

***N*-Lines and Chromium-Pairs in the Luminescence Spectra of the Spinels $\text{ZnAl}_2\text{O}_4 : \text{Cr}^{3+}$ and $\text{MgAl}_2\text{O}_4 : \text{Cr}^{3+}$**

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It is shown that the *N*-lines in the luminescence spectra of the two spinels $\text{ZnAl}_2\text{O}_4 : \text{Cr}^{3+}$ and $\text{MgAl}_2\text{O}_4 : \text{Cr}^{3+}$ exhibit quite similar dependencies on chromium concentration, excitation frequency, and thermal treatment of the samples. While most of these lines are structure dependent, the line N_4 at $\bar{\nu}_R - \bar{\nu} \approx 400 \text{ cm}^{-1}$ and two very weak lines are in both cases due to chromium-pairs. The exchange Hamiltonian $H_{ex} = J\mathbf{S}_1 \cdot \mathbf{S}_2 + j(\mathbf{S}_1 \cdot \mathbf{S}_2)^2$ used for the ground-state splitting is fitted by the parameters $J = 40.9 \text{ cm}^{-1}$, $j = 1.5 \text{ cm}^{-1}$ and $J = 45.6 \text{ cm}^{-1}$, $j = 2.0 \text{ cm}^{-1}$ for ZnAl-spinel and MgAl-spinel, respectively. The differences between the spectra of low-doped and high-doped samples are in both cases caused by the existence of a phonon sideband of the N_4 -line, which is in many respects similar to the well-known phonon side band of the *R*-line.

1. Introduction

In a recent paper (1) it was shown that in the luminescence spectra of $\text{MgAl}_2\text{O}_4 : \text{Cr}^{3+}$ two kinds of *N*-lines exist: Lines which are primarily a function of the chromium concentration in the host lattice, and those which are dependent only upon the structure of the host lattice. The concentration-dependent *N*-lines are caused by chromium-pairs. The structure-dependent *N*-lines arise from six-coordinated Cr^{3+} ions whose short-range orders are distorted. This difference is a purely phenomenological one, however, since all *N*-lines can be interpreted as zero-phonon lines of different luminescence centers and are therefore spectroscopic analogs of the *R*-line.

Since the spinels $\text{ZnAl}_2\text{O}_4 : \text{Cr}^{3+}$ and $\text{MgAl}_2\text{O}_4 : \text{Cr}^{3+}$ exhibit quite similar optical properties, a comparison of their *N*-lines

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should be useful. Some earlier $\text{ZnAl}_2\text{O}_4 : \text{Cr}^{3+}$ papers (2, 3) contain partly differing results so that a reinvestigation seemed to be appropriate. In the following sections some results of a luminescence study are given which emphasize the problem of chromium-pairs.

2. Experimental

ZnAl_2O_4 -powders with 0-10 mole% Cr_2O_3 were prepared from appropriate amounts of ZnO , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and Cr_2O_3 which were ground, thoroughly mixed, and then pre-annealed at 600°C . Afterward the samples were again powdered, mixed, pressed into pellets, sintered at 1100°C for 15 hr, and finally cooled slowly¹ in air. The samples were checked by X-ray diffraction.

The luminescence spectra were measured on a Jarrel-Ash 25-300 Raman spectrometer. For excitation a Kr^+ -ion laser, Coherent

¹ The cooling rate was approximately 25°C hr^{-1} .

TABLE I
RELATIVE WAVENUMBERS OF THE *N*-LINES OF $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ AND $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ AT 77°K

$\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$			$\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$		
Line designation ^a	$\Delta\bar{\nu}^{(R)}$ [cm ⁻¹] ^b	Intensity ^c	Line designation ^a	$\Delta\bar{\nu}^{(R)}$ [cm ⁻¹] ^b	Intensity ^c
	22	m		(19)	sh
$N_1 \dots$	41	m	$N_1 \dots$	30 ^d	st
	52 ^d	st		37 ^d	st
	(62)	w		(52)	sh
	72	m	$N_2 \dots$	57	st
	(88)	w		(70)	sh
	(104)	sh	$N_3 \dots$	87 ^d	st
$N_2 \dots$	112 ^d	m			
	129 ^d	st			
$N_4 \dots$	398 ^e	st	$N_4 \dots$	398 ^e	st

^a For designation see text.

^b Accuracy in line position at least ± 2 cm⁻¹ for the sharper lines and ± 5 cm⁻¹ for the poorly resolved lines, which are indicated by brackets.

^c st, strong; m, medium; w, weak; sh, shoulder.

^d Intensity strongly affected by increasing disorder.

^e Intensity affected by chromium concentration.

Radiation Model 52, was used. The low-temperature measurements were made with the CF-100 cryogenic unit and the VC-30 PTC control system, Oxford Instrument, to keep the temperature constant within 0.3°K.

3. *N*-Lines of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$

Table I lists the relative wavenumbers² of the *N*-lines of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ compared with those of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$. Line designations are chosen according to Ref. (3) referring to normal temperature spectra, where only the strongest *N*-lines can be distinguished. Low-temperature measurements show some additional lines as well as splittings of the main *N*-lines (1, 4).

In order to decide which of the *N*-lines are pair-lines we have measured the luminescence spectra of ZnAl_2O_4 -samples containing 0–10 mole% Cr_2O_3 . While the relative intensity³ of

² The wavenumber of a line *i* relative to a line *X* is given by $\Delta\bar{\nu}^{(X)} = \bar{\nu}_X - \bar{\nu}_i$.

³ Relative intensity = intensity relative to the intensity of the *R*-line.

the N_4 -line increases with increasing chromium concentration (see Fig. 1),⁴ no such dependence was observable for the other lines in the range of $\Delta\bar{\nu}^{(R)} < 200$ cm⁻¹. Therefore only the line N_4 can be due to chromium-pairs. This is in some respects contrary to other results (2, 3), but it is very similar to the case of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ (1).

By varying the preparation conditions, sintering temperature, sintering duration, cooling rate, slight deviations from stoichiometric composition, one can produce samples with different imperfections and concentrations of imperfections. An increase in the disorder is always apparent through an increased background and a general line broadening in the luminescence spectra. Further, as Fig. 2 shows, in those cases where background and line broadening indicate increasing disorder in the lattice (Figs. 2b, c), the relative intensities of the lines N_1 and N_2 are much greater than in the "normal case" (Fig. 2a). These lines there-

⁴ Stokes and anti-Stokes lines of the phonon sideband of the *R*-line are indicated by V_i^S and V_i^A , respectively.

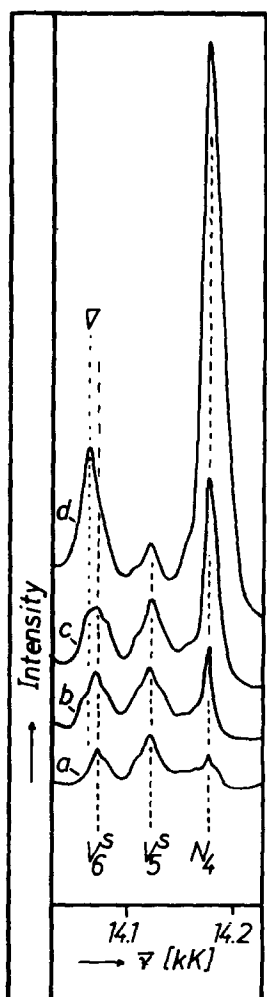


FIG. 1. Effect of chromium concentration on the relative N_4 -line intensity of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ ($\bar{\nu}_{\text{exc}} = 15454 \text{ cm}^{-1}$; $T = 77^\circ\text{K}$). a, 0.1 mole% Cr_2O_3 ; b, 0.5 mole% Cr_2O_3 ; c, 1.0 mole% Cr_2O_3 ; d, 2.0 mole% Cr_2O_3 .

fore must belong to the structure-dependent N -lines again analogous to $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ (1). However, the line V_1^S at $\Delta\bar{\nu}^{(R)} = 161 \text{ cm}^{-1}$, designated " N_3 " in Ref. (3, 4), must belong to the phonon sideband of the R -line (R -PSB), as also indicated by a corresponding anti-Stokes line V_1^a appearing at $\Delta\bar{\nu}^{(R)} = -160 \text{ cm}^{-1}$ in the normal temperature spectra.

In order to decide, whether two lines result from different luminescence centers, measure-

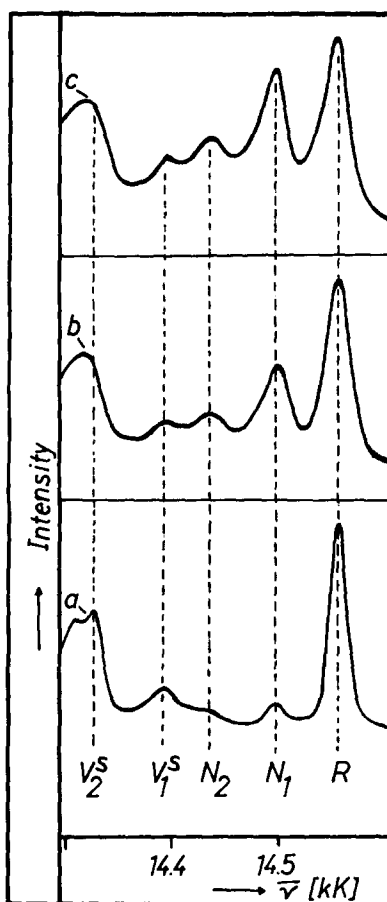


FIG. 2. N_1 -line and N_2 -line of various synthetic $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ samples ($\bar{\nu}_{\text{exc}} = 15454 \text{ cm}^{-1}$; $T = 77^\circ\text{K}$; 0.5 mole% Cr_2O_3). a, minimal disorder; b, c, increased disorder.

ments of the spectra with various excitation frequencies are often helpful. Figure 3 shows parts of the luminescence spectra from a powdered $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ sample using different laser lines for excitation. The relative vibronic intensities remained constant but the relative intensity of the N_4 -line changed. Thus, besides an increase in chromium concentration or the use of a time-resolved spectroscopy technique (5), the choice of an appropriate excitation frequency offers a possibility for increasing the relative N_4 -line intensity ("specific excitation").

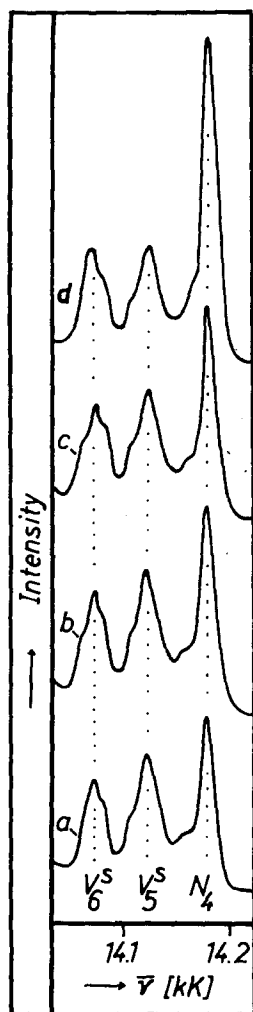


FIG. 3. Effect of excitation frequency on the relative N_4 -line intensity of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ ($T = 77^\circ\text{K}$; 1.5 mole% Cr_2O_3). a, $\bar{\nu}_{\text{exc}} = 21\,000\text{ cm}^{-1}$; b, $\bar{\nu}_{\text{exc}} = 19\,201\text{ cm}^{-1}$; c, $\bar{\nu}_{\text{exc}} = 17\,599\text{ cm}^{-1}$; d, $\bar{\nu}_{\text{exc}} = 15\,454\text{ cm}^{-1}$.

4. Phonon sidebands of the N_4 -Lines of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ and $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$

An interesting phenomenon appears in those luminescence spectra where the R -line and the N_4 -line are of comparable intensities. As Fig. 4a shows, in such a case there is a group of additional lines at $\Delta\bar{\nu}^{(R)} > 700\text{ cm}^{-1}$, which with lower N_4 -line intensity essentially disappear (Fig. 4b). The dependence of these lines on the chromium concentration and on the

excitation frequency is fully analogous to the case of the N_4 -line. Thus, these should also be attributable to chromium-pairs. The same effect can be observed in the spectra of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$.

The number of these lines as well as their frequencies relative to the N_4 -line exclude an interpretation by spin-spin coupling effects between neighboring Cr^{3+} ions. However, an obvious interpretation results if one assumes that the N_4 -lines are zero-phonon lines. The additional lines could then be considered as a phonon sideband of the N_4 -line (N_4 -PSB). This is illustrated in Fig. 4c where the R -PSB from Fig. 4b has been so transposed that the R -line frequency coincides with the N_4 -line. Thus, Fig. 4c portrays a hypothetical N_4 -PSB whose intensity and frequency distribution would correspond to that of the R -PSB. A complete equivalence of the phonon sidebands is of course not to be expected since different luminescence centers are responsible for the emission. It is clear however that spectrum 4a can easily be explained through the assumption of an N_4 -PSB, which is indicated by dotted lines in Fig. 4. From Table II, where the vibronic frequencies are listed, one can see that the same is also true for the spectra of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$.

This interpretation is supported by the presence of corresponding anti-Stokes lines of the N_4 -PSB in the normal temperature spectra (6). Also, as should be noted, such phonon sidebands can be identified for a series of other structure-dependent N -lines through the choice of a suitable excitation frequency. This will be discussed in another paper.

5. Discussion

The experimental results show, that in the luminescence spectra of the two spinels only one of the dominant N -lines, N_4 at $\Delta\bar{\nu}^{(R)} = 398\text{ cm}^{-1}$, can be due to chromium-pairs. We believe that these are ion pairs occupying first nearest neighbor ($16d$)-positions, because the mutual interaction between second nearest

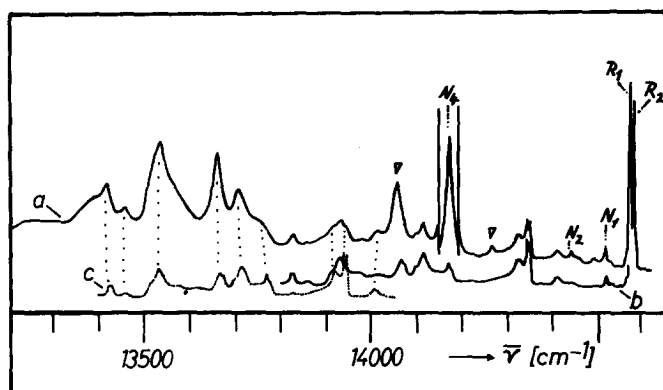


FIG. 4. Luminescence spectra of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ powders ($T = 77^\circ\text{K}$). a, 2 mole% Cr_2O_3 ; $\bar{\nu}_{\text{exc}} = 15454 \text{ cm}^{-1}$. (In the range of the N_4 -line the amplification was decreased by half.) b, 0.5 mole% Cr_2O_3 ; $\bar{\nu}_{\text{exc}} = 19201 \text{ cm}^{-1}$; c, spectrum (b) shifted by 398 cm^{-1} .

neighbor chromium ions should already be negligible. The large frequency differences between R -lines and N_4 -lines, $\Delta\bar{\nu}_{N_4}^{(R)}$ at 77°K , must be caused not only by exchange interactions, but also by distortions of the octahedral CrO_6 -complexes, which are influenced by the neighboring Cr^{3+} ions.

Splittings in the luminescence spectra due to spin-spin coupling could not be proved with absolute certainty. Besides the N_4 -lines and the N_4 -PSB in each spinel spectrum two weak lines can be seen, whose relative intensities are concentration dependent: The lines at $\Delta\bar{\nu}^{(N)} = 116 \text{ cm}^{-1}$ and -92 cm^{-1} for the ZnAl -spinel

TABLE II
VIBRONIC SIDEBAND WAVENUMBERS OF $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ AND $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ AT 77°K

$\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$				$\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$			
R-PSB ^a		N_4 -PSB ^a		R-PSB ^a		N_4 -PSB ^a	
$\Delta\bar{\nu}^{(R)}$ [cm^{-1}] ^b	Intensity ^c	$\Delta\bar{\nu}^{(N)}$ [cm^{-1}] ^b	Intensity ^c	$\Delta\bar{\nu}^{(R)}$ [cm^{-1}] ^b	Intensity ^c	$\Delta\bar{\nu}^{(N)}$ [cm^{-1}] ^b	Intensity ^c
161	m	(156)	m	218	st	(220)	m
227 ^d	st	(222)	m	256	st	(260)	w
247 ^d	st	(250)	w	302	st	(305)	w
398 ^e	m	(405)	sh	396 ^e	m	410	w
455	st	462	st	445	st	455	m
503	st	507	st	490	st	495	st
(600)	sh	(600)	sh	(620)	sh	(630)	st
635	st	634	st	650	st	655	st
710	m	712	m	(708)	w	707	m
746	st	753	st	750	st	770	st

^a For abbreviations see text.

^b Accuracy in line position at least $\pm 2 \text{ cm}^{-1}$ for sharper lines and approximately $\pm 5 \text{ cm}^{-1}$ for poorly resolved lines, which are indicated by brackets.

^c st, strong; m, medium; w, weak; sh, shoulder.

^d Doublet due to R_1 - R_2 -separation; only the wavenumber of the R_1 -vibronic line is given.

^e Vibronic line covered by N_4 -line.

(indicated by ∇ in Figs. 1 and 4a) and the equivalent lines at $\Delta\bar{\nu}^{(N_4)} = 128 \text{ cm}^{-1}$ and -105 cm^{-1} for the MgAl-spinel. Using the exchange Hamiltonian (7)

$$H_{\text{ex}} = JS_1 \cdot S_2 + j(S_1 \cdot S_2)^2 \quad (1)$$

to describe the ground-state splitting and assuming a total spin $S = 2$ for the lowest excited state of the chromium-pairs,⁵ the three lines can easily be assigned to the transitions from the quintet-excited state to the septet, quintet, and triplet ground states, respectively. The large N_4 -line intensity can then be explained by an exchange-induced dipole moment (8) which gives rise to a $\Delta S = 0$ selection rule, while the other two lines should result from $\Delta S = \pm 1$ magnetic dipole transitions. The Hamiltonian (1) is fitted by the parameters⁶

$$J = 40.9 \text{ cm}^{-1}; \quad j = 1.5 \text{ cm}^{-1} \quad \text{for} \\ \text{ZnAl}_2\text{O}_4:\text{Cr}^{3+},$$

$$J = 45.6 \text{ cm}^{-1}; \quad j = 2.0 \text{ cm}^{-1} \quad \text{for} \\ \text{MgAl}_2\text{O}_4:\text{Cr}^{3+}.$$

Though the values of the coupling constants are reasonable and the interpretation seems to be consistent, additional investigations, for instance relaxation studies or measurement of excitation spectra (see Ref. (5)), are necessary to establish, beyond doubt, a complete energy-level scheme of the chromium-pairs.

If one disregards the imperfections which are responsible for the appearance of the structure-dependent N -lines, the luminescence spectra are superimpositions of two partial spectra, each of them consisting of a zero-phonon line and its corresponding vibronic sideband: the R -line and the R -PSB, due to the Cr^{3+} single ions in ideally coordinated octahedral positions; the N_4 -line and the N_4 -PSB, due to the first nearest neighbor pair system.⁷ The differences between the spectra of low-doped and high-doped spinels are attributable

⁵ This was actually found for chromium-pairs in $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ (5).

⁶ A positive value of the constant J indicates an anti-ferromagnetic coupling.

⁷ The weak lines assigned to the $\Delta S = \pm 1$ transitions may be treated as components of the N_4 -line and therefore do not affect the interpretation.

to the different relative intensities of both partial spectra. On the other hand, overall structural changes in the lattice with increasing chromium concentration, as discussed by Lou and Ballentyne (9), can apparently be excluded since the partial spectra themselves must also be changed in this case. Figure 3 is an example of how the choice of excitation frequency can also change the relative intensities of the partial spectra and therewith, in principle, analogous changes in the total spectrum can be attained as those through the variation of the chromium concentration. These conclusions can however be applied with certainty only for spinels doped with 0–4 mole% Cr_2O_3 , since by crystals with higher dopings the evaluation of the spectra is complicated by increasing line widths and decreasing luminescence intensities.

Although this paper emphasizes the problem of chromium-pairs a few remarks on the structure-dependent N -lines are appropriate. When dealing with spinels, imperfection or disorder is often equalized with cation inversion, which in many cases is very sensitive to the preparation conditions and thermal treatment of the samples. Besides this, however, one should also consider vacancies and occupation of interstitial sites, which are found in all real crystals, and in some cases domain structures too (1). It is of major interest to know which of the possible imperfections are responsible for the appearance of the different N -lines. A complete interpretation of the origin of the N -lines can give much information about structural imperfections in the host lattice. X-ray and neutron diffraction studies, measurement of excitation spectra, and theoretical computations of appropriate models seem to be suitable to solve this problem, which will be the topic of a following paper.

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