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EXCITATION OF MAGNONS AND PHONONS ON ABSORPTION OF LIGHT IN ANTIFERROMAGNETIC NiF_2

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The structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in the absorption spectrum of antiferromagnetic NiF_2 in the temperature interval 4.2 to 77°K is analyzed on the basis of experimental data on its oscillation frequencies. It is shown that the $\nu_I = 20{,}622$ cm^{-1} and $\nu_{II} = 20{,}717$ cm^{-1} bands are due to electron-magnon transitions with generation of one or two magnons, respectively, of maximal frequencies. The maximal magnon frequency $\nu_M = 100$ cm^{-1}. The magnon nature of the ν_I band is confirmed by analysis of its shape, the temperature dependence of its spectral position, and its half-width.

THE optical absorption spectrum of most antiferromagnetic crystals containing ions of the iron group (Mn^{2+}, Co^{2+}, Ni^{2+}) consists of quite narrow bands, which are connected with transitions between levels of the unfilled 3d-shell of these ions. In most cases such transitions are forbidden both according to symmetry and according to spin.

In the case of antiferromagnetic crystals, it may be conjectured that in addition to the usual phonon enabling mechanism, there is a magnon mechanism, by which a transition of an ion into an excited state is accompanied by the generation of a spin wave.

The present paper analyzes, from this point of view, the structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in the optical absorption spectrum of antiferromagnetic NiF_2. The transition is observed only when $T \ll T_N$, the Néel temperature; its components exhibit properties different from the characteristic features of purely electronic 0–0 transitions in antiferromagnetic crystals.

The paper will use the known NiF_2 spectral identification.[1]

NOTES ON METHOD

Single crystals of NiF_2 were grown in a helium atmosphere in a self-hermeticizing ampoule. The possibility of using this method is related to the weak oxidizability of NiF_2 as compared with the crystals of MnF_2 and CoF_2 that were obtained earlier in an atmosphere of HF.[2]

The raw material used was anhydrous NiF_2, obtained from $NiF_2 \cdot 4H_2O$ in two stages: 1) $NiF_2 \cdot 4H_2O$ was heated in a nickel boat on an electric plate at T ~ 200°C, whereupon two molecules of water of crystallization were removed; 2) for final dehydration, the powder thus obtained was heated in a stream of argon to T ~ 800°C, and then reduced and sintered in an atmosphere of HF at T ~ 1200 to 1300°C for a period of several hours. During this time there occurred an enlargement of the coarser crystallites at the expense of the finer, and thus the active sorbing surface of the NiF_2 powder was decreased.

The apparatus consisted of a high-frequency furnace (LGZ-10), through whose inductor there passed a quartz tube of length 1.5 m. Mounted in the tube was a tantalum heater of diameter 20 mm and height 50 mm. Helium, evaporating from a Dewar, entered at the bottom of the quartz tube; at the top, a platinum ampoule with the NiF_2 powder, previously sintered in an HF atmosphere, was introduced on a quartz fiber. The ampoule terminated at the top in a capillary, through which, under constant heating, the gases and moisture sorbed by the NiF_2 powder were given off and the powder was washed by helium.

At temperature ~1400°C the capillary was sealed by sublimated NiF_2, insuring hermeticity of the ampoule at the time of the growth of the single crystal. Control of the temperature was accomplished by means of an optical pyrometer. The ampoule was fed through the tantalum heater (~ 1500°C) by means of a small motor with a reducing gear, at speed ~0.8 mm/min.

The NiF_2 crystal obtained, transparent and of emerald color, cracked upon extraction from the ampoule into grains of size 3 × 2 × 2 mm. Examination with a polarizing microscope showed that these grains were single crystals.

The method of low-temperature spectral investigation of the crystals was similar to that described earlier.[3] The spectrum was investigated in the region of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition (21 000 to 20 000 cm^{-1}), at temperatures 77 to 4.2° K. The linear dispersion of the instrument used (DFS-8) was ~ 6 Å/mm.

EXPERIMENTAL RESULTS

Figure 1a shows the region of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in the spectrum of NiF_2 at T = 77 and 4.2° K, in agreement with the data in the literature,[1] there is observed a wide absorption band, 21 000 to 20 800 cm^{-1}; at T = 4.2° K, there develops from its long-wavelength side a series of comparatively narrow absorption bands, among which stands the most intense, $\nu_I = 20\ 622\ cm^{-1}$.

Figure 2 illustrates the shape of this band for various temperatures. Notice the very rapid diminution of intensity of the band on increase of temperature, its abrupt widening (Fig. 3), and its shift toward longer wavelengths (Fig. 4). At T ~ 40° K the fine structure completely disappears (Fig. 1a).

DISCUSSION OF RESULTS

Consideration of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition is simplified by the fact that the excited state $^1T_{2g}$ is nonmagnetic (S = 0) and should not become split in the exchange field upon transition of the crystal to a magnetically ordered state. The behavior of the state $^3A_{2g}$—the ground state for $T < T_N$—has been studied in NiF_2 with the analogous transition $^3A_{2g} \rightarrow {}^1E$ as a model.[1] In the exchange field H_{exch}, the state $^3A_{2g}$, with S = 1, splits into three spin-sublevels (Fig. 5); the energy of the ground state thereupon is lowered by $\Delta E = g\mu_B H_{exch}$, where $H_{exch} = 3kT_N/g\mu_B(S+1)$ is the exchange field, k is Boltzmann's constant, and μ_B is the Bohr magneton.

From these considerations, on transition of the crystal to an antiferromagnetic state a shift of the 0–0 band, by the amount ΔE, is to be expected. In the case of the $^3A_{2g} \rightarrow {}^1E$ transition in NiF_2, the shift $\Delta E = 100\ cm^{-1}$.[1] Furthermore, at a distance ~ 100 cm^{-1} from the fundamental $^3A_{2g} \rightarrow {}^1E$ transition band, on the short-wavelength side, a

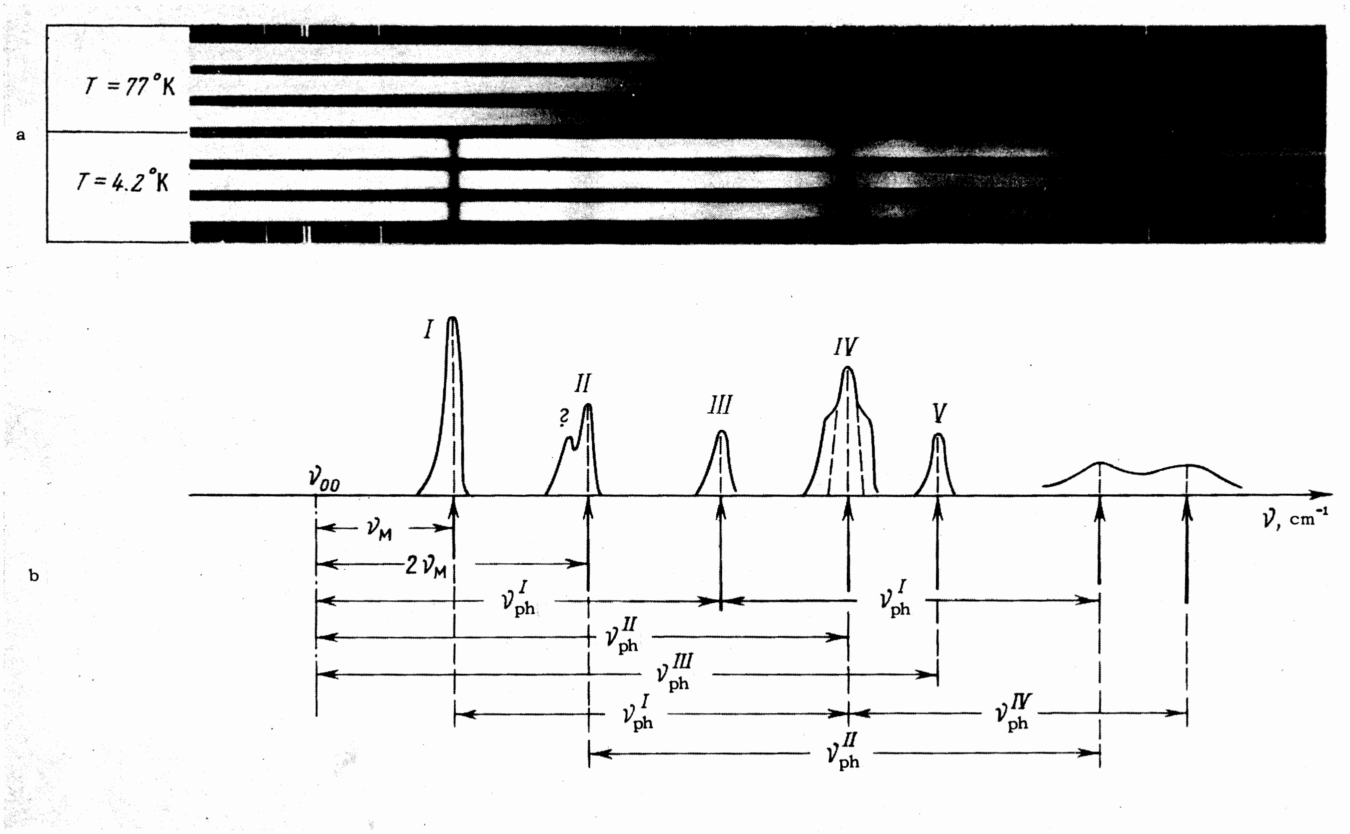

FIG. 1. a, Region of the spectrum connected with the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in NiF_2 at T = 77 and 4.2°K. b, Possible identification of the structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition.

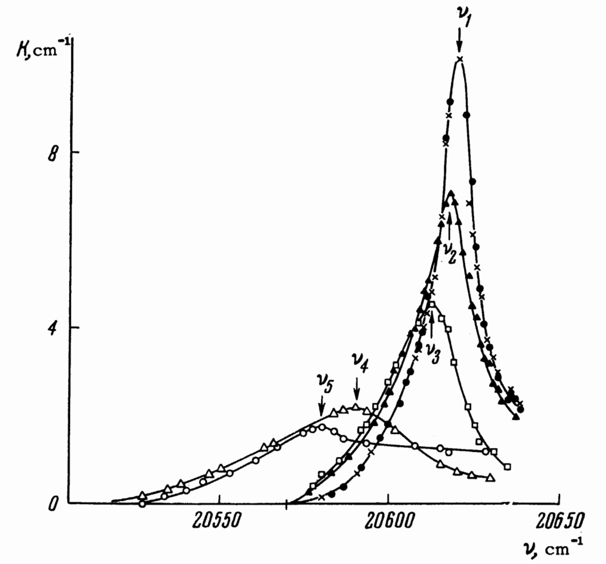

FIG. 2. Behavior of the $\nu_I = 20\,622\ \mathrm{cm}^{-1}$ band in NiF_2 at various temperatures: crosses, 4.2°K ($\nu_1 = 20\,622\ \mathrm{cm}^{-1}$); dark circles, 20.4°K ($\nu_1 = 20\,622\ \mathrm{cm}^{-1}$); dark triangles; 28°K ($\nu_2 = 20\,619\ \mathrm{cm}^{-1}$); open squares, 35°K ($\nu_3 = 20\,614\ \mathrm{cm}^{-1}$); open triangles, 40°K ($\nu_4 = 20\,591\ \mathrm{cm}^{-1}$); open circles, 46°K ($\nu_5 = 20\,581\ \mathrm{cm}^{-1}$). K = absorption coefficient.

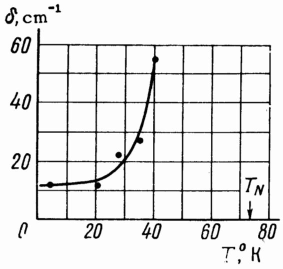

FIG. 3. Temperature dependence of the half-width δ of the $\nu_I = 20\,622\ \mathrm{cm}^{-1}$ band in NiF_2: solid curve, calculation by formula (1) of this paper; dark circles, experimental points.

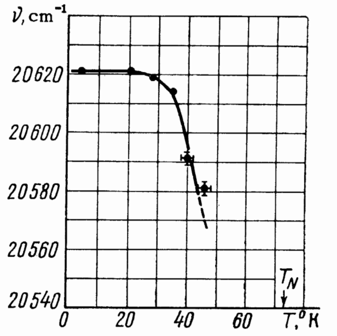

FIG. 4. Temperature dependence of the frequency of the $\nu_I = 20\,622\ \mathrm{cm}^{-1}$ band in NiF_2, obtained experimentally.

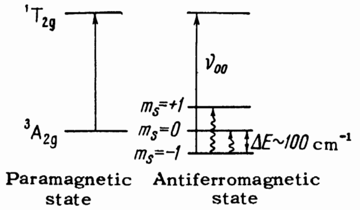

FIG. 5. Energy-level scheme of the ${}^3A_{2g} \to {}^1T_{2g}$ transition in NiF_2 in the paramagnetic and antiferromagnetic states.

satellite has been observed. Tanabe and Sugano[4] attributed the appearance of a satellite in this band to "double" transitions, in which, upon transition of one ion of an exchange-coupled pair of ions into the excited state ${}^1E$, the second acquires an energy ΔE (cf. Fig. 5).

This hypothesis, however, does not touch upon the question of conservation of momentum in the optical transition. In fact, a transition from the level $m_S = -1$ to the level $m_S = 0$ implies excitation of a spin wave with maximal energy ($\nu_M = 100\ \mathrm{cm}^{-1}$) and maximal quasimomentum $q_S = \pi/a$. The picture is clarified by admission of the exciton mechanism for absorption of light in antiferromagnetic crystals. Such a hypothesis was suggested earlier[3] and has been developed and given a theoretical basis.[5,6]

From this point of view, the appearance of a band-satellite implies the simultaneous generation of an exciton with quasimomentum $q_{exc} = \pi/a$ and of a magnon with equal but opposite quasimomentum $q_S = -\pi/a$. The energy interval between the 0–0 band and the magnon satellite should in this case be equal to the maximal energy of a magnon, $h\nu_M \sim kT_N$, if the exciton band is sufficiently narrow—as is apparently true for excitation of 3d-states.[3]

It is clear that the band-satellites that appear in the presence of such a mechanism will behave differently from the fundamental bands. First, they will be shifted twice as fast upon cooling, with a total shift $\Delta\nu \sim 2\Delta E$ (Fig. 5). Furthermore, if we take into account that the population of the ground state with $m_S = -1$ will decrease through thermal transitions to the state with $m_S = 0$, which leads to a widening of the band, then the half-width of the magnon band will change with temperature according to the law

$$\delta_T = \delta_+ + \delta_- \exp(-\Delta\nu / 2kT), \tag{1}$$

where δ_+ and δ_- are the half-widths due, respectively, to generation and absorption of phonons, and Δν is the experimental value of the shift of the band at temperature T. For purely electronic bands, of course, the coefficient 2 in the denominator of the exponent in formula (1) will be absent, and Δν/2 will be replaced at the appropriate temperature T by the value of ΔE (Fig. 5) or by the value of the experimental shift of the band, Δν(T).

Possible Identification of Fine Structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ Transition in NiF_2

Band notation	Frequency, cm^{-1}, T = 20°K	Possible identification	Band notation	Frequency, cm^{-17}, T = 20°K	Possible identification
0	20522	ν_{00}	III	20807	$\nu_{00} + \nu_{ph}^{I}$
	20622	$\nu_{00} + \nu_M$			
II	20702 20717	? $\nu_{00} + 2\nu_M$	I	20891	$\nu_{00} + \nu_{ph}^{II}$ $\nu_{00} + \nu_M + \nu_{ph}^{I}$
			V	20947	$\nu_{00} + \nu_{ph}^{III}$

Note: Maximal magnon frequency $\nu_M = 100\ cm^{-1}$; vibrational frequencies (cm^{-1}) $\nu_{ph}^{I} = 285$, $\nu_{ph}^{II} = 370$, $\nu_{ph}^{III} = 445$, $\nu_{ph}^{IV} = 225$.

The electron-magnon mechanism mentioned above for enabling of forbidden optical transitions, in the case of antiferromagnetic crystals, is no less real than the usual electron-vibration mechanism (interactions of the electronic transition with lattice vibrations). The magnon satellites, by virtue of the lifting of the prohibition with respect to evenness, may be more intense as compared with forbidden purely electronic transitions, which in general cannot be observed.

From this point of view, the fine structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in NiF_2 is of interest. For its analysis, use was made of the experimentally measured values of four optically active oscillations of the crystal lattice of NiF_2, 445, 285, 225, and 370 cm^{-1}.[1] The results are presented in Fig. 1b, where the ν_{00}-transition is chosen for the beginning of the scale (corresponding to a forbidden purely electronic transition), and in the table. Thus the most intense band $\nu_I = 20\ 622\ cm^{-1}$, distant from the ν_{00}-band by the amount of the maximal magnon frequency $\nu_M = 100\ cm^{-1}$, can be considered an electron-magnon transition, i.e., a band due to an electric-dipole transition permitted because of interaction of the electronic transition with a short-wavelength magnon, having the maximal frequency $\nu_M = 100\ cm^{-1}$.

Band II, distant from the ν_{00}-band by $2\nu_M = 200\ cm^{-1}$, can be related to the excitation of an exciton with zero momentum and of two magnons with equal but opposite momenta. (In the language of "double" transitions of Tanabe and Sugano,[4] this is equivalent to excitation, along with the fundamental transition, to the level with $m_S = +1$ (Fig. 5).)

Bands III, IV, and V are distant from the ν_{00}-band by distances corresponding to known optically active oscillations of the NiF_2 lattice and may be regarded as electronic-vibrational. Band IV is obviously a superposition of two bands: an electronic-vibrational band, distant by $\nu_{ph}^{II} = 370\ cm^{-1}$ from the ν_{00}-band, and an electron-magnon-phonon band, distant from band I by a frequency that is close to the frequency of the optical phonon $\nu_{ph}^{I} = 285\ cm^{-1}$; this is confirmed by analysis of its shape (cf. the scheme of Fig. 1b).

Confirming the electron-magnon nature of the $\nu_I = 20\ 622\ cm^{-1}$ band are, first, the significantly larger temperature dependence of its frequency, a shift that exceeds by a factor two the similar dependence of the $^3A_2 \rightarrow {}^1E$ band (Fig. 4); and second, the fact that the change of half-width of the band with temperature agrees satisfactorily with the calculation according to formula (1) (Fig. 3). Also to be noted is the "red" asymmetry of the $\nu_I = 20\ 622\ cm^{-1}$ band (Fig. 2), which is characteristic of electron-magnon transitions;[5,6] this is due to interaction with the spin-wave range of the spectrum, where $\partial^2\nu/\partial q_S^2 < 0$.

CONCLUSIONS

Analysis of the structure of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition in antiferromagnetic NiF_2 in the interval 4.2 to 77° K, on the basis of the extant experimental data on the vibration spectrum of NiF_2 and of the behavior of the $^3A_{2g}$ ground state of Ni^{2+} on transition of the crystal to a magnetically ordered state, enables us to draw the following conclusions.

1. The $\nu_I = 20{,}622\ cm^{-1}$ band can be related to an electric-dipole transition, allowed because of interaction of an electronic transition with a magnon of maximal frequency $\nu_M = 100\ cm^{-1}$.

2. The $\nu_{II} = 20\ 717\ cm^{-1}$ band is due to generation of an exciton and two magnons with equal but opposite momenta.

3. Confirming the electron-magnon nature of the $\nu_I = 20\ 622\ cm^{-1}$ band are its red asymmetry, its more pronounced dependence of frequency on temperature as compared with the analogous dependence for the usual electronic transitions ($^3A_{2g} \rightarrow {}^1E$), and the agreement of the temperature de-

pendence of its half-width with formula (1).

4. The remaining bands of the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition can be explained within the framework of the usual electronic-vibrational analysis, with use of the known optical vibration frequencies of the NiF$_2$ spectrum.

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[1] M. Balkanski, P. Moch, and R. G. Shulman, J. Chem. Phys. **40**, 1897 (1964).

[2] N. N. Mikhaĭlov and S. V. Petrov, Kristallografiya **11**, 451 (1966), Soviet Phys. Crystallography in press.

[3] V. V. Eremenko and A. I. Belyaeva, FTT **5**, 2877 (1963), Soviet Phys. Solid State **5**, 2106 (1964).

[4] S. Sugano and Y. Tanabe, Technical Report of ISSP, Japan, ser. A, No. 71 (1963).

[5] R. L. Greene, D. D. Sell, W. M. Yen, A. L. Schawlow, and R. M. White, Phys. Rev. Letters **15**, 656 (1965).

[6] J. Woods Halley and I. Silvera, Phys. Rev. Letters **15**, 654 (1965).

[7] M. Balkanski, P. Moch, and G. Parisot, Phys. Semiconduct., Paris, 1107-1110 (1964).

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