superexchange interactions in the Ni^{2+}–F^-–Ni^{2+} ($J_1 \simeq 70$ cm^{-1} [2, 3, 4, 7]) and Ni^{2+}–O^{2-}–Ni^{2+} ($J_1 \simeq 150$ cm^{-1}

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[8, 9, 10]) linear atom chains. Besides, 90°-superexchange Ni^{2+}–O^{2-}–Ni^{2+} interactions ($J_2 \simeq 24$ cm^{-1} [11]) contribute in NiO as well.

The two- and four-magnon Raman scatterings have been observed in both compounds [8]. The two-magnon peak at $\sim$ 750 cm^{-1} in $KNiF_3$ and at $\sim$ 1560 cm^{-1} in NiO is exceptionally strong and detectable up to T_N [8]. The four-magnon peak at $\sim$ 1270 cm^{-1} in $KNiF_3$ and at $\sim$ 2800 cm^{-1} in NiO is very weak even at $T = 1.5$ K [8].

At the same time, the one-magnon Raman scattering has been detected, to our knowledge, only in NiO: its frequency is equal to 38 cm^{-1} at $T = 0$ K [6]. This value agrees well with the energy of the antiferromagnetic resonance (AFMR) [12], observed in NiO in far-infrared (IR) at 36.6 cm^{-1}. The one-magnon excitations were also found in the fine structure of near-IR optical absorption in NiO, where two narrow lines at 7810 and 7849 cm^{-1} have been observed in the range of the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ at 5 K [13]. The two lines were attributed to pure exciton and exciton-magnon transitions, respectively, and are separated by 39 ± 3 cm^{-1} [13]. Such interpretation is supported by IR absorption spectra of NiO:Co [14], where the intensity of the exciton-magnon transition decreases upon doping with Co, whereas the difference between exciton and exciton-magnon transitions increases in agreement with the AFMR results.

No AFMR measurements exist to our knowledge for $KNiF_3$. Therefore, we were interested to estimate the one-magnon energy in $KNiF_3$ from low temperature IR absorption spectra.

2. Experimental

Experiments were performed on a transparent bright-green single-crystal sample of $KNiF_3$. A green-colored NiO single-crystal, grown by the method of chemical transport reactions on the (100) face of a MgO crystal, was used for comparison [15]. Optical absorption spectra of $KNiF_3$ and NiO single-crystals were measured at 5 K in the energy range from 4000 to 50000 cm^{-1} using the Jasco spectrometer (Model V-570).

3. Results and Discussion

The optical absorption spectrum of $KNiF_3$ (Figure 1) consists of several bands due to the *d–d*-transitions, labelled according to the energy levels diagram for Ni^{2+} (d^8) ion in a cubic crystal field (Figure 2). The bands in UV and visible spectrum are the electric-dipole of nature, whereas the near-IR band at $\sim$ 8000 cm^{-1} corresponds to the magnetic-dipole transition [15]. The difference between the absorption spectra of $KNiF_3$ and NiO [15, 16] can be estimated from the calculated Tanabe-Sugano diagrams (Figure 2). It manifests mainly as a change in the order of $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and

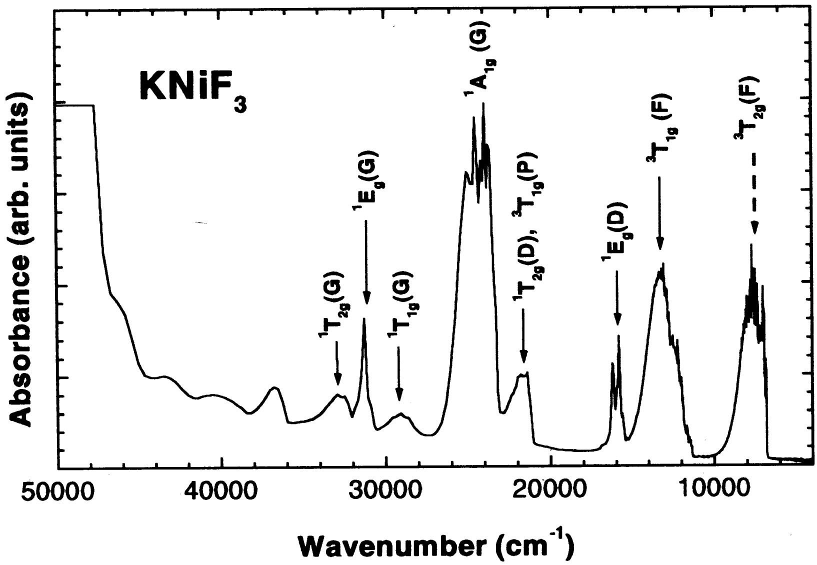

Figure 1. The absorption spectrum of $KNiF_3$ at 5 K. The electronic transitions are indicated.

$^3A_{2g}(F) \rightarrow {}^1E_g(D)$ bands: in $KNiF_3$ the Dq value is smaller than the cross-point energy of $^1E_g(D)$ and $^3T_{1g}(F)$ terms, whereas it is larger in NiO.

The crystal-field parameter Dq, estimated from the center of gravity of the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ band, is 766 cm^{-1} in $KNiF_3$. This value is smaller than that (890 cm^{-1}) in NiO, in spite of the $Ni^{2+}-F^-$ bonds being by ~ 0.08 Å shorter than the $Ni^{2+}-O^{2-}$ bonds. Using Anderson's theory with dominant σ-bonding contribution (which is the case of $KNiF_3$ and NiO), one can relate the antiferromagnetic exchange J_1 to the Dq parameter and the Coulomb interaction for the Ni $3d$ electrons U_{eff} as $J_1 = (10Dq/3)^2/U_{\text{eff}}$ [17]. The value of U_{eff} for NiO was found to be ≈ 7.5 eV [10], and, thus, we estimate U_{eff} for $KNiF_3$ to be ≈ 11.7 eV. The larger value of U_{eff} suggests that the $3d$ electrons in $KNiF_3$ are more localized than in NiO, and the $Ni^{2+}-F^-$ bonding has higher degree of ionicity.

At the low energy side of the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ band, two peaks (denoted A and B in Figure 3) can be detected at 6799 and 6824 cm^{-1} in $KNiF_3$ and at 7810 and 7849 cm^{-1} in NiO. In the latter case, they are very strong and well separated. There have been several attempts to explain the origin of the peaks A and B. They have been attributed to the exchange splitting of the excited $^3T_{2g}$ state in $KNiF_3$ [5]. Later the spin-orbital splitting was suggested as an explanation, however, it was not consistent with

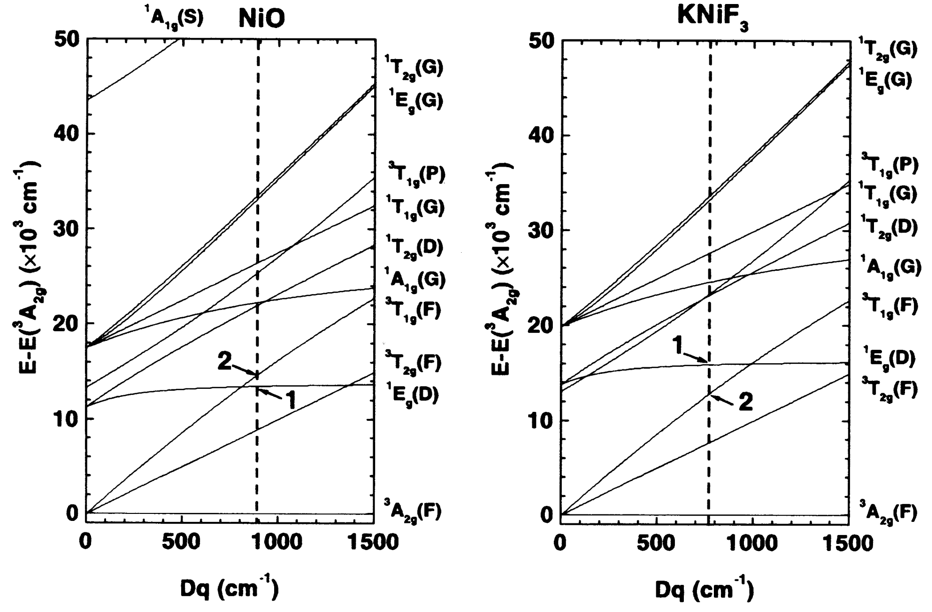

Figure 2. Calculated energy levels (Tanabe-Sugano) diagrams for Ni^{2+} ($3d^8$) ion in $KNiF_3$ ($Dq = 766$ cm^{-1}, $B = 874$ cm^{-1}, $C = 4733$ cm^{-1}) and NiO ($Dq = 890$ cm^{-1}, $B = 780$ cm^{-1}, $C = 3432$ cm^{-1}). The crystal-field (Dq) and Racah (B and C) parameters were determined from $KNiF_3$ and NiO absorption spectra. The point corresponding to the transition $^3A_{2g}(F)\rightarrow{}^1E_g(D)$ is shown by 1 and to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ by 2.

theoretical calculations showing that there should be four zero-phonon lines instead of two [18]. Recently, the origin of the doublet structure in NiO was attributed to spin-orbital interaction, rhombohedral exhange striction and an orthorhombic transverse molecular field due to antiferromagnetic long-range order [16].

The difference (39 ± 3 cm^{-1}) between the two lines in NiO agrees with the energy of the zone-centre ($k = 0$) one-magnon excitation, which was observed previously in zero magnetic field AFMR spectra at 36.6 cm^{-1} [12]. Such interpretation is supported by IR absorption measurements of NiO single-crystals doped with up to 5% of Co ions [14]. It was found [14] that upon an increase of the cobalt concentration, the energy difference between two zero-phonon peaks at 7828 and 7864 cm^{-1} and their half widths decrease. Besides, the intensity of the high-energy peak decreases drastically. Such a behaviour of the two IR absorption peaks correlates nicely with that observed for the AFMR lines of Co^{2+}-doped NiO in [12]. Therefore, the low-energy peak was attributed to the pure exciton transition, whereas the high-energy peak to the coupled exciton-magnon excitation

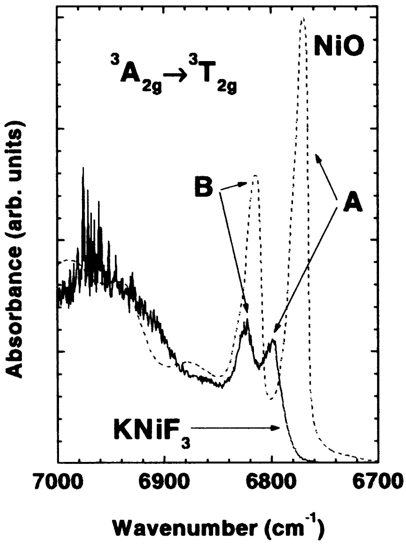

Figure 3. The $^3A_{2g}(F)\rightarrow ^3T_{2g}(F)$ magnetic-dipole transition band in $KNiF_3$ and NiO at 5 K. The energy scale of the absorption spectrum for NiO was shifted for comparison by -1020 cm^{-1} to compensate the difference in the Dq values. The intervals between A and B peaks are $\sim$ 39 cm^{-1} for NiO and $\sim$ 25 cm^{-1} for $KNiF_3$.

[13]. Our temperature and polarization dependent measurements of IR optical absorption in NiO also support such interpretation [19]. We suppose that similar processes are responsible for the origin of the lines at 6799 and 6824 cm^{-1} in $KNiF_3$. They are less separated, compared to NiO, due to a twice smaller value of the Néel temperature for $KNiF_3$.

4. Summary and Conclusions

A study of low temperature (5 K) optical absorption of $KNiF_3$ and NiO stoichiometric single-crystals in the energy range from 4000 to 50000 cm^{-1} is presented. The obtained absorption bands are interpreted in accordance with the energy levels (Tanabe-Sugano) diagrams for Ni^{2+} ($3d^8$) ion parameters Dq, B and C being optimized to fit the experimental data. Two peaks at the low energy side of the band, ascribed to the magnetic-dipole $^3A_{2g}(F)\rightarrow ^3T_{2g}(F)$ transition, are discussed in details. The energy difference between the two peaks is found to correspond to the zone-centre ($k = 0$) one-magnon energy, so that the low-energy peak is attributed to the pure exciton transition, whereas the high-energy peak to the exciton-magnon excitation. The estimated one-magnon energies are 25 ± 5 cm^{-1} in $KNiF_3$ and 39 ± 3 cm^{-1} in NiO. The value for NiO is consistent with experimental data of AFMR [12] and Raman scattering [6].

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