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Luminescence of Cr^{3+} Ions in Ordered and Disordered $LiAl_5O_8$

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The phosphorescence and excitation spectra of Cr^{3+} ions in the ordered and disordered phases of $LiAl_5O_8$ have been measured and interpreted. In both phases Cr^{3+} substitutes for Al^{3+}. In the ordered phase the rhombic symmetry is responsible for a relatively large splitting of the $^2E(^2G)$, $^2T_1(^2G)$ and $^2T_2(^2G)$ levels and the occurrence of an intense zero-phonon line in the broad $^4A_2 \rightarrow {}^4T_2$ absorption band. In the disordered phase three different sites for the Cr^{3+} ions have been found. This can be explained in terms of different nearest-neighbor Li^+ and Al^{3+} ion distributions.

I. Introduction

Oxide spinels containing small concentrations of Cr^{3+} exhibit interesting luminescence phenomena (*1*). In most cases the emission is a narrow-line phosphorescence (*R* lines) with associated vibrational side bands, which is known to be from a $^2E_g \rightarrow {}^4A_{2g}$ transition of the Cr^{3+} ions in nearly octahedral point symmetry.

In normal and inverse spinels there are two types of site for the metal ions, the A site, which lies in the center of a tetrahedron of four oxygens, and the B site, which lies in the center of a trigonal distorted octahedron formed by six oxygen ions (*2*). When spinels are doped with small quantities of Cr^{3+}, the Cr^{3+} ions, having strong preference for octahedral coordination, will substitute for Al^{3+} ions in B sites. These sites have a centre of symmetry, making all zero-phonon electric dipole transitions in Cr^{3+} forbidden. Wood *et al.* (*1*a) concluded that the *R* lines in $MgAl_2O_4$ are principally magnetic dipole in character.

$LiAl_5O_8$ as a spinel is exceptional in the sense that the ionic arrangement is intermediate between normal and inverse spinel (*3*). A good description of its structure is given in a recent publication by Glynn *et al.* (*4*). $LiAl_5O_8$ has a long-range 1:3 ordering in the occupancy of the B sites by Li and Al ions. Each Li^+ ion is surrounded by six Al ions as nearest-neighbor cations, whereas each Al ion has as its nearest-neighbor cations four Al and two Li ions. Therefore, when Cr^{3+} substitutes for Al^{3+}, the site symmetry will not be trigonal, like in normal and inverse spinels, but orthorhombic belonging to the C_2 point group. The Cr^{3+} ions in Cr^{3+} doped $LiAl_5O_8$ have no center of symmetry and hence the transitions are not electric-dipole forbidden. This will increase the transition probabilities of the $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ transition, thus more efficiently populating the phosphorescing ^2E level. We therefore expect a much more intense phosphorescence in $Cr^{3+}/LiAl_5O_8$ than in other spinels such as $MgAl_2O_4$ and $ZnAl_2O_4$.

By heating $LiAl_5O_8$ above 1295°C the long-range order in the Li ions is destroyed and by rapid quenching to room temperature a disordered phase is obtained (*5, 6*).

Apart from an earlier publication on the cathodoluminescence of Cr^{3+}-doped $LiAl_5O_8$ giving no details about the emission, crystal field strength and symmetry (*7*), recently two more detailed publications on the luminescence of Cr^{3+} in the ordered phase of $LiAl_5O_8$ appeared (*8, 9*). The splitting between the *R* lines at about 14 000 cm^{-1} was found to be approximately 300 cm^{-1}, which is one order of magnitude larger than in Cr^{3+}-doped $MgAl_2O_4$ or $ZnAl_2O_4$. Glynn *et al.* (*10*) measured the Cr^{3+} emission spectrum of both Cr^{3+}-doped $LiGa_5O_8$ and $LiAl_5O_8$. The *R*-line splittings in these isomorphous compounds were found to be 278 and 262 cm^{-1}, respectively.

In other publications we have reported on the luminescence of Fe^{3+}, Mn^{2+} and Mn^{4+} in the ordered and disordered phases of $LiAl_5O_8$ (*6*, *11*). As an extension of this work we are now reporting on the luminescence of Cr^{3+} in ordered and disordered $LiAl_5O_8$. In the ordered phase we have been able to observe the forbidden $^4A_2 \rightarrow {}^2T_1(^2G)$ and $^4A_2 \rightarrow {}^2T_2(^2G)$ transitions in the excitation spectrum. Moreover, an intense zero-phonon line is observed in the $^4A_2 \rightarrow {}^4T_2(^4F)$ excitation band. In the disordered phase the R_1 line emission broadens and consists of three components with different luminescence decay times. This could be interpreted as different nearest-neighbor cation surroundings in the disordered phase.

II. Experimental Methods

Disordered and ordered samples of $LiCr_xAl_{5-x}O_8$ with $x \simeq 0.004$ were prepared from the nitrates of Al^{3+} and Cr^{3+} and Li_2CO_3 as described before (*6*). Only spectroscopically pure chemicals were used. As for Fe^{3+}-doped $LiAl_5O_8$ two types of Cr^{3+}-doped ordered samples were made, one by heating above the order–disorder transition (temp > 1295°C) followed by slow cooling to ambient in 48 hr, and the other form by heating the gel—which had been preheated to 600°C—at 1000°C for 4 hr, followed by slow cooling to room temperature.

Phosphorescence and excitation spectra were measured on a Becquerel-type phosphorescence spectrometer specially designed for powdered samples. The monochromator was a Bausch and Lomb 33-86-45 grating monochromator (dispersion 3.3 nm/mm). More details of the apparatus were given in a previous publication (*6*).

III. Results

1. Ordered Phase

The phosphorescence and excitation spectrum of a polycrystalline sample of Cr^{3+}-doped $LiAl_5O_8$ in the ordered phase measured at 77 K is shown in Fig. 1a and b. Figure 2 gives the phosphorescence spectrum measured at room temperature showing the R_2 line as well. The two R lines measured at room temperature are at 13 966 cm^{-1} (R_1) and at 14 249 cm^{-1} (R_2), the splitting between the ^2E levels thus being 283 cm^{-1}. From the excitation spectrum measured at 77 K the R_1 line is found at 13 992 cm^{-1} and the R_2 line at 14 259 cm^{-1}. The splitting of the ^2E levels at 77 K is thus 16 cm^{-1} smaller than at room temperature.

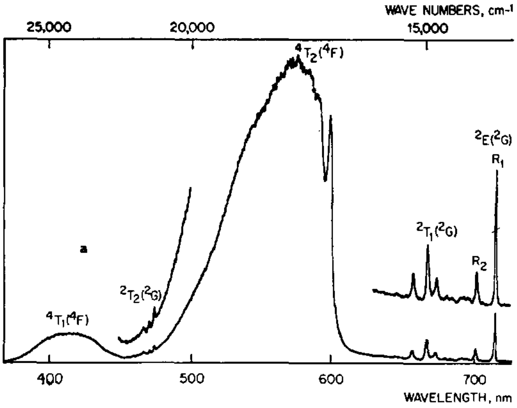

FIG. 1a. Excitation spectrum of Cr^{3+}-doped $LiAl_5O_8$ in the ordered phase, measured at 77 K.

From the excitation spectrum in Fig. 1a it is apparent that the transition probabilities of the two R lines in absorption ($^4B(^4F) \rightarrow {}^2A(^2G)$ and

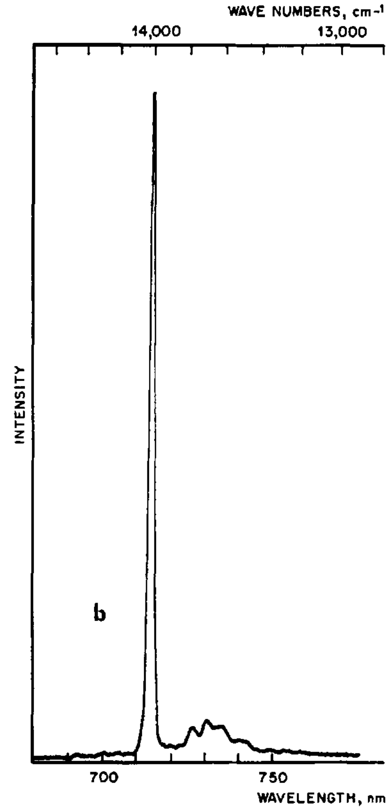

FIG. 1b. Phosphorescence spectrum of Cr^{3+}-doped $LiAl_5O_8$ in the ordered phase, measured at 77 K.

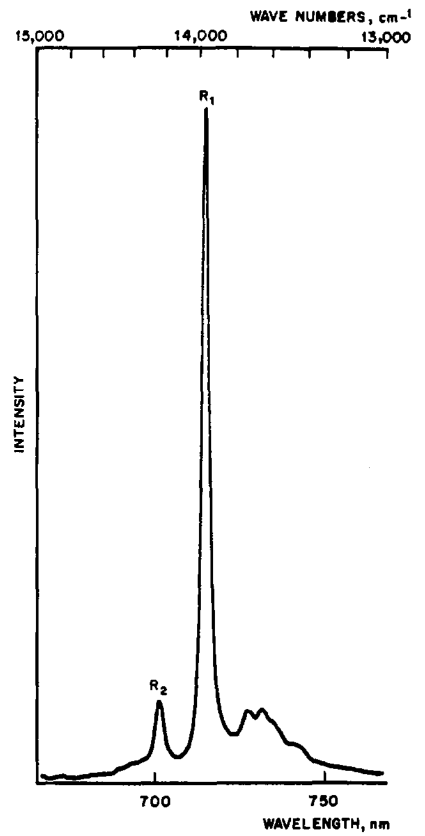

FIG. 2. Phosphorescence spectrum of Cr^{3+}-doped $LiAl_5O_8$ in the ordered phase, measured at room temperature.

${}^4B({}^4F) \rightarrow {}^2B({}^2G)$ in C_2 point symmetry) differ by a factor of almost 4. Taking this into account we calculated that the intensity ratio of the R_1 and R_2 lines measured at 77, 200, 298 and 373 K satisfy a Boltzmann distribution over the split ${}^2E$ levels.

From the Tanabe-Sugano diagram (*12*) and by analogy with Cr^{3+} in other matrices (*1*) the interpretation of all spectral bands and lines is straightforward. Although the site symmetry is rhombic (C_2), in Fig. 4a we have used the irreducible representations of the O_h group for convenience and for better comparison with spectra of Cr^{3+} in other oxide matrices. The ${}^2T_1$ and ${}^2T_2$ levels are both split in the three sublevels (${}^2A + 2\,{}^2B$ and ${}^2A + {}^2B$, respectively). On the low-energy side of the ${}^4A_2({}^4F) \rightarrow {}^4T_2({}^4F)$ absorption band a sharp zero-phonon line at 16 730 cm^{-1} is observed together with a few discrete vibronic transitions.

From the Tanabe-Sugano matrices (*13*) we calculated $B = 800$ cm^{-1}, $C = 2900$ cm^{-1} and the crystal field parameter Dq is 1750 cm^{-1}. The measured and calculated energies (cm^{-1}) are given in Table I. The value for B is higher than the value calculated for Cr^{3+} in α-Al_2O_3 ($B = 650$ cm^{-1}) (*13*) and $ZnAl_2O_4$ and $MgAl_2O_4$ ($B = 700$ cm^{-1}) (*1*a).

TABLE I

CALCULATED AND EXPERIMENTAL TRANSITION ENERGIES (cm^{-1}) OF Cr^{3+} IN THE ORDERED PHASE OF $LiAl_5O_8$[a]

	${}^2E({}^2G)$	${}^2T_1({}^2G)$	${}^4T_2({}^4F)$	${}^2T_2({}^2G)$	${}^4T_1({}^4F)$
Exptl	13 992 (R_1)	14 845		21 119	
		14 990	17 470	21 218	24 080
	14 259 (R_2)	15 220		21 487	
Calcd	14 071	15 022	17 500	20 064	25 200

[a] $Dq = 1750$ cm^{-1}; $B = 800$ cm^{-1}; $C = 2900$ cm^{-1}.

The sharpest lines in the phosphorescence and excitation spectra were obtained from the ordered sample made by heating the sample—which had been preheated to 600°C—at 1000°C

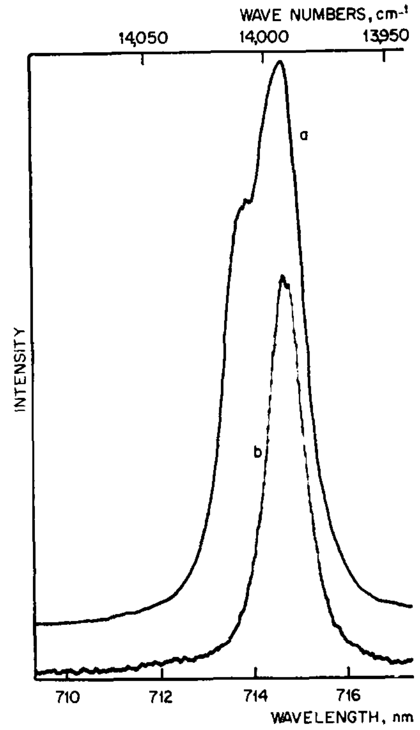

FIG. 3. The R_1 line of Cr^{3+}-doped ordered phase of $LiAl_5O_8$ measured in emission (a) and excitation (b). Spectral slit width 0.1 mm (0.3 nm).

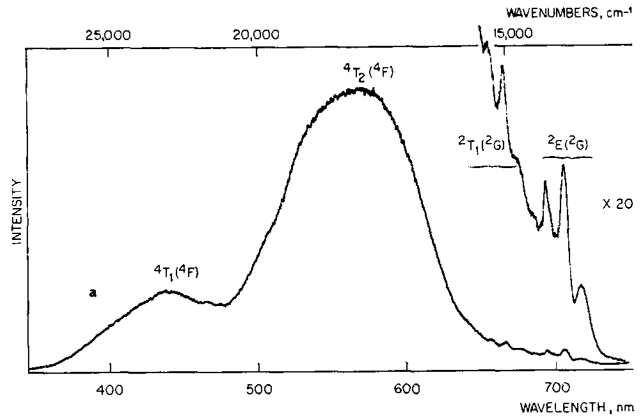

FIG. 4a. Excitation spectrum of Cr^{3+}-doped $LiAl_5O_8$ in the disordered phase, measured at 77 K.

for 12 hr. Samples first heated to 1400°C and then cooled gradually to room temperature in 48 hr had broader lines, which was especially noticeable by the intensity and width of the zero-phonon line at 16 730 cm^{-1}.

The R_1 line measured in emission at 77 K with 0.1-mm slits of the B & L monochromator shows a splitting into two components (Fig. 3, curve a). The splitting and relative intensity of the two components was about the same when measured at 200, 77 and 20 K. At room temperature the line is too broad to make the splitting observable. The R_1 line measured in absorption is a perfect symmetrical line and is not split (Fig. 3, curve b). The width at half height of the R_1 line in absorption is 14 cm^{-1}, whereas the total width at half height of the R_1 line in emission is approximately 30 cm^{-1}. The phosphorescence decay time of both components is the same (3.7 msec). The R_1 line in absorption is at the same wavelength as the strongest line (at longer wavelength) in emission.

2. *Disordered Phase*

As was found for the excitation and phosphorescence spectra of Fe^{3+} in $LiAl_5O_8$ (*6*), all spectral lines are substantially broadened. The excitation spectrum measured at 77 K is shown in Fig. 4a, the phosphorescence spectra measured at 77 K in Fig. 4b.

In the phosphorescence spectra three peaks can clearly be distinguished: at 14 390, 14 180 and 13 950 cm^{-1}. The broad band at lower energies must be a vibronic side band because this band is absent in the excitation spectrum. The phosphorescence decay times measured at the wavelengths of the three peaks were found to be:

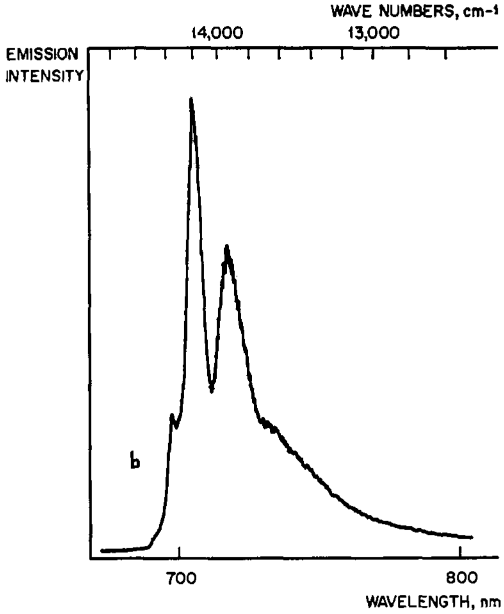

FIG. 4b. The phosphorescence spectrum of Cr^{3+}-doped $LiAl_5O_8$ in the disordered phase, measured at 77 K.

cm^{-1}	msec
$\tau(14\,390)$	3.1
$\tau(14\,180)$	3.5
$\tau(13\,950)$	4.8

With the aid of another Bausch and Lomb monochromator to select the emitting wavelengths we measured the excitation spectra at the three peaks of the phosphorescence spectrum and

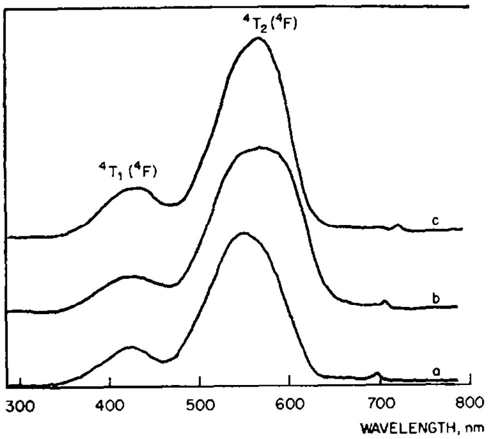

FIG. 5. The excitation spectra of the 14 390 cm^{-1} (a), 14 180 cm^{-1} (b) and 13 950 cm^{-1} (c) phosphorescence peaks of Cr^{3+} in disordered LiAl$_5$O$_8$, measured at 77 K.

found slight differences in the maxima of the excitation bands (Fig. 5a, b and c).

From the results on the decay times and the excitation spectra it is obvious that the three peaks in the phosphorescence spectrum belong to Cr^{3+} ions in different crystallographic environments.

In Table II we have given the phosphorescence peak maxima and decay times together with the 10 *Dq* values for the three different coordinated Cr^{3+} ions in the disordered phase of LiAl$_5$O$_8$. For comparison the data for the ordered phase are also given.

IV. Discussion

1. Ordered Phase

The well-resolved excitation spectrum of Cr^{3+} in the ordered phase of LiAl$_5$O$_8$ does not leave much doubt as regards interpretation. The rhombic symmetry combined with spin-orbit coupling is responsible for the relatively large splittings of the $^2E(^2G)$, $^2T_1(^2G)$ and $^2T_2(^2G)$ levels. The occurrence of a zero-phonon line at 16 730 cm^{-1} in the low-energy crystal field dependent transition is presumably due to two circumstances. First, the low symmetry of the B sites causes the electric dipole transitions to increase, making the 0–0 transition stronger as compared with the transition induced by odd parity vibrations. Secondly the lower electronegativity of Li$^+$ compared with Al^{3+} reduces the covalency of the ions in the B sites in LiAl$_5$O$_8$ with respect to normal aluminum spinels (e.g., MgAl$_2$O$_4$) and α-Al$_2$O$_3$(g). A higher ionicity gives less delocalization of the antibonding e_g electrons in particular and therefore the normal coordinates of the excited state deviate less from the ground state than they would in the case of higher covalency. This in turn results in an increased overlap between the zero-vibrational levels of ground and excited states and thus causes an increased intensity of the 0–0 transition.

TABLE II

PHOSPHORESCENCE DECAY TIMES AND CRYSTAL-FIELD PARAMETERS OF THE THREE PEAKS MEASURED IN THE DISORDERED PHASE^a

	Phosphorescence		
	Peak (cm^{-1})	Decay time (msec)	10 *Dq* (cm^{-1})
Disordered phase	13 950	4.8	17 600
	14 180	3.5	16 600
	14 390	3.1	18 200
Ordered phase	14 000	3.7	17 500

^{a} The results of the ordered phase are given for comparison.

The decreased covalency in Cr^{3+}-doped LiAl$_5$O$_8$ with respect to Cr^{3+}-doped α-Al$_2$O$_3$, ZnAl$_2$O$_4$ or MgAl$_2$O$_4$ is reflected in the increased value of the Racah parameter *B*. The increased electric-dipole transition is also shown by the fact that the ratio of the intensity of the pure electronic transition and the vibronic side band in the $^2E \rightarrow {}^4A_2$ phosphorescence in Cr^{3+}-doped LiAl$_5$O$_8$ is much larger than in other compounds. Gillen and Salomon (*9*), measuring diffuse reflectance spectra of Cr^{3+}-doped LiAl$_5$O$_8$ at 77 K, found a sharp peak at 16 800 cm^{-1}, which is very probably the same as the line that we measured in excitation at 16 730 cm^{-1}. These authors, however, interpreted this sharp line either as one of the spin-orbit split components of the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ band or as a transition in four coordinated Cr^{3+} ions. We have no explanation for the fact that the R_1 line in emission is split while the same line in absorption is single. The double R_1 line is not related to a ground-state splitting because the weaker component is at the high-energy side of the main line and, moreover, from ESR spectra a ground-state splitting of only 0.7 cm^{-1} was found (*14*), whereas the R_1 line splitting is approximately 20 cm^{-1}.

2. Disordered Phase

As is evident from the spectra and the phosphorescence decay time of Cr^{3+} in the disordered

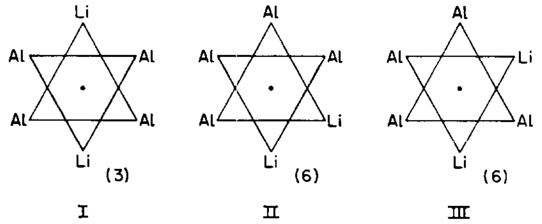

FIG. 6. Positions of nearest-neighbor cations around a Cr^{3+} ion in a projection perpendicular to the "trigonal axis."

phase of $LiAl_5O_8$ there are three different sites for the Cr^{3+} ions.

In the ordered phase every Al^{3+} ion in a B site is surrounded by six oxygen ions as nearest neighbors and four Al^{3+} and two Li^+ ions (in B sites) as next nearest neighbors. The following "shell" is formed by the cations in A sites. In going to the disordered phase it is most likely that the disordering occurs over the B sites only (*3*) in such a way that the number of Li^+ ions immediately surrounding an Al^{3+} ion in a B site is still two. On the basis of this assumption three different possible cation coordinations for the Cr^{3+} ions can be envisaged, as shown in Fig. 6. In this figure the position of the six nearest-neighbor cations (in B sites) are given in a projection perpendicular to the "trigonal axis." At the center of each octahedron a Cr^{3+} or Al^{3+} ion is located. The degrees of degeneracy of each distribution of Li^+ and Al^{3+} ions are three, six and six, respectively. Thus, when the Li^+ and Al^{3+} ions in octahedral coordination are randomly distributed over the available B sites in such a way that each Al^{3+} ion in a B site has two Li^+ and four Al^{3+} ions as nearest-neighbor cations, then there will be three different sites for the Cr^{3+} ions, their numbers being in the ratio of 1:2:2. Inspection of the phosphorescence spectrum (Fig. 4b) shows that the above gives a very likely explanation for the three phosphorescence peaks. Owing to the overlap of the three lines it is difficult to determine exactly the intensity of each line separately. Moreover, an exact 1:2:2 ratio is not to be expected in consequence of the differences in transition probabilities. Distribution II is the one occurring in the ordered phase; therefore, this distribution will give rise to the peak at 13 950 cm^{-1} (13 992 cm^{-1} in the ordered phase), whereas the peak at 14 180 cm^{-1} is correlated with distribution III and the peak at 14 390 cm^{-1} with distribution I. The 10 *Dq* values for the three different Cr^{3+} sites is also indicative of the correctness of the interpretation.

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