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Substitutional disorder and the ground state spectroscopy of gallogermanate crystals

Mitsuo Yamaga†, Peter I Macfarlane‡, Brian Henderson‡, Keith Holliday‡, Hideo Takeuchi§, Taturu Yosida‖ and Minoru Fukui‖

† Department of Physics, Faculty of General Education, Gifu University, Gifu 501-11, Japan
‡ Department of Physics and Applied Physics, University of Strathclyde, Glasgow G1 1XN, UK
§ Department of Electronics and Information, Faculty of Engineering, Nagoya University, Nagoya 464-01, Japan
‖ Nakanihon Automotive College, Sakahogi Kamo 504, Japan

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Abstract. Electron spin resonance (ESR) spectra at X-band microwave frequencies are reported for Cr^{3+} dopant ions in $Ca_3Ga_2Ge_4O_{14}$ (CGGO), $Sr_3Ga_2Ge_4O_{14}$ (SGGO), $La_3Ga_5GeO_{14}$ (LGGO) and $La_3Ga_5SiO_{14}$ (LGS). The ESR measurements identify two distinct sites for Cr^{3+} in CGGO and SGGO and a single site in LGGO and LGS characterized by spin $S = 3/2$ for Cr^{3+} ions in the ground state. In CGGO a sharp line ESR spectrum, fitted to an axially symmetric spin Hamiltonian with $g_\parallel = 1.980 \pm 0.005$, $g_\perp = 1.98 \pm 0.01$ and $2D = 1.6 \pm 0.4$ cm^{-1}, is assigned to Cr^{3+} substituents at trigonally distorted octahedral sites with a regular array of Ga^{3+} and Ge^{4+} ions in second-nearest-neighbour sites. A second spectrum of broader lines, due to Cr^{3+} ions in orthorhombically distorted sites associated with random occupation of the second-nearest-neighbour sites by Ga^{3+} and Ge^{4+} ions, has slightly different spin Hamiltonian parameters; $g_x \simeq g_y \simeq g_z = 1.97 \pm 0.01$, $2D = 1.6 \pm 0.4$ cm^{-1} and $3E = 0.23 \pm 0.05$ cm^{-1}. In this spectrum the principal axis is rotated by about 5° from the c-axis towards the a-axis. In SGGO there are also ESR spectra from Cr^{3+} ions in trigonal and orthorhombic symmetry sites with almost identical spin Hamiltonian parameters. The ground state splittings of the trigonal centres measured optically by fluorescence line narrowing gives $|2D| = 1.6 \pm 0.1$ cm^{-1} for both crystals. In contrast, only the trigonal centres are identified in LGGO and LGS, their ESR spectra being very similar to those of the trigonal Cr^{3+} centres in CGGO and SGGO. These results are discussed in terms of the substitutional disorder in these crystals and the nature of the site environment of Cr^{3+} substituents. The spectra correspond to Cr^{3+} ions in strong and weak crystal field sites, respectively, in agreement with earlier optical studies.

1. Introduction

The disorder in gallogermanate crystals arises from statistical occupation of various sites by Ga^{3+} and Ge^{4+} ions such that the perfect crystal composition is maintained [1–4]. The sites that are occupied in this way vary between different members of the gallogermanate family and a summary for the four crystals studied here, $Ca_3Ga_2Ge_4O_{14}$ (CGGO), $Sr_3Ga_2Ge_4O_{14}$ (SGGO), $La_3Ga_5GeO_{14}$ (LGGO) and $La_3Ga_5SiO_{14}$ (LGS), is given in table 1. In all crystals the Cr^{3+} ion substitutes in the 1a site where its nearest neighbours are a distorted octahedron of O^{2-} ions.

Recent optical studies of Cr^{3+}-doped CGGO, SGGO, LGGO and LGS showed that Cr^{3+} ions experience different, disorder-induced distributions of strong and weak crystal field strengths depending on the host crystal [3, 4]. A model of the inhomogeneous broadening

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Table 1. The site occupation of the gallogermanates.

Crystal	3e sites (cube)	1a site (octahedral)	2d sites (tetrahedral)	3f sites (tetrahedral)	2d sites	6_{g1} sites	6_{g2} sites
CGGO	Ca^{2+}	$0.5Ga^{3+} + 0.5Ge^{4+}$	Ge^{4+}	$1.5Ga^{3+} + 1.5Ge^{4+}$	O^{2-}	O^{2-}	O^{2-}
SGGO	Sr^{2+}	$0.4Ga^{3+} + 0.6Ge^{4+}$	Ge^{4+}	$1.6Ga^{3+} + 1.4Ge^{4+}$	O^{2-}	O^{2-}	O^{2-}
LGGO	La^{3+}	Ga^{3+}	$Ga^{3+} + Ge^{4+}$	Ga^{3+}	O^{2-}	O^{2-}	O^{2-}
LGS	La^{3+}	Ga^{3+}	$Ga^{3+} + Si^{4+}$	Ga^{3+}	O^{2-}	O^{2-}	O^{2-}

of the optical spectra of Cr^{3+} in CGGO and SGGO has been developed on the basis of fluorescence line narrowing (FLN), selective excitation and site selective fluorescence lifetime measurements [3]. It was shown that the Cr^{3+} ions occupy a distribution of both strong field sites, in which fluorescence is via the ^2E state in the form of R-lines, and weak field sites, characterized by broadband fluorescence from the $^4T_2$ state. In both cases the broadening was shown to be dominated by the distribution in the non-octahedral component of the crystal field rather than by changes in the magnitude of the octahedral crystal field. This model has been extended to the cases of LGGO and LGS [4] in which only a single distribution of sites was required to account for the optical behaviour; in the former case these were weak field sites and in the latter the crystal field strength distribution spanned the region in which the ^2E and $^4T_2$ states cross over. Again, despite the larger separation between the disordered site and the optically active ion, the broadening was shown to be dominated by variation in the distortions to rather than the strength of the octahedral field. Optical measurements, however, cannot differentiate between the structures of the strong field and weak field sites.

The present paper continues the discussion of substitutional disorder in the gallogermanates through its influence on the spectroscopy of Cr^{3+} dopants. Earlier investigations focused on optical spectroscopy. Here we report studies of the $^4A_2$ ground state using high-resolution FLN and ESR measurements and interpret these in terms of models of the disorder in the immediate lattice environment of the Cr^{3+} dopants.

2. Experimental details

The experimental samples of Cr^{3+}:CGGO, SGGO, LGGO and LGS were purchased from the Crystal Laser Physics Laboratory in Moscow: they were grown by the Czochralski technique to contain ~ 0.5 at.% Cr^{3+} [1]. The samples were cut and polished to dimensions of $5 \times 2 \times 2$ mm^3, the long dimension being parallel to the c-axis of the crystal. The ESR experiments were performed at X-band microwave frequencies ($\nu \sim 9.275$ GHz) at room temperature, with magnetic field modulation at 100 kHz. In this mode the spectrometer records the first derivative of the absorption line. The microwave absorption spectrum as a function of magnetic field can be obtained by integrating the digitalized ESR signals using a computer.

FLN spectra were excited by a single-mode Ti–sapphire laser tuned to resonance with the R-lines of the Cr^{3+}:SGGO or Cr^{3+}:CGGO samples. The resonant fluorescence was analysed using a Fabry–Pérot étalon set with its plates 0.5 mm apart to give a free spectral range of 5 cm^{-1} and an effective resolution of 0.2 cm^{-1}. The fluorescence was measured using single-photon counting during the off period of the chopped excitation.

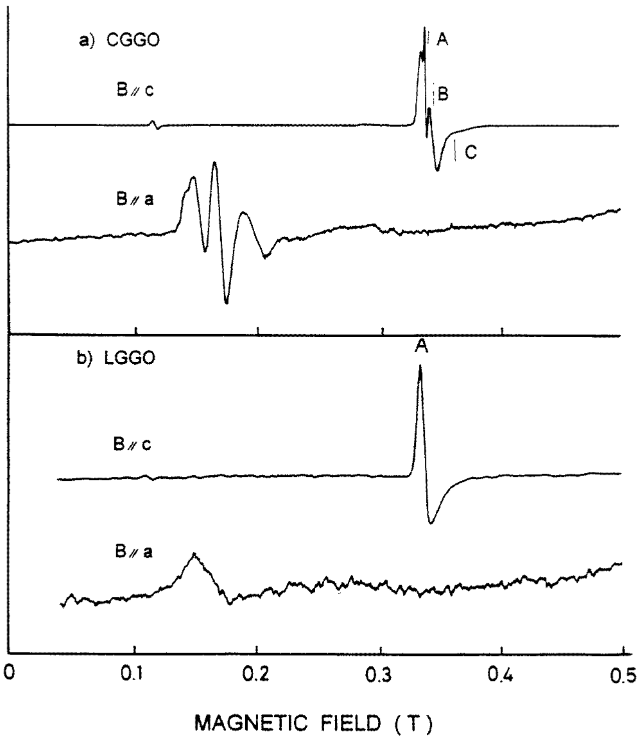


Figure 1. The ESR spectra of Cr^{3+} ions in (a) CGGO and (b) LGGO, measured at X-band microwave frequencies ($\nu \simeq 9.275$ GHz) and room temperature. The static magnetic field, B, was set parallel to the crystallographic c- and a-axes.

3. Experimental results

Figure 1 shows ESR spectra of Cr^{3+}-doped CGGO and LGGO measured with the static magnetic field, B, parallel to the crystallographic c- and a-axes. For Cr^{3+}:CGGO, the spectrum with $B \parallel c$ in figure 1(a) consists of three lines around $B = 0.33$ T. The sharp line A at 0.3347 T corresponds to $g_{\parallel} = 1.980 \pm 0.005$ and the broader line B at a slightly higher field to $g = 1.97 \pm 0.01$. The much weaker, broader line C overlaps the high-field wing of line B. The weak line at 0.117 T is due to the forbidden $\Delta M_S = 3$ transition. The spectrum with $B \parallel a$ consists of three lines. The central line is associated with the A-line, while the other two lines are due to the splitting of the B-line. The ESR spectra of Cr^{3+}:SGGO reveals A-, B- and C-lines as in CGGO. The comparable spectra for Cr^{3+}-doped LGGO and LGS differ in the sense that only line A and its associated $\Delta M_S = 3$ transition is observed (figure 1(b)). In both cases, line A is broader than in CGGO and SGGO and is particularly broad in Cr^{3+}:LGS.

The local structure of Cr^{3+} in the gallogermanates is trigonal, so the plane perpendicular to the c-axis contains three identical a-axes, at an angle of 120° to each other. The Cr^{3+} ESR lines are anisotropic against rotations of the magnetic field away from the c-axis. In figure 2 the orientation dependences of the A- and B-lines in CGGO are shown as a function of angular rotation in the ca- and aa-planes. The resonant fields of lines A and B are denoted by solid and open circles, respectively, in figure 2. The extreme resonance fields of line A in the ca-plane are $g(B \parallel c) = 1.98$ and $g(B \perp c) = 3.96$. There are no splittings of this line with orientation and it is invariant against rotations in the aa-plane. This shows that the A-line is axially symmetric about the crystal c-axis. The resonance fields of the forbidden $\Delta M_S = 3$ lines increase dramatically when the magnetic field is applied perpendicular to the c-axis. Similar orientation dependences are observed for line A in each of the other crystals SGGO, LGGO and LGS. The orientation dependence of line B in Cr^{3+}:CGGO is also shown in figure 2. For rotation in the ca-plane line B splits into two lines which flank the A-line. The turning points for the two line B field dependences are at 5° from the c-axis. In the aa-plane line B splits into three orientationally sensitive lines having a 60° repetition cycle. This coupled with the fact that the orientation dependence is asymmetric around the c-axis shows that Cr^{3+} centres appear with 120° repetitions. Although the rather weak C-line is not shown in figure 2, it is notable that the g-shift is larger than those of the A- and B-lines and that the principal axis is rotated more than that of the B-line.

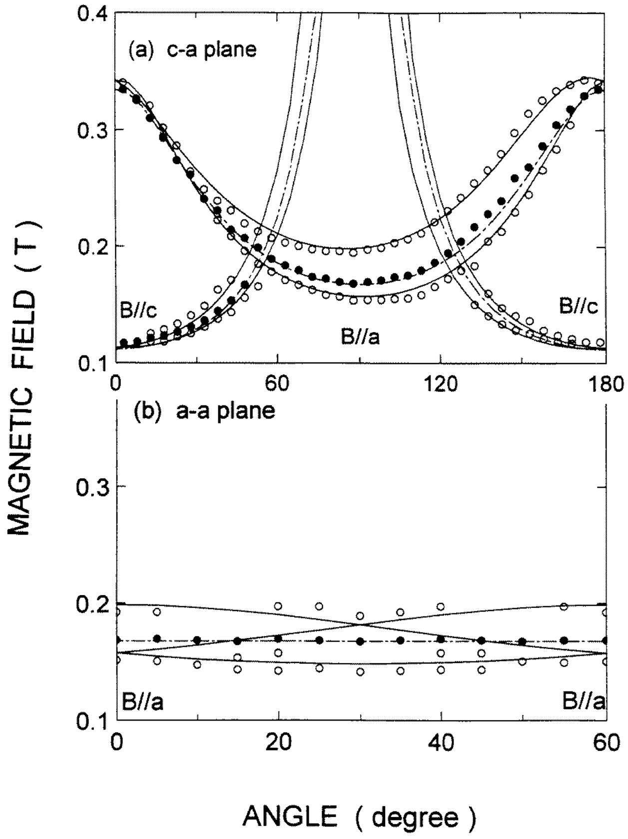


Figure 2. The orientation dependence of the A-lines (●) and B-lines (○) of the Cr^{3+} ESR spectra in CGGO for magnetic field variations in (a) the ca- and (b) the aa-plane.

In figure 1 the ESR spectra are presented as the derivative of the absorbed microwave power at resonance; they are recorded using 100 kHz field modulation and phase sensitive detection. Integrating this signal yields a spectrum corresponding to the absorbed microwave power plotted as a function of magnetic field results. Figure 3 compares the derivative signal for A- and B-lines in the field range 0.32–0.38 T with the microwave absorption spectrum for both CGGO and SGGO. Evidently line B is much more intense than line A, the relative intensities of line A to lines B plus C being 1:55 for CGGO and 1:40 for SGGO.

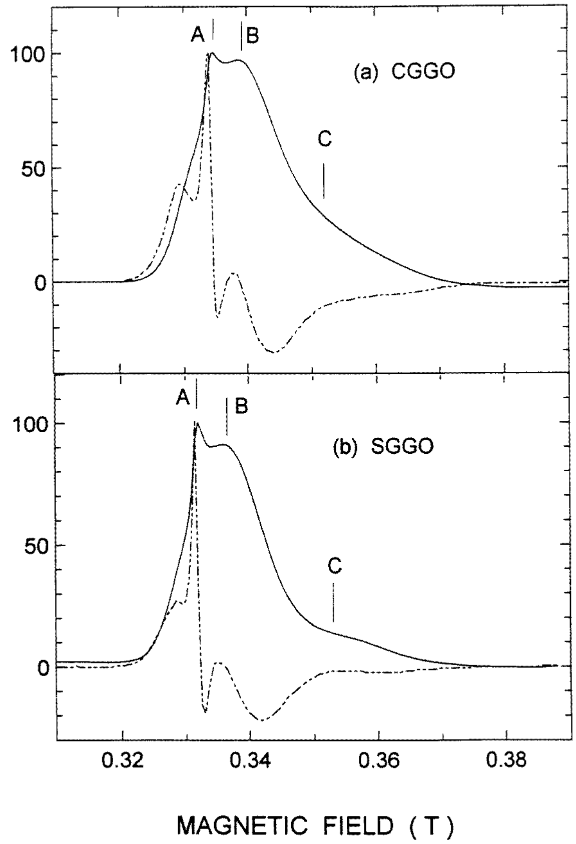


Figure 3. The derivative representation of the ESR signal (— · · —) and the integrated spectrum (——) for (a) Cr^{3+}:CGGO and (b) Cr^{3+}:SGGO.

Photoluminescence due to Cr^{3+} ions in strong crystal field sites in CGGO and SGGO is revealed as inhomogeneously broadened R-lines and their weak vibronic sidebands [2, 3]. The width of the R-lines is due to disorder which causes a distribution in the splittings of the ^2E excited state. In figure 4 we show the splitting of the ground state measured using the FLN technique. From these optical spectra we determine $|2D| = 1.6 \pm 0.1$ cm^{-1} for Cr^{3+} ions in both CGGO and SGGO.

4. Analysis of the ESR spectra

The Cr^{3+} ion has an electronic spin $S = \frac{3}{2}$: in trigonal symmetry the fourfold spin degeneracy is partially lifted such that the $M_S = \pm\frac{1}{2}, \pm\frac{3}{2}$ levels are separated in zero magnetic field by the crystal field splitting, $2D$. Assuming trigonal symmetry the ESR spectrum is interpreted using the spin Hamiltonian

$$H_S = \mu_B B \cdot g \cdot S + D(S_z^2 - \tfrac{5}{4}). \qquad (1)$$

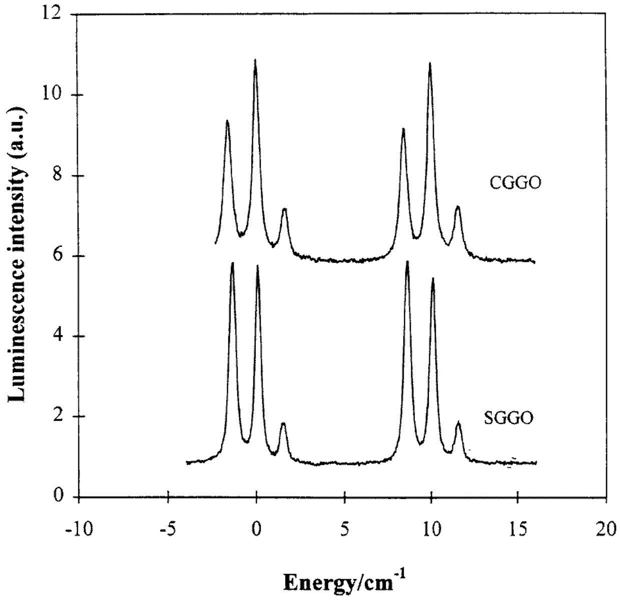


Figure 4. The ground state splittings of Cr^{3+} in CGGO and SGGO measured at 15 K using FLN in which the Cr^{3+} ion R-line is excited at the line centre and the low-energy wing in CGGO and SGGO, respectively.

The optical experiments show that $|2D| \simeq 1.6$ cm^{-1}, an energy splitting much larger than the microwave quantum ($h\nu \sim 0.3$ cm^{-1}). In such a situation only transitions between the $M_S = \pm\frac{1}{2}$ levels can be excited by the X-band microwave quantum. The observed ESR spectra, figure 1, correspond to Cr^{3+} ions with an effective spin $S' = \frac{1}{2}$ and effective g-values $g_\parallel^e = g_\parallel$ and $g_\perp^e = 2g_\perp$. The orientation dependence of the A-line in the ca-plane, in which the A-line shifts from $g_\parallel = 1.980$ to $g_\perp^e = 3.957$, shows that the spectrum is due to an $S = \frac{3}{2}$ ion in a strong, axial crystal field. A perturbation calculation for the $S = \frac{5}{2}$ ions in strong tetragonal crystal fields [5] is easily adapted to the case of $S = \frac{3}{2}$. The orientation dependence of $g_e(\theta)$ of the effective spin $S' = \frac{1}{2}$ is given by

$$g_e(\theta) = (g_\parallel^2 \cos^2\theta + 4g_\perp^2 \sin^2\theta)^{1/2}[1 - \tfrac{3}{4}(g_\perp \mu_B B/2D)^2 F(\theta)] \qquad (2)$$

where

$$F(\theta) = \sin^2\theta[(4g_\perp^2 \sin^2\theta - 2g_\parallel^2 \cos^2\theta)/(4g_\perp^2 \sin^2\theta + g_\parallel^2 \cos^2\theta)]$$

showing that the spin Hamiltonian parameters $g_\parallel$, $g_\perp$ and $2D$ may be derived from measurements of the resonance fields as a function of the angle θ between the static field, B, and the c-axis. The A-spectra in CGGO, SGGO, LGGO and LGS all have axial symmetry about the threefold symmetry axis of these crystals. They are very similar as is emphasized by the spin Hamiltonian parameters in table 2. The only difference is the much greater width of lines A in LGS compared with the three gallogermanates.

The B spectrum is only detected in CGGO and SGGO: its orientation dependence is similar to that of the A spectrum. However, the splitting into two lines in the ca-plane shows that an additional term $E(S_x^2 - S_y^2)$ must be added to the spin Hamiltonian. Further, the fact that the two components have different turning points, either side of the c-axis in figure 2(a), shows that the principal z-axis of the system is rotated through $\sim 5^\circ$ away from the c-direction towards one of three equivalent a-axes.

The spin Hamiltonian parameters of both A- and B-spectra may also be determined from the measured resonance fields by computer fitting to the spin Hamiltonian

$$H_S = \mu_B \boldsymbol{B} \cdot \tilde{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \tilde{D} \cdot \boldsymbol{S}. \tag{3}$$

The spin Hamiltonian parameters given in table 2 were used to reproduce orientation dependences shown in figure 2 for lines A and B. In fitting the A- and B-spectra to the spin Hamiltonian for Cr^{3+} ions in axial and orthorhombic symmetry in (3) the angular dependences are rather insensitive to changes in D at values greater than about 7000×10^{-4} cm^{-1}. This has the effect of limiting the inhomogeneous broadening of the ground state ESR lines for both spectra.

Table 2. Spin Hamiltonian parameters for Cr^{3+} in gallogermanates.

Parameters	CGGO	SGGO	LGGO	LGS
Line A				
$g_\parallel$	1.980 ± 0.005	1.980 ± 0.005	1.970 ± 0.005	1.97 ± 0.02
$g_\perp$	1.98 ± 0.01	1.98 ± 0.01	1.97 ± 0.01	1.97 ± 0.02
D (10^{-4} cm^{-1})	8000 ± 2000	9000 ± 2000	8000 ± 2000	9000 ± 3000
Line B				
$g_x \approx g_y \approx g_z$	1.97 ± 0.01	1.97 ± 0.01		
D (10^{-4} cm^{-1})	8000 ± 2000	8000 ± 2000		
E (10^{-4} cm^{-1})	800 ± 300	800 ± 300		

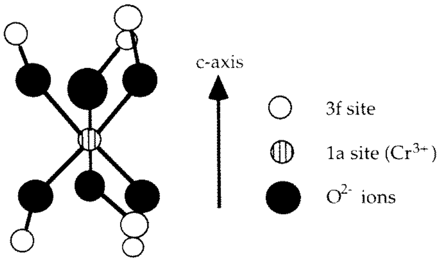
5. Discussion

The ESR studies show that Cr^{3+} ions in CGGO and SGGO occupy two different sites, with trigonal and orthorhombic symmetries. In contrast, for LGGO and LGS there is just a single crystal field site occupied by Cr^{3+}. The earlier optical studies confirm that there are two Cr^{3+} sites in CGGO and SGGO, strong field sites that emit into sharp R-lines and weak field sites that emit into broad $^4T_2 \rightarrow {}^4A_2$ bands [3]. In both cases the luminescence spectra are broadened by disorder. LGGO and LGS each provide only a single site for Cr^{3+} substitution and emission from these crystals is characteristic of weak field sites with the exception of some very weak R-line fluorescence in LGS which is thought to be due to the strong field tail of the crystal field distribution [4]. The numbers of site distributions detected both optically and using ESR seem to show some correlation but further analysis is required before definite links between individual features in the two sets of spectra can be made.

Generally, local disorder of the environment of the optical centre reduces the strength of the crystal field. For example, in Cr^{3+}:MgO charge compensating vacancies are the source of disorder. Most of the vacancies are remote from the Cr^{3+} ions so that octahedrally coordinated Cr^{3+} ions are dominant. A fraction of the charge compensating vacancies occupy near neighbour sites of particular Cr^{3+} ions. As vacancies are brought closer to Cr^{3+} the site symmetry reduces from octahedral to tetragonal to orthorhombic, with concomitant reductions in the strength of the octahedral crystal field. In octahedral and tetragonal sites in MgO Cr^{3+} ions occupy strong field sites and emit into sharp R-lines; Cr^{3+} ions in orthorhombic sites emit into the broad $^4T_2 \rightarrow {}^4A_2$ band [6]. In consequence, it is argued that the strong octahedral crystal field sites in CGGO and SGGO are then of higher symmetry, in respect of their neighbouring occupancy by Ga^{3+} and Ge^{4+} ions, whereas the weak field sites have less symmetrical arrangements of second-nearest-neighbour ions. This is consistent with the conclusions of the optical studies of Cr^{3+}:CGGO and Cr^{3+}:SGGO, where it was shown that the broadening of the weak field fluorescence was due to variation in the Huang–Rhys factor caused by non-octahedral distortions to the crystal field which shift the emission peak to lower energy [3]. The most likely site assignment would therefore be that the site determined to be of higher symmetry in SGGO and CGGO is the same site that fluoresces through R-line emission. The single site in LGGO and LGS is also trigonally symmetric and might be expected to fluoresce via R-lines as does the A-site in CGGO and SGGO. However, the higher ionization state of La^{3+} compared to Ca^{2+} and Sr^{2+} causes the oxygen ions to be shifted from the Cr^{3+} centre, resulting in a larger octahedron of nearest neighbour oxygen ions [1] and a weaker crystal field. The relative intensities of the R-line to broadband fluorescence are found to be 1:40 in CGGO and 1:60 in SGGO, in close accord with the ESR site ratios derived from figure 3, lending further weight to the assignment, particularly as values of $|2D| = 1.6 \pm 0.1$ cm^{-1} for both CGGO and SGGO splittings are in good agreement with the values of $2D$ obtained from the ESR measurement.

The ESR spectra in figure 1(a) also show that the width of the lines in the B-spectrum are $\sim$ 10 times broader than the A-line in CGGO (and SGGO, not shown). This complies with the assignment made above in that the A-spectrum is associated with those Cr^{3+} ions in the most highly ordered octahedral sites, which satisfy the condition for strong crystal fields, and the B-spectrum is associated with Cr^{3+} in more disordered, lower-symmetry sites, which give rise to weak crystal fields. The width of the ESR features in LGGO and LGS might then be expected to have a width similar to that of the A-site in CGGO but it can be seen in figure 1(b) to be considerably broader. To explain this a more detailed model of the site structure is required.

In the gallogermanates, the Cr^{3+} octahedron is sandwiched between two planes consisting of three tetrahedrally coordinated cations (3f site) arranged in an equilateral triangle in each aa-plane (see figure 5). The octahedral site therefore has six next-neighbour O^{2-} ions and six second-nearest-neighbour cations. The 3f site is substitutionally disordered in CGGO and SGGO (see table 1) and so there are 64 different ways that the Ga^{3+} and Ge^{4+} ions can occupy the 3f sites. The statistical probabilities for the numbers of Ga and Ge ions are also presented in figure 5. There are only four ways that the differently charged cations can be arranged in the 3f sites so as to maintain trigonal symmetry; all involve filling the three 3f sites in the aa-plane with the same ion. The sum of the statistical probabilities for these particular arrangements is 0.06 or 4 in 64 in CGGO. This probability is certainly an overestimate of the actual occupation of the sites as it takes no account of charge compensation. It is very unlikely that all six sites would be occupied by the same ion because of the local charge imbalance. This also decreases the probability that the three ions that share a plane have the same charge but the effect is reduced compared to the two adjacent planes. The observed ESR intensity ratio of the A-line to the sum of the intensities of the B- plus C-lines, $\sim$ 1:55, is close to that expected from the random site occupation with site A being attributed to the arrangement of 3f ions that produces a trigonal crystal field. The B- and C-sites are assigned to a superposition of all the other sites that have irregular arrangements of Ga^{3+} and Ge^{4+} ions. Such an assignment also fits well with the data for LGGO and LGS where the 3f site is not disordered and the only feature that is observed in the ESR spectrum has trigonal symmetry. In these crystals the tetrahedral 2d sites are disordered: since they are more remote from the central Cr^{3+} ion they are less effective in reducing that symmetry.



no. of Ga^{3+} in 3f sites	no. of Ge^{4+} in 3f sites	probabality for occupation in CGGO	probability for occupation in SGGO
0	6	0.015	0.010
1	5	0.094	0.071
2	4	0.234	0.202
3	3		
	all sites:	0.313	0.308
	trigonal:	0.031	0.031
4	2	0.234	0.264
5	1	0.094	0.121
6	0	0.015	0.023

Figure 5. A schematic drawing of the Cr^{3+} centre in the gallogermanates. The Cr^{3+} ion is (approximately) octahedrally coordinated to six O^{2-} ions. Equilateral triangles of 3f sites lie both up and down the *c*-axis from the Cr^{3+} site. These triangles lie directly above each other along the *c*-axis with no rotation. The 3f sites are the most important influence on the broadening of the optical and ESR spectra and the statistical probability of their occupation by different numbers of Ga^{3+} and Ge^{4+} ions is given in the table below. In LGGO and LGS, all 3f sites are occupied by Ga^{3+} ions.

It seems likely that in SGGO and CGGO there is a close correlation between the sites that fluoresce via the R-lines and the sites that give rise to the A-spectrum in ESR. The ratios between R-line and broadband fluorescence intensities are of the same order as the ratio between the ESR intensities. However, it is noted that the optical and ESR spectra distinguish directly between sites in different ways: the ESR in terms of the local symmetry and the optical spectra in terms of crystal field strengths, although the optical spectra are sensitive to symmetry lower-order splittings and polarization effects. In this context, both intensity ratios, ESR and optical, are about 1:60. The ESR spectra indicate the numbers of Cr^{3+} ions occupying trigonal and non-trigonal (B+C) sites. The higher-symmetry (trigonal) sites are expected to be characteristic of the Cr^{3+} ions in the stronger crystal field. Although, as discussed above, this observation is consistent with the experimental data it is possible that the optical spectra do not so accurately represent the distribution of Cr^{3+} ions in the different strong and weak field sites. Not all sites contributing to the high-symmetry ESR spectrum (line A) necessarily fluoresce via the R-line. The different Cr^{3+} sites containing six Ga^{3+} ions or six Ge^{4+} ions in the closest 3f sites are unlikely to have identical crystal field strengths of identical magnitude, as is evident from the different charge in the 3e sites in CGGO and SGGO relative to LGGO (table 1), for instance. Furthermore, non-radiative decay of excited Cr^{3+} ions is more probable in weak field sites than strong field sites so that the R-lines appear relatively stronger than in effect they are. In consequence, it is concluded that all trigonally symmetric sites contribute to the trigonal ESR spectra but that only a subset of these sites contribute to the R-line. The two effects appear to counterbalance such that the optical and ESR intensity ratios appear to match well. Indeed our recent studies of non-radiative decay of Cr^{3+} ions in the gallogermanates show that the actual number of weak field sites is somewhat larger than measured from CW optical spectra [7].

The widths of the ESR spectra are also consistent with the model suggested above. The very narrow A-spectrum in CGGO and SGGO corresponds to highly ordered centres. The B- and C-spectra are much broader and their rotation patterns in the ac-plane are shifted by 5° from the principal axis of the trigonal centre due the effects of disorder. In LGS and LGGO the spectrum is trigonal but broadened. This represents an intermediate case where broadening is due to substitutional disorder on the 2d tetrahedral sites that are further removed from the Cr^{3+} centre than the 3f sites. In consequence, LGGO shows a single Cr^{3+} centre, of which the principal axis is distributed around the c-axis with small bending angles.

6. Conclusions

It has been shown that ESR spectra of Cr^{3+}:CGGO and Cr^{3+}:SGGO confirm that there are two types of crystal field site as was apparent from optical spectra [3, 4]. Their crystal fields are close to intermediate and strongly modified by disorder. The strong field sites are shown to be mainly due to Cr^{3+} ions in the more ordered unit cells and weak field sites are sites where there is a greater degree of local disorder in the next-nearest-neighbour shell of cations local to the Cr^{3+} ion probe. The ESR spectra of Cr^{3+}:LGGO shows a trigonal centre, corresponding to the weak crystal field estimated from optical spectra. The larger charge of the La^{3+} ion compared to Ca^{2+} and Sr^{2+} reduces the crystal field at the Cr^{3+} site. Disorder in the 2d site is still sufficient to broaden both the ESR and optical spectra.

Acknowledgments

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