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TEMPERATURE DEPENDENCE OF THE OPTICAL ABSORPTION IN THE ANTIFERROMAGNET $NaNiF_3$

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The temperature dependence of the transition $^3A_{2g} \rightarrow {}^1E_g$ in the antiferromagnet $NaNiF_3$ (T_N = 149°K) was investigated in the temperature range from 77 to 295°K. The observed temperature shift of the absorption line is explained by a change in the value of the crystal field and by the exchange interaction between nickel ions below T_N. The increase in the line intensity with decreasing temperature is ascribed to the spin-orbit interaction between the states ^1E_g and $^3T_{1g}$. The complex form of the line, characterized by a series of maxima of decreasing intensity, is interpreted as the result of electronic-vibrational interactions.

THE optical absorption line of the Ni^{2+} ion, corresponding to the electron transition $^3A_{2g} \rightarrow {}^1E_g$, exhibits complex splitting in magnetically ordered crystals. This was noted first by Knox et al. in the spectrum of $KNiF_3$ [1] and was later reported also in [2-4]. Sugano and Tanabe [5] proposed a qualitative explanation of the appearance of a satellite line below the magnetic ordering temperature. They based their model on the idea of a correlation between the exchange interactions of paramagnetic ions in the ground and excited states. However, Ferguson et al. [2] suggested that the complex splitting of the ^1E_g level was caused by the spin-orbit coupling of this level with the neighboring triplet level $^3T_{1g}$. Apart from the unusual splitting, it was also found that the intensity of the transition $^3A_{2g} \rightarrow {}^1E_g$ increased as the temperature was lowered although, according to modern ideas about the electronic-vibrational nature of this transition, its intensity should have decreased. Further experimental investigations on this problem are of considerable interest. The present paper reports the results of an investigation of the splitting, the position and the intensity of the $^3A_{2g} \rightarrow {}^1E_g$ transition in the antiferromagnet $NaNiF_3$ (T_N = 149°K) in the temperature range from 77 to 295°K.

PRELIMINARY REMARKS

$NaNiF_3$ single crystals were grown from a melt of NaCl and NiF_2. [6] $NaNiF_3$ crystallizes in the perovskite type structure, but the crystal symmetry is described by the space group D_{2h}^{16} [7] (orthorhombic distortion). The symmetry of the environment of the Ni^{2+} ion, which is in an octahedron of six F^- ions, is not purely cubic O_h. The x-ray analysis data indicate, however, that the deviations from cubic symmetry are slight. We may therefore assume with sufficient justification that the interpretation of the optical spectrum, based on the assumption of a purely cubic environment, is valid. A single crystal of $NaNiF_3$ was oriented in a magnetic field at T = 77°K. The c-axis was perpendicular to the plane of the plate-shaped sample. The investigation of the optical absorption was carried out using a double-prism monochromator,

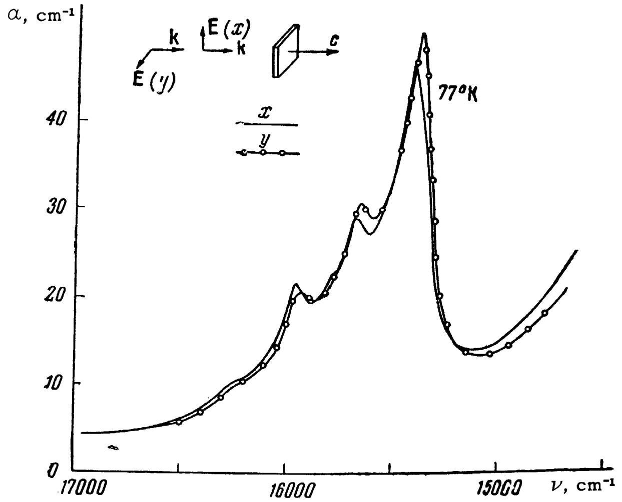

FIG. 1. $^3A_{2g} \rightarrow {}^1E_g$ transition at T = 77°K; k is the direction of propagation of light; E(x), E(y) are two directions of the electric vector in the light wave.

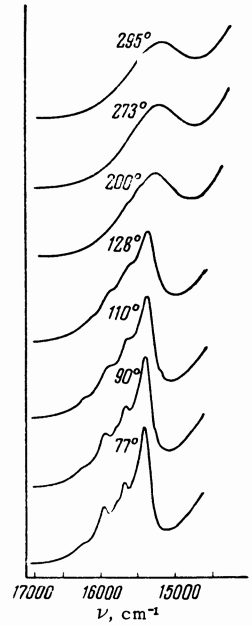

FIG. 2. Structure of the transition at various temperatures.

DMR-4, with an average resolution of 15 cm^{-1}. The crystal was mounted in a metal vacuum cryostat.

STRUCTURE OF THE LINE $^3A_{2g} \rightarrow {}^1E_g$

The investigated absorption line, corresponding to the electron transition from the ground state $^3A_{2g}$ of the Ni^{2+} ion to the excited state ^1E_g, is shown in Figs. 1 and 2. Curves x and y in Fig. 1 were obtained for two mutually perpendicular directions of the electric vector in the light wave. The displacement of the polarized lines with respect to one another amounts to 20—30 cm^{-1} at 77°K and is, most probably, the result of the deviation of the structure of NaNiF$_3$ from cubic symmetry. The frequencies of the main and secondary maxima are listed in Table I. The neighboring peaks are separated by approximately equal distances. Figure 2 shows the structure of the investigated line at various temperatures. It is interesting to note that the secondary absorption maxima had already appeared at 200°K, i.e., at temperatures much higher than T_N = 149°K. A possible explanation of the series of the secondary maxima will be given in the final section of the present paper.

Table I. Frequencies of the absorption maxima at T = 77°K (in cm^{-1})

x	Difference	y	Difference
15430		15405	
	270		275
15700		15680	
	275		270
15975		15950	
	275		280
16259		16230	

TEMPERATURE SHIFT OF THE $^3A_{2g} \rightarrow {}^1E_g$ LINE

The main absorption maximum shifts toward higher frequencies as the temperature is decreased (Fig. 3). The total shift amounts to 230 cm^{-1}. The shift is greatest in the temperature range from 120 to 180°K. Cooling also changes the two factors which most strongly alter the position of the $^3A_{2g} \rightarrow {}^1E_g$ line. First, a change in the lattice parameters alters the value of the crystal field and, secondly, at T_N = 149°K the crystal goes over into a magnetically ordered state. The change in the crystal field should alter the energy of the level ^1E_g (the energy of the level $^3A_{2g}$ is assumed to be zero). On the other hand, the magnetic ordering affects only the position of the ground level $^3A_{2g}$, since in the ^1E_g state the spin is S = 0. We shall estimate quantitatively the influence of these two factors.

The position of the ^1E_g level can be quite well described by the solution of the matrix equation of Tanabe and Sugano: [8]

$$E = {}^{17}/_2 B + 2C + 10Dq - {}^1/_2[(B + 20Dq)^2 + 48B^2]^{1/2},$$

where E is the energy of the ^1E_g level; B and C are the Racah coefficients which represent the electrostatic interaction within the 3d-shell; Dq is a crystal field parameter. At T = 295°K, Dq = 760 cm^{-1}, and at 77°K, Dq = 780 cm^{-1}. [1] The values of the Racah coefficients were selected in the author's earlier paper (B = 935 cm^{-1} and C = 4160 cm^{-1}). [4] The change in Dq with temperature should lead to a shift in the ^1E_g level by about 40 cm^{-1}.

Below 149°K, the exchange interaction splits the $^3A_{2g}$ level into three sublevels, corresponding to the three orientations of the spin S = 1 in the exchange field. The reduction in the ground state energy, estimated from the formula $\Delta E = 3kT_N/(S + 1)$, [5] amounts to 170 cm^{-1} (k is the Boltzmann constant, S = 1 is the spin in the $^3A_{2g}$ state). It is evident

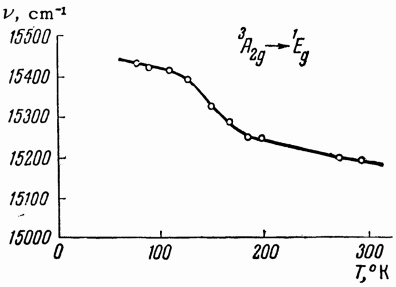

FIG. 3. Temperature shift of the maximum of the $^3A_{2g} \rightarrow {}^1E_g$ transition.

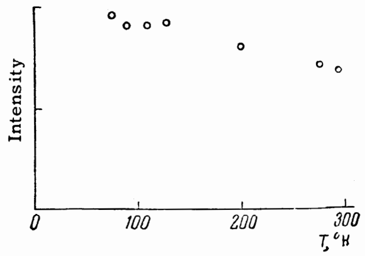

FIG. 4. Temperature dependence of the integral intensity of the $^3A_{2g} \rightarrow {}^1E_g$ transition.

from Fig. 3 that the shift in the line due to the exchange interaction takes place over a temperature range of about 60 deg. Physically, this means that already at temperatures of 180—200°K the lifetime of the ion in the excited state ^1E_g is longer compared with the lifetime at higher temperatures (this is also indicated by the narrowing of the absorption line) and becomes comparable with the time for the exchange of the states between paramagnetic ions, which is inversely proportional to the frequency of the exchange resonance and is weakly temperature-dependent.

Thus, the estimates obtained indicate that the shift in the absorption line can be explained mainly by the change in the position of the excited level ^1E_g, caused by a change in the crystal field, and by the splitting of the ground level $^3A_{2g}$ by the exchange interaction below T_N.

CHANGE IN THE DEPENDENCE OF THE INTENSITY OF THE TRANSITION $^3A_{2g} \rightarrow {}^1E_g$

The ^1E_g line has an anomalous temperature dependence of the intensity as the temperature decreases.[1,2,4] Both electric and magnetic dipole transitions between the states $^3A_{2g}$ and ^1E_g are forbidden. In crystals with an inversion center, the appearance of a nonzero probability of the transition is associated with the electronic-vibrational interactions. Due to these interactions, the electron states contain an admixture of the wave functions of the odd lattice vibration modes (for example, the T_{1u} and T_{2u} modes in the perovskite structure) and the transition becomes allowed. A theoretical consideration of this mechanism leads to the conclusion that the intensity of the transition is proportional to coth ($h\nu/2kT$) (where ν is some effective vibrational frequency), i.e., the intensity should decrease as the temperature falls. The temperature dependence of the integral intensity of the transition $^3A_{2g} \rightarrow {}^1E_g$ in $NaNiF_3$ is shown in Fig. 4. The transition intensity increases approximately by a factor of 1.5 on lowering the temperature from 295°K to 77°K.

Table II

Crystals	Temperature, °K	$\Delta E(^1E_g - {}^3T_{1g})$, cm^{-1}
$NaNiF_3$	300	2300
	77	2020
$KNiF_3$ [1]	300	2910
	77	2580
	4.2	2570
$KMg(Ni)F_3$ [1]	300	2710
	77	2420
	4.2	2440

A possible explanation of the observed effect is as follows. The $^3A_{2g} \rightarrow {}^1E_g$ transition violates the selection rules by conserving the total spin of the ion during the optical transition. In our case, in the ground state the spin is $S = 1$, while in the excited state $S = 0$. The selection rule $\Delta S = 0$ may be violated by including, in the Hamiltonian, the spin-orbital interaction operator which couples the states differing by $\Delta S = 1$.[10] In $NaNiF_3$, such an interaction may occur between the $^1E_g(^1\Gamma_3)$ state and the nearby triplet state $^3T_{1g}$. The spin-orbit interaction splits the $^3T_{1g}$ level into the components $^3\Gamma_1$, $^3\Gamma_3$, $^3\Gamma_4$, and $^3\Gamma_5$,[11] and, in accordance with the symmetry considerations, the triplet level $^3\Gamma_3$ interacts with the singlet level $^1\Gamma_3(^1E_g)$. The degree of mixing of the levels is in this case governed by the value of the spin-orbital parameter λ and by the separation of the two interacting states. In view of this, it is interesting to compare the separation of the ^1E_g and $^3T_{1g}$ levels in $NaNiF_3$ and other crystals. Table II lists the separations which are of interest. In $NaNiF_3$, these levels lie much more closely than in other crystals and the interaction between the states ^1E_g and $^3T_{1g}$ is stronger. When the temperature is decreased, these states approach each other, and this is very likely to increase the intensity of the transition. In the temperature range from 77°K to 4.2°K, the separation between these states in $KNiF_3$ and $KMgF_3$:Ni changes little and, therefore, we would expect that in this range of temperatures the intensity of the transition in these crystals will either decrease or change only slightly.

VIBRATIONAL NATURE OF THE ^1E_g LINE IN $NaNiF_3$

The fact that the ^1E_g and $^3T_{1g}$ states in $NaNiF_3$ may interact more strongly than in other crystals can account also for the unusual structure of the ^1E_g line in $NaNiF_3$. In the ground state $^3A_{2g}$ of the $Ni^{2+}(d^8)$ ion we have the following distribution of the eight d-electrons in the t_{2g} and e_g orbitals in a cubic field: $t_{2g}^6e_g^2$. The transition $^3A_{2g} \rightarrow {}^1E_g$ represents a jump of an electron from the e_g orbital to an orbital of the same symmetry but with an opposite direction of spin. In the ^1E_g state, the distribution of electrons in the orbitals is the same as in the ground state $^3A_{2g}$: $t_{2g}^6e_g^2$. Such transitions, which take place without a change in the orbital electron configuration in the ion, usually correspond to narrow absorption lines, since the electronic-vibrational interaction is the same in the initial and final states and does not broaden the line. The $^3T_{1g}$ state represents the following electron distribution in the orbitals: $t_{2g}^5e_g^3$, and this state is strongly coupled to the lattice vibrations. The mixing of the ^1E_g and $^3T_{1g}$ states may result in the narrow ^1E_g line reflecting in its structure the interaction between the $^3T_{1g}$ level and the lattice vibrations. In all probability, the series of approximately equidistant maxima of decreasing intensity (Figs. 1 and 2) reflects such interaction.

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