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Fluorescence-line-narrowing Zeeman spectroscopy of Cr^{3+} -doped silicate and Li borate glass

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Abstract. This paper discusses the inhomogeneous broadening of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission (R line) in Cr^{3+} -doped glasses. The impurity ion occupies approximately octahedral sites in silicate and borate glasses in which the R-line transition is broadened by site-to-site disorder associated with the glassy structure. The spectroscopic effects of disorder are to some extent removed by fluorescence line narrowing (FLN), which seeks to recover the homogeneous width of the R-line transitions. In the three glasses investigated, two silicate and a Li borate glass, the R-line width is $\simeq 190\text{--}200\text{ cm}^{-1}$. The width of the fluorescence-narrowed line in each case is only $\simeq 2.1\text{--}2.4\text{ cm}^{-1}$. In magnetic fields up to 3.46 T and at low temperatures ($T \simeq 2\text{ K}$) the narrowed R line splits into three components, one resonant with the excitation and two shifted to longer wavelengths. At higher temperatures these three lines are supplemented by two other blue-shifted lines, the intensities of which are strongly temperature dependent. The Zeeman splitting patterns are consistent with a g -value in the ${}^4\text{A}_2$ ground state of $\simeq 1.98$ and small differences in g -values between ground and excited states.

1. Introduction

There is much current interest in the physics of tunable solid state lasers based on the Cr^{3+} ion as a dopant in ionic crystals. Cr^{3+} -doped glasses are also of interest in this context because the emission band is much broader than in ionic crystals. The optical properties of Cr^{3+} ions are modified by the random, disordered structure of glasses, because the environment of each Cr^{3+} ion in the glass varies as a consequence of differences in bonding to nearest-neighbour ions. This results in site-to-site differences in the energy level structure, and in the radiative and non-radiative transition probabilities of the Cr^{3+} ions in glasses. Since the frequencies and radiative transition probabilities vary from site to site, the optical absorption and emission spectra as well as luminescence decay patterns are superpositions of contributions from individual crystal-field sites. In consequence, the R-line emissions are inhomogeneously broadened and the luminescence decay patterns are non-exponential [1–5].

The general spectroscopic properties of lineshape, luminescence intensity and decay time of the R lines and broad-band ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transitions of the three

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Cr³⁺-doped glasses discussed in this paper have been described in earlier papers [3, 4]. Such properties do not resolve the homogeneous widths of the transitions. At low temperature the lineshapes of Cr³⁺ ion spectra in glasses are dominated by inhomogeneous broadening processes. The greater resolution of the fluorescence-line-narrowing (FLN) technique is limited ultimately by the homogeneous broadening of the transition. In our earlier studies of these glasses, for which the compositions are given in table 1, FLN was used to measure the temperature dependence of the homogeneous width of the R line. This measurement was used to give information on the coupling of the electronic centre to two-level vibrations in these glasses [3, 4]. Subsequently the inhomogeneous broadening of the ⁴T₂ → ⁴A₂ broad-band emission was probed experimentally [6, 7]. The broad band was also shown to be inhomogeneously broadened by disorder and a theoretical model was derived in which the disorder was represented by a Gaussian distribution of crystal-field sites. Comparisons of the experimental and theoretical lineshapes were used to derive the widths γ and Γ of the disorder distribution and intrinsic lineshape functions [6, 7]. These values are collected together in table 2.

The present paper is also concerned with FLN, this time in the R line of Cr³⁺-doped silicate and borate glasses. Three glasses have been investigated: their compositions are given in table 1. FLN spectroscopy has been used at temperatures in the range 1.4–18 K and with applied magnetic fields in the range 0–3.5 T.

Table 1. Composition of Cr³⁺-doped glasses.

Glass	Sample composition (mol%)				
Silicate (G8035)	68.6SiO ₂	15.8Li ₂ O	10.7CaO	4.87Al ₂ O ₃	0.03Cr ₂ O ₃
Silicate (ED-2)	60.0SiO ₂	27.3Li ₂ O	10.0CaO	2.5Al ₂ O ₃	0.15CeO
Li borate (G8382)	54.4B ₂ O ₃	41.9Li ₂ O	3.6MgO	0.1Cr ₂ O ₃	

Table 2. The parameters of the ⁴T₂ → ⁴A₂ lineshape functions γ and Γ (unit cm⁻¹) for three glasses (after [7]).

Glass sample	Fluoride (G8197)	Silicate (G8035)	Silicate (ED-2)	Li borate (G8382)
Γ	1178	935	970	1070
γ	236	260	340	445

2. Experimental method

The compositions of the three glasses used in this study are given in table 1. A commercial silicate glass, ED-2, was provided by G F Imbusch of University College, Galway, whereas silicate glass G8035 and lithium borate glass G8382 were provided by S E Stokowski of Lawrence Livermore Laboratory. The samples were cut and polished

to dimensions of $1 \times 2 \times 5 \text{ mm}^3$. For variable-temperature measurements in the range 14–300 K the samples were contained in a cryorefrigerator, whereas for Zeeman effect studies in the temperature range 1.4–18 K the samples were contained in an Oxford Instruments variable temperature cryostat complete with superconducting solenoid which generates magnetic fields up to 3.5 T. The magnetic field homogeneity was better than $\pm 0.1 \text{ mT}$ over the field range 50 mT–3.5 T. Both systems provided optical access via four mutually perpendicular quartz windows.

Photoluminescence measurements were carried out using a Spectraphysics 2020-05 Ar^+ laser or an Ar^+ -laser-pumped Spectraphysics 380D ring dye laser. The output of the dye laser was typically 50 mW. Generally, neutral density filters were used to keep the laser power incident on the sample low so as to minimize beam-heating effects and non-linear transient bleaching effects. Light from the laser system passed through the slots on a mechanical chopper placed near an optical access to the cryorefrigerator or cryostat. The beam spot at the sample was approximately 1 mm in diameter. In conventional photoluminescence studies the emitted radiation is observed in a direction perpendicular to the excitation direction. For FLN Zeeman studies the excitation propagates along the magnetic field and the back-scattered fluorescence collected also in this direction. The experimental arrangement is shown in figure 1(a): the radiation emitted by the sample is focused onto the chopper blade and then onto the entrance slit of a 1 m grating monochromator. After passing through the monochromator the luminescence is detected at the exit slit by a Hamamatsu R666 GaAs photomultiplier tube.

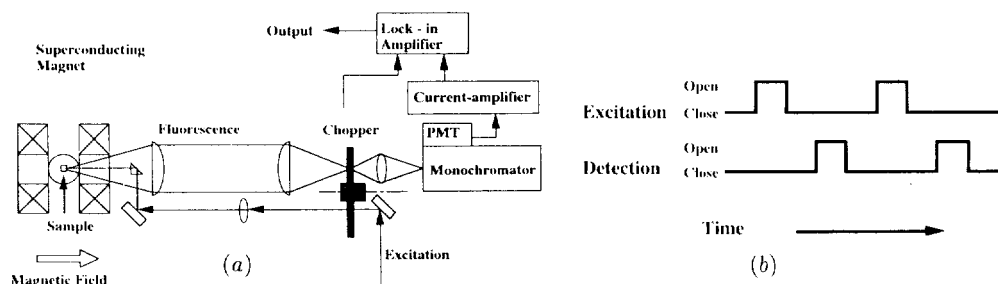


Figure 1. (a) Spectrometer systems used for FLN Zeeman measurements. (b) Chopping sequence for excitation and detection channels in FLN measurements.

The luminescence spectra of the three glasses cover wide spectral ranges from $\approx 650 \text{ nm}$ to $\approx 1000 \text{ nm}$ depending on glass composition. A GaAs photomultiplier tube (PMT) was used to detect the emission, the sensitivity of this photomultiplier tube falls to very low levels above 870 nm. For the silicate glasses ED-2 and G8035 the peak wavelength of the ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ band is below about 820 nm and the spectra detected by the photomultiplier tube reflect the real lineshape, except at wavelengths above 860 nm. However, this is not a consideration in dealing with the R-line shape which peaks near 700 nm.

After amplification the electrical signal from the phototube is processed either by a lock-in detector or a boxcar averager. Using the former system a reference signal from the mechanical chopper is compared with the magnitude and phase of the photoluminescence signal by the lock-in detector. The phase control of the reference

channel is adjusted to give maximum signal, which is displayed on a pen recorder or stored for data processing on a computer. The boxcar detector system is used for time-resolved emission spectroscopy. Essentially such spectra are recorded at various times after the excitation pulse. A time delay may be set at any desired value and periodically repeated any number of times. The emission is observed through the monochromator and the wavelength scanned as usual. The intensity-wavelength spectra are then presented as a sequence following a number of pre-set time delays.

In fluorescence line narrowing a narrow-laser line is used to pump within the inhomogeneously broadened R line. The laser interacts only with the subset of 2E levels which span the laser bandwidth. These levels only re-radiate to the 4A_2 ground state, thereby resulting in a fluorescence linewidth which approaches the homogeneous width of the transition. (Actually the FLN linewidth is equal to the sum of the laser linewidth and twice the homogeneous linewidth in resonant FLN studies.) In consequence a narrow peak of fluorescence is observed at the excitation wavelength of ≈ 690 nm, i.e. at a wavelength within the inhomogeneously broadened 2E band. The measurement of the photoluminescence signal is complicated by the more intense scattered light, and excitation and detected light are chopped alternatively as illustrated in figure 1(b), so that the detection system is closed when the excitation passes the chopper. The chopping period is about 4 ms and the fluorescence is monitored following a time delay of about 1 ms after the excitation light has been shut off. The same electronic detection/signal processing system is separated from the superconducting magnet by a distance of ≈ 1 m to avoid magnetic focusing effects on the photomultiplier tube.

3. Experimental results

The fluorescence spectra of the three glasses discussed here are quite similar, consisting of the inhomogeneously broadened R line and its side band, overlapping the short-wavelength wing of the broadband ${}^4T_2 \rightarrow {}^4A_2$ emission [3, 4]. However, there are large variations in the intensity ratio of the R line to the broadband depending on the excitation wavelength. This is a characteristic of the disordered structures in which the Cr^{3+} impurities are dissolved [4]. The timescale of the radiative decay processes for the R line and the broad-band emission are quite different so that they may be separated using time-resolved emission spectroscopy. Representative time-resolved emission spectra of lithium borate glass (G8382) measured at 16 K is shown in figure 2. The spectrum measured with zero delay time is composed of the intense R lines with their phonon-assisted side-bands and the ${}^4T_2 \rightarrow {}^4A_2$ broad band. With the increasing delay time, the intensity of the broad band decreases: when the delay time reaches 200 μs , the spectrum consists mainly of the R lines and their phonon side band, with almost no contribution from the broad band. When the delay time reaches 2 ms, the intensity of the broad band is essentially zero.

In figure 3 we show the FLN spectra of the Li borate glass excited at various wavelengths within the inhomogeneously broadened R line, and measured at $T = 10$ K. The homogeneous R-line width is less than 1 cm^{-1} after using FLN and allowing for the laser line width, providing a striking illustration of the inhomogeneous broadening associated with site-to-site disorder in these glasses. Very similar FLN spectra are observed for the ED-2 and G8035 silicate glasses [3]. There is always a resonant component accompanied by a weaker, broader component at longer

wavelengths. Essentially crystal-field distortions split the excited 2E level into $2\bar{A}$ and \bar{E} levels, (assuming trigonal distortions), which under normal circumstances give rise to the R_1 and R_2 lines, respectively. The R_1 line occurs at lower photon energies. The strong resonant line is due to direct excitation of centres, which have a lowest-lying excited state resonant with the laser. For those centres this is the R_1 line. The weaker line is the R'_1 component from centres excited directly in the R_2 line: at low temperature, rapid non-radiative decay populates the lower level, from which the emission takes place in the R_1 line of these weaker field sites. The separation of these two lines then measures the energy level splitting between the $2\bar{A}$ and \bar{E} levels. This splitting increases slightly with increasing wavelength, from 87 cm^{-1} to 105 cm^{-1} across the width of the inhomogeneously broadened line.

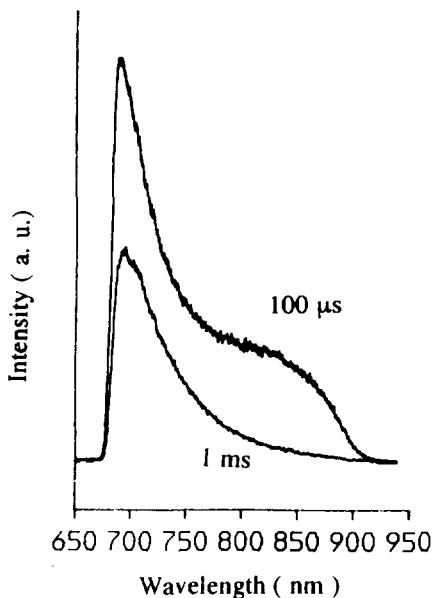


Figure 2. Time-resolved photoluminescence spectra of Cr^{3+} ions in the Li borate glass (G8382) measured at $T = 16\text{ K}$.

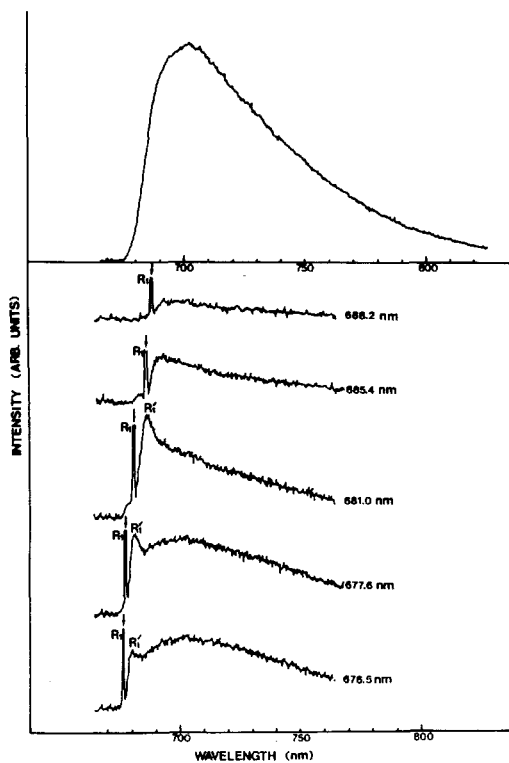


Figure 3. The FLN spectrum of Cr^{3+} ions in Li borate glass (G8382) measured at different wavelengths in the inhomogeneously broadened R line and at $T = 10\text{ K}$.

Figure 4 shows the FLN spectra of Cr^{3+} -doped silicate glasses, (a) ED-2 and (b) G8035, excited at 683.3 nm and measured at $T \sim 2\text{ K}$ in various magnetic fields from 0 T to 3.46 T . Related data are shown in figure 5 for the Li borate (G8382) glass. These FLN spectra were also excited at 683.3 nm and measured at fixed field ($B = 3.46\text{ T}$) as a function of temperature in the range $2.1\text{--}15\text{ K}$. The trends in the FLN spectra of all three glasses as a function of magnetic field at low temperature,

and fixed field at various temperatures, are very similar. In a magnetic field, the line splits into several Zeeman components, the number of components depending on the magnetic field strength and temperature. Initially with increasing magnetic field, the FLN lines broaden. However, above ≈ 2 T, clear splittings occur. At lower temperatures, $T < 2$ K, there are only three components (figures 4 and 5). The strongest peaks are resonant with the excitation. At $T > 4$ K, the line has split into five Zeeman components. This is illustrated by the results for the G8382 glass in figure 5, this temperature-dependent behaviour being typical of each of the glasses. Two peaks are red-shifted and the other two are blue-shifted relative to the resonant one. The intensities of the blue-shifted peaks increase with increasing temperature, figure 5; they are almost undetectable when the temperature is below 2.0 K. The lines have almost equal energy separations of $\Delta E = 3.2\text{--}3.4$ cm^{-1} in a magnetic field of 3.46 T.

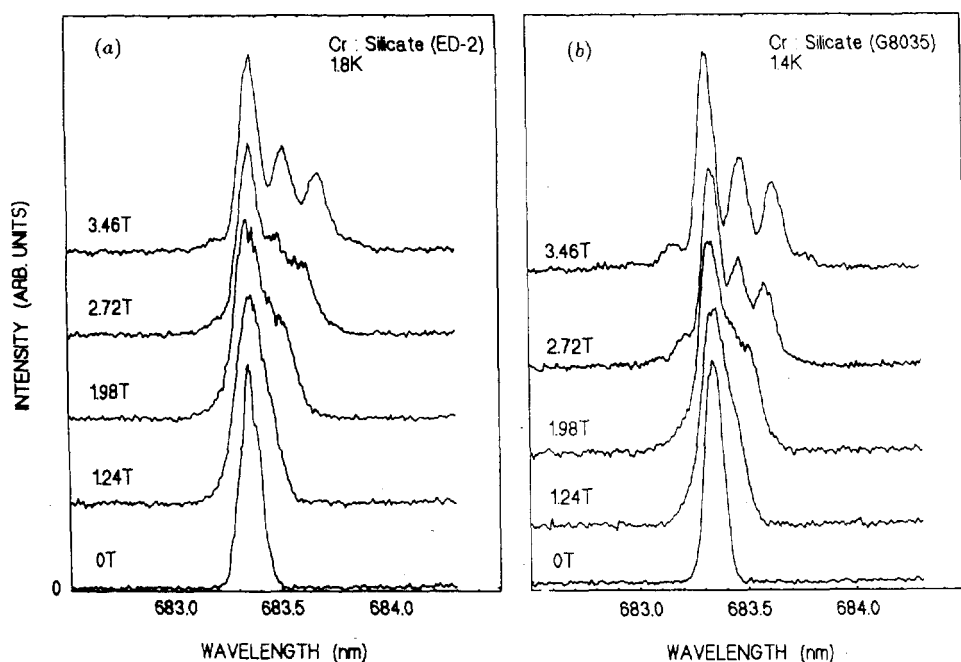


Figure 4. The magnetic field dependence of the Zeeman splitting of the FLN line of Cr³⁺ ions in the silicate glasses (a) ED-2 and (b) G8035. The spectra were excited at $\lambda = 683.3$ nm.

4. Discussion

The photoluminescence spectra of Cr³⁺-doped silicate and Li borate glasses are dominated by overlapping spectral features associated with ${}^2E \rightarrow {}^2A_2$ (R lines) and ${}^4T_2 \rightarrow {}^4A_2$ (the vibronic broad band). Both are strongly broadened by the site-to-site disorder characteristic of the glassy matrix in which the Cr³⁺ ions are embedded. This crystal-field disorder results in sites with a distribution of octahedral field splittings,

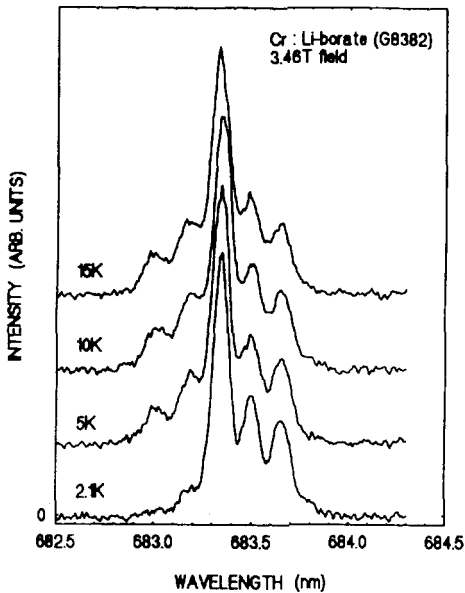


Figure 5. The FLN spectrum of Cr^{3+} ions in the Li borate glass G8382, excited at $\lambda = 683.3$ nm. The Zeeman splitting pattern is shown at fixed field $B = 3.46$ T and at different temperatures in the range 1.6–18 K.

$10Dq$, of the Cr^{3+} ion states spanning some 1000 cm^{-1} [6, 7]. The net result for the three glasses discussed here, table 1, is that the excited energy level splittings $E(^4T_2) - E(^2E)$ may be negative, zero or positive and the 2E level may be higher in energy than 4T_2 , degenerate with 4T_2 or below this state, and all in the same sample. In consequence, excitation in the vibronically broadened $^4A_2 \rightarrow ^4T_2, ^4T_1$ transitions leads to simultaneous occupation of the 2E and 4T_2 relaxed excited states and a photoluminescence spectrum that is a mélange of $^2E \rightarrow ^4A_2$ (R line) and $^4T_2 \rightarrow ^4A_2$ broadened emission processes. This is shown in figure 2, the photoluminescence spectrum of the Li borate glass. Very similar spectra have been reported for both ED-2 and G8035 silicate glasses [3, 4]. Since the $^2E \rightarrow ^4A_2$ transition is both spin and parity forbidden, whereas $^4T_2 \rightarrow ^4A_2$ is only parity forbidden, the two transitions decay with different timescales. Indeed the radiative lifetimes of $^2E \rightarrow ^4A_2$ transitions range from 10–100 ms whereas those of the $^4T_2 \rightarrow ^4A_2$ are 100–1000 μs . These differences in decay times permit the use of time-resolved emission spectroscopy to separate the R line and the $^4T_2 \rightarrow ^4A_2$ broad band as shown in figure 2.

The widths of both sharp line and broad band spectra are much greater than in single crystals. This is obvious for the R line in figure 2 since in systems such as $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ and $\text{Cr}^{3+}:\text{MgO}$ the R line width is only $\approx 0.1\text{ cm}^{-1}$ whereas in these glasses (e.g. figure 2) the half-width is some 200 cm^{-1} or so. The inhomogeneous broadening of the R line in glasses is dramatically illustrated in figure 3, the FLN spectrum of the Cr^{3+} -doped Li borate glass. The line labelled R_1 is due to emission from Cr^{3+} ions which have $^2E(\tilde{E}) \rightarrow ^4A_2$ transitions resonant with the laser excitation. In the case of R'_1 , the laser excites some Cr^{3+} ions directly in the 2E (\tilde{A}) level: non-radiative decay on these ions results in population of the lower-lying

2E (\bar{E}) level of these ions. The R'_1 line is due to emission from the 2E (\bar{E}) level of this subset of levels. This splitting therefore does measure the R_1 – R_2 line separation, associated with the removal of the 2E degeneracy by the distortions of the octahedral of nearby ligand ions. The symmetry of these distortions is not revealed in optical spectroscopic studies: they may be revealed in electron spin resonance (ESR) studies. For the glasses currently under discussion, ground-state ESR measurements reveal only a broad (10–50 mT) ESR line at a magnetic field near $g = 1.98$ [3, 4]. Nor is it possible to determine in these distorted sites the ordering of the two levels of the 2E state. In excited-state ESR experiments on ruby Geschwind *et al* [10] showed that the \bar{E} level is lower than $2\bar{A}$ as a consequence of the octahedron of O^{2-} ions around the Cr^{3+} ion being compressed along the trigonal axis. The determination of the excited state g -value, using Zeeman spectroscopy, helps to resolve this issue.

The ${}^2E \rightarrow {}^4A_2$ transitions are both parity and spin forbidden. In Cr^{3+} -doped glasses there are always some low-symmetry distortions at Cr^{3+} sites, which relax the parity selection rule, and spin–orbit coupling relaxes the selection rule on spin of the transition. The matrix element for such weakly allowed electric dipole transitions between $|{}^2E\phi' M_{S'}\rangle$ and $|{}^4A_2 M_S\rangle$ is given by [8, 9]

$$P_{M_S - M_{S'}} \propto \sum_{\phi'' M_{S''}} \frac{\langle {}^2E\phi' M_{S'} | H_{SO} | {}^4T_2\phi'' M_{S''} \rangle \langle {}^4T_2\phi'' M_{S''} | \mu_e E | {}^4A_2 M_S \rangle}{E({}^2E) - E({}^4T_2)}. \quad (1)$$

Since the denominators in (1) are small for terms involving 4T_2 states close in energy to the 2E states we can neglect all other terms. The total spin of the 4A_2 ground state is $S = \frac{3}{2}$, while that of the 2E excited state is $S' = \frac{1}{2}$. The projection quantum number M_S takes the value $+S, S-1, \dots, -S$, for $S' = \frac{1}{2}$ in the 2E state and $S = \frac{3}{2}$ in the ground state, 4A_2 . The spin–orbit matrix elements are tabulated in [8]. The matrix elements in (1) are non-zero if

$$\Delta M_S = M_{S'} - M_S = 0, \pm 1. \quad (2)$$

This relation gives the selection rule for the weakly allowed ${}^2E \rightarrow {}^4A_2$ transitions. The excited 2E state splittings, measured from the R_1 – R_2 separation in FLN, are 87–105 cm^{-1} for lithium borate glass G8382, $\simeq 50$ –53 cm^{-1} for silicate glass ED-2 and $\simeq 49$ –57 cm^{-1} for silicate glass G8035 [2, 3]. Assuming that the average g -value for the excited state of Cr^{3+} doped glasses is around 2, for magnetic fields from 0–3.5 T and at low temperature, only the lower component of the 2E state will participate in the radiative transitions to the ground state. The lower 2E excited state is a spin doublet (i.e. $S = \frac{1}{2}$) which in a magnetic field splits into two levels $M_{S'} = \frac{1}{2}$ and $M_{S'} = -\frac{1}{2}$: the ground state 4A_2 splits into four levels, $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. As figure 6(a) shows, there are then six radiative transitions between these split levels.

Assuming that the zero-field splitting is negligible, the g -values of the ground state 4A_2 and excited state 2E are close to 2 as illustrated in figure 6(a) and at low enough temperature ($T \simeq 1.4$ K), only the lowest Zeeman level $|{}^4A_2, -\frac{3}{2}\rangle$ of the ground state is populated. In consequence, the $|{}^4A_2, -\frac{3}{2}\rangle$ to $|{}^2E, -\frac{1}{2}\rangle$ transition is the only excitation transition. Moreover, since phonons are not available to transfer population from $|{}^2E, -\frac{1}{2}\rangle$ to the $|{}^2E, +\frac{1}{2}\rangle$ level, there are just three radiative emission transitions from the $|{}^2E, -\frac{1}{2}\rangle$ level to $|{}^4A_2, \frac{1}{2}\rangle$, $|{}^4A_2, -\frac{1}{2}\rangle$ and $|{}^4A_2, -\frac{3}{2}\rangle$ levels. The splitting between the components is the Zeeman splitting of the 4A_2

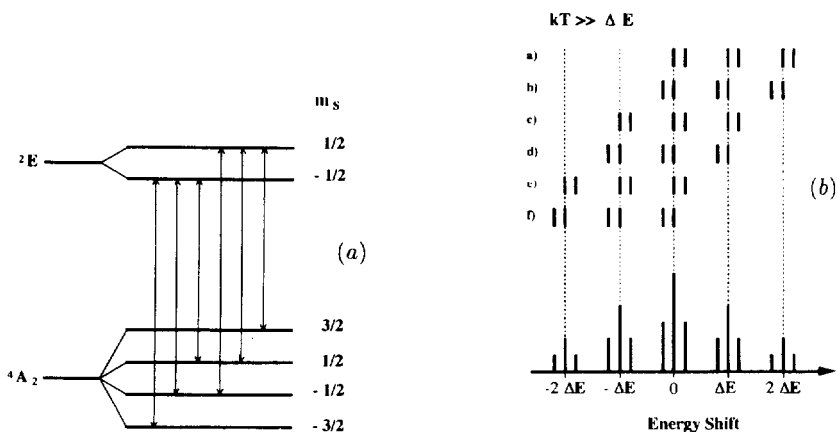


Figure 6. (a) The Zeeman splitting of the 2E and 4A_2 states of Cr^{3+} and the allowed $\Delta m_s = 0, \pm 1$ transitions. (b) The FLN spectrum of Cr^{3+} ions in glasses measured at high field and high temperature expected on the basis of the ${}^2E \rightarrow {}^4A_2$ selection rules.

ground state. In terms of this splitting, ΔE , the g -value of the ground state 4A_2 is given by

$$g_g = \Delta E / \mu_B B. \tag{3}$$

For the three glasses, the measured energy separations vary from 3.2 cm^{-1} to 3.4 cm^{-1} , and the corresponding ground-state g -values are between 1.99 and 2.11, close to $g = 1.98$ measured in ESR experiments (3) and (4), and within the experimental error of $\approx 10\%$.

The intensity of the resonant FLN line observed at 1.8 K and $B = 3.46 \text{ T}$, figures 4(a) and 5, is 1.5–2.0 times larger than those of the other Zeeman components. The three lines should have the same intensities if the transition probabilities are independent of angle and equal. In order to explain the discrepancy, we take account of the angular dependence of transition probability. Since the excitation and emission occur at the same site, the probability of this cycle is given by

$$P_{n,n'} = \int P_n(\theta, \phi) P_{n'}(\theta, \phi) \sin \theta \, d\theta \, d\phi \tag{4}$$

where $P_n(\theta, \phi)$ are the electric dipole transition probabilities which are proportional to the matrix elements given by (1) as functions of angles between the symmetry axis of the Cr^{3+} site and the direction of a magnetic field. The subscripts n and n' label the six transitions for the excitation and luminescence transitions, respectively. This integration satisfies the Schwarz inequality:

$$P_{n,n'}^2 \leq P_{n,n} P_{n',n'} \tag{5}$$

If $P_{n,n}$ is independent of n , then

$$P_{n,n'} \leq P_{n,n} \tag{6}$$

for any n and n' , showing that the transition probability is higher when excitation and fluorescence occur between the same pair of Zeeman levels (i.e. $n = n'$) than for other processes ($n \neq n'$). In consequence the resonant FLN peak is stronger than the other peaks and at any temperature.

That above 8 K the spectrum consists of five lines shows that the observed spectrum reflects the temperature-dependent populations of the Zeeman levels of the 4A_2 ground states and 2E excited states. The detailed distribution of intensities in the FLN spectrum follows from the disorder distribution. In these Cr^{3+} -doped glasses the energy of the 2E state is continuously distributed within the 2E sub-band. At high temperature, where all magnetic sub-levels of the 4A_2 ground state are occupied, any one of the six possible Zeeman transitions may selectively excite a different subset of Cr^{3+} ions (i.e. one of sites a, b, ..., f in figure 6(b)) provided that they fall within $\pm \Delta E$ of the resonant transitions, ΔE being the Zeeman splitting energy of the 4A_2 ground state. The observed FLN spectrum of Cr^{3+} -doped glass in a magnetic field is a superposition of the emissions from different Cr^{3+} sites, each having different 2E energies. For a particular site, when the laser frequency is close to the energy of any one of the six transitions, luminescence will occur. The spectrum is composed of 15 lines, as shown in figure 6(b), which reduces to five lines when the ground- and excited-state g -values are the same. When the g -values of the 2E states are distributed around that of the 4A_2 level the five lines are broadened to an extent determined by the distribution. With increasing temperature, more ions at higher levels of the ground state are populated at the expense of the population of the lower levels, so the proportion of emission with higher energy is enhanced and that with lower energy reduced. Consequently, the intensities of the two blue-shifted peaks increase and that of the two red-shifted peaks decrease with increasing temperature.

Next we discuss the linewidth of the FLN spectrum and estimation of excited-state g -value. In principle the linewidth of FLN is the sum of the laser linewidth and homogeneous linewidth as noted earlier. The distribution of the zero-field splitting of the 4A_2 ground state broadens the resonant FLN line at zero field. However, the broadening is removed completely from resonant peak by applying a magnetic field so that the spectrum splits into Zeeman components. We can estimate the distribution of zero-field splitting from the difference in the linewidths of the resonant FLN lines in the absence and presence of a magnetic field at low temperature. The spectra in figures 4(a) and (b) show no difference of the linewidths and suggests that the distribution of zero-field splitting is less than 0.1 cm^{-1} as is expected from ground-state ESR measurement.

The g -value of the 2E excited state, g_e , also affects the Zeeman pattern and the linewidth of each Zeeman component. Assuming that the difference in the Zeeman splitting of the ground and excited states is $\Delta E' = |g_e \mu_B B - g_g \mu_B B| = \Delta g \mu_B B$ and $kT \gg \Delta E$, the Zeeman pattern is expected to be that illustrated in figure 6(b). This pattern indicates that the linewidth of each Zeeman component is approximately twice $\Delta E'$. In calculating the Zeeman pattern, the g -value of both ground and excited states must be taken into account, the g -value of the excited state being somewhat anisotropic [10–13]. This anisotropy is determined by whether the distortion is of trigonal, tetragonal or lower symmetry. Optically detected magnetic resonance (ODMR) studies have been used in the cases of $3d^3$ ions in Al_2O_3 [10, 11] and MgO [12, 13] to measure the 2E -state g -values. In ODMR experiments on $Cr^{3+}:Al_2O_3$ Imbusch *et al* [11] showed that for the \bar{E} (2E) state in C_{3v} symmetry the g -value was highly anisotropic with $g_{\parallel} = 2.446$ and $g_{\perp} = 0.06$. The g -values for the $2\bar{A}$

(²E) state obtained from Zeeman studies on the optical absorption spectrum were $g_{\parallel} = 1.48$ and $g_{\perp} \simeq 0.06$ [14, 15]. In tetragonal symmetry sites the limiting values of the g -tensor are $g_{\parallel} = 1.980$ and $g_{\perp} = 1.724$ for the lowest-lying component of ²E which transforms as the irreducible representation of ²E_v in tetragonal symmetry [12, 13]. The corresponding g -values of the higher-lying ²E_u state are only slightly higher.

As the zero-field splitting of ⁴A₂ is negligible within the experimental precision, the linewidths of non-resonant FLN lines at low temperature ($T \leq 1.8$ K) reflect the distribution of the g -values in the excited state. As the value of g_{\perp} for a trigonally distorted Cr³⁺ site is close to zero, the $|+\frac{1}{2}\rangle$ spin state of the excited state is populated even at low temperature. The transition of the $|+\frac{1}{2}\rangle$ excited state to the $|+\frac{3}{2}\rangle$ ground state is allowed, so the four Zeeman components are expected. However, the Zeeman pattern observed at low temperature ($T \leq 1.8$ K) is composed of three lines. This suggests either that the transition probability is fairly weak for those Cr³⁺ sites with the trigonal distortion axis perpendicular to the magnetic field or that the Cr³⁺ sites in glasses undergo tetragonal or orthorhombic distortions rather than trigonal distortions.

As the temperature increases, the linewidths of the Zeeman components slightly increase as shown in figure 5. The difference between the linewidth of the resonant FLN line at 2.1 K and those of the five Zeeman components at higher temperature is associated with $\Delta E'$. The estimated value is $\Delta E' = 0.3 \text{ cm}^{-1}$. This limits the average difference in g -values between the ground and excited states to be $\Delta g = 0.18$. In consequence, the g -value of the excited state is determined to be in the range $g_g - 0.18$ to $g_g + 0.18$.

5. Conclusions

The g -value of the Cr³⁺ ground state in three glasses measured in EPR experiments on the ground state is in agreement with that measured using the Zeeman splitting of FLN lines by a magnetic field. The splitting of FLN lines is due to the Zeeman effect in the ⁴A₂ ground state. Comparison of the linewidths of resonant FLN lines in the absence and in the presence of a magnetic field indicates that no apparent zero-field splitting due to low-symmetry distortion was detectable within the experimental precision of $\lesssim 1 \text{ cm}^{-1}$. The Zeeman splitting patterns of the FLN spectra, which for three glasses are quite similar, also indicate the Cr³⁺ ions occupy approximately octahedral sites, the random distortion being quite similar in each case. The distribution of the g -value for the excited state is small. The fact that the splitting of the FLN lines, and the number and intensity of the peaks depend on the strength of the magnetic field and the temperature is in agreement with this conclusion. The observed g -value of the ground state, g_g , around 1.98 to 2.11, agrees fairly well with the expected value. The excited-state g -value is estimated from the linewidths of the Zeeman components of the FLN line to be $g_e = g_g \pm 0.18$. This result suggests that the environment of the Cr³⁺ is tetragonal or orthorhombic in symmetry.

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