Strathprints Institutional Repository

This version is available at http://strathprints.strath.ac.uk/55347/

Crystalfield symmetries of luminescent Eu^{3+} centers in GaN: The importance of the $^5D_0$ to $^7F_1$ transition

K. P. O'Donnell,[1,a)] P. R. Edwards,[1] M. Yamaga,[2] K. Lorenz,[3] M. J. Kappers,[4] and M. Boćkowski[5]

[1]SUPA Department of Physics, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, United Kingdom
[2]Department of Mathematical and Design Engineering, Gifu University, Gifu 501-1193, Japan
[3]IPFN, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal
[4]Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, England, United Kingdom
[5]Institute of High Pressure Physics PAS, Sokolowska 29/37, 01-142 Warsaw, Poland

Eu-doped GaN is a promising material with potential application not only in optoelectronics but also in magneto-optical and quantum optical devices "beyond the light emitting diode." Its interesting spectroscopy is unfortunately complicated by spectral overlaps due to "site multiplicity," the existence in a given sample of multiple composite centers in which Eu ions associate with intrinsic or extrinsic defects. We show here that elementary crystalfield analysis of the $^5D_0$ to $^7F_1$ transition can critically distinguish such sites. Hence, we find that the center involved in the hysteretic photochromic switching observed in GaN(Mg):Eu, proposed as the basis of a solid state qubit material, is not in fact Eu1, as previously reported, but a related defect, Eu1(Mg). Furthermore, the decomposition of the crystalfield distortions of Eu0, Eu1(Mg), and Eu1 into axial and non-axial components strongly suggests reasonable microscopic models for the defects themselves. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4939631]

Semiconductors activated with lanthanide ("rare earth") ions have been studied since the late 1980s[1] with the main aim of converting the band gap emission of optoelectronic devices into more useful spectral regions.[2] Following the demonstration of a red-emitting GaN:Eu LED (light-emitting diode) by Fujiwara and co-workers in 2009,[3] much attention has focused on the emission spectra of Eu^{3+} ions in GaN (bandgap 3.4 eV), in particular, the strong multiplet of lines due to the $^5D_0$ to $^7F_2$ transition near 620 nm (2 eV).[4–9] More recently, attention has extended "beyond the LED" to the potential application of RE-doped III-nitrides in magneto-optical[10] and quantum optical devices.[11–13]

Optical absorption and emission spectra of tri-positive rare earth ions in crystalline solids feature sharp peaks at characteristic wavelengths that depend rather weakly on the host. These transitions are due to *intra-4f-shell* transitions that are forbidden in the free ion by the Laporte selection rule. Thus RE doping of a solid lattice first *localises* the ion and then *develops* its latent spectroscopy (in the photographic sense) through the mixing-in of quantum states of opposite parity by the crystalfield (CF), according to principles established by Judd[14] and Ofelt.[15] A CF perturbation that is very much smaller in magnitude than the energy separations of the atomic terms opens up otherwise invisible transitions to observation and measurement. The CF also induces energy splittings, which, although small, produce spectral line patterns that reveal the *symmetry* of the local environment. We show here that symmetry, in particular, as

it affects the $^7F_1$ energy level, provides the key to solving long-standing problems caused by site multiplicity of Eu^{3+} emission in GaN. Our guide to transition assignments is a comprehensive analysis of Eu cathodoluminescence in AlN,[16] for which a single center, with C_{3v} point symmetry, has been shown to be dominant.[17]

In an extension of previous studies, we measure photoluminescence (PL) spectra of the relatively simple $^5D_0$ to $^7F_{0,1}$ transitions of Eu^{3+} to reveal the site symmetries of the most commonly encountered defects. On the basis of these symmetry determinations, we suggest tentative microscopic models for the centers.

Luminescent GaN:Eu (n-type) and GaN(Mg):Eu (p-type) samples were prepared by ion implantation of up to $\sim 10^{15} cm^{-2}$ Eu ions at 300 keV, followed by high-temperature, high-pressure annealing at 1400 °C in 1 GPa of N_2 as detailed in the previous work [e.g., Refs. 4 and 5]; at room temperature, the PL spectra of fresh samples, excited by ultraviolet light above the GaN band edge, feature only the spectra of those defects which we call Eu1 and Eu0, in GaN:Eu and GaN(Mg):Eu samples, respectively.[5,12] High-resolution PL spectra were recorded using a cooled 1024×127-pixel CCD camera in spectral regions of interest (ROI) centred on 594 nm, 608 nm, 622 nm, and 635 nm, with wavelength spans of approximately 15 nm. The ROI correspond to inter-term (atomic) transitions of Eu^{3+}, originating on the lowest excited level, $^5D_0$, and ending on: $^7F_0$ (at ~ 590 nm); $^7F_1$ (at ~ 600 nm) and $^7F_2$ (at ~ 620 nm and 635 nm; see below). In this sequence, the emission lines of Eu^{3+} in GaN become both brighter and broader as the peak wavelengths increase.

a)E-mail: k.p.odonnell@strath.ac.uk

Since the emitting $^5D_0$ level is a singlet, any line splitting that we observe will reveal the symmetry of the luminescent center in its receiving state. The lowest ground state of Eu^{3+}, $^7F_0$, is also a singlet, and the so-called "sensitive" transitions, from $^5D_0$ to $^7F_0$, act as a simple spectroscopic counter of defect species (called sites) that are active in a given Eu-doped sample, discounting accidental overlaps. As an example, Figure 1 shows the sensitive spectral region at room temperature for a GaN(Mg):Eu sample with a prominent Eu0 line near 587 nm and its Stokes' (S) and anti-Stokes' (A-S) replicas. For reasons that will become clear later, the corresponding Eu1 transition, which should dominate the spectrum of an undoped GaN:Eu sample in the sensitive region, proves to be relatively weak; it is therefore much harder to observe.

The $(2S+1)$ multiplicities of the $^7F_1$ and $^7F_2$ states, 3 and 5, respectively, determine the maximum possible number of lines to expect for transitions from $^5D_0$ to these states in a low-symmetry site. However, degeneracies occur in higher symmetry. In the trigonal case, considered by Gruber *et al.* for AlN:Eu,[16] the $^7F_1$ level splits into a doublet (E) and a singlet (A), while $^7F_2$ splits as $E+E+A$. Hence, in a purely trigonal symmetry, we expect to see 2 $^5D_0$ to $^7F_1$ lines near 600 nm, with a relative intensity ratio close to 2:1, and 3 $^5D_0$ to $^7F_2$ lines near 620 nm. Remarkably, one component of the $^5D_0$ to $^7F_2$ transition splits away from the others and is located close to 635 nm. This anomaly, overlooked in the previous GaN:Mg studies, both by some of the present authors[5] and by others,[8] turns out to be useful as well as interesting, since it allows a clear demonstration in an isolated spectral region of hysteretic photochromic switching (HPS) in GaN(Mg):Eu samples, as described in Refs. 11 and 12.
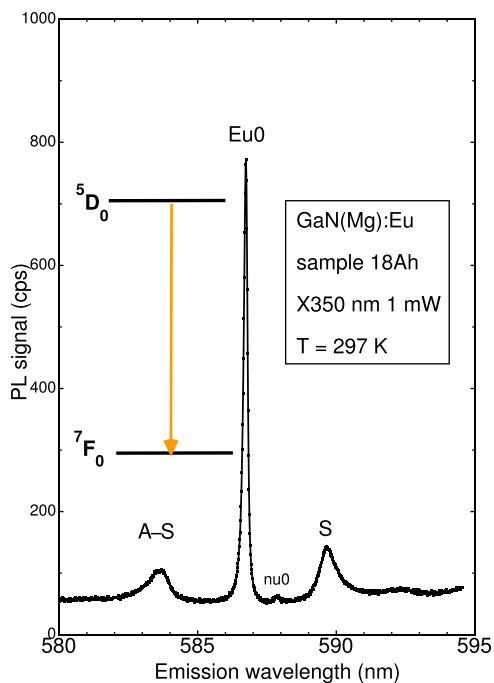
It will be clear from the following summary that HPS provides a useful and unique additional "handle" for the identification of groups of transitions belonging to a particular site. The Eu0 spectrum has a characteristic temperature dependence, first reported in Ref. 6 and shown by the present authors to implicate HPS.[11,12] Upon sample cooling below room temperature, Eu0 transitions first grow rapidly, reaching a maximum intensity at ∼200 K and then saturating. In a narrow temperature range below 30 K, the Eu0 signal abruptly decreases to zero intensity. It is progressively replaced by a new set of lines which we here ascribe to Eu1(Mg). Figure 2 shows the spectral changes observed in the $^5D_0$ to $^7F_1$ spectral region between 100 K and 25 K.

The photochromic switch from Eu0 to Eu1(Mg) is hysteretic, because it does not reverse itself when a cooled sample warms from 10 K through 30 K. In fact, the Eu0 lines only reappear when the temperature exceeds 100 K. The same HPS behaviour is of course observed for all monitored transitions, allowing the labelled transitions, near 596 nm, 600.8 nm, and 606 nm in Figure 2, to be easily identified as "belonging" to Eu0. In a similar way, lines at ∼600.8 nm (again), 601.2 nm, and 602.5 nm "belong to" Eu1(Mg), the hysteretic switching partner of Eu0. The Eu1(Mg) lines are noticeably sharper than those of Eu0, leading to higher peak values, but the integrated intensities of both sets of lines are similar.

In a preliminary conference report of this work,[18] the line at 608 nm was assigned to Eu1(Mg). This assignment is now considered unlikely for 2 reasons: (1) the line at 608 nm is broader than any other in this spectral ROI and shows unresolved structure: it is clearly not the singlet expected from splitting of a $^7F_1$ level into 3 components; and (2) the line positions of Eu1(Mg) closely resemble those observed by Gruber *et al.* for the trigonal Eu1 centre in AlN[16] and we expect the CF of GaN and AlN to be similar. However, the actual origin of the 608 nm line is presently unknown and a matter for further study.

In GaN:Eu samples without Mg, the dominant center at RT, Eu1, is distinguished by its excitation spectrum, which
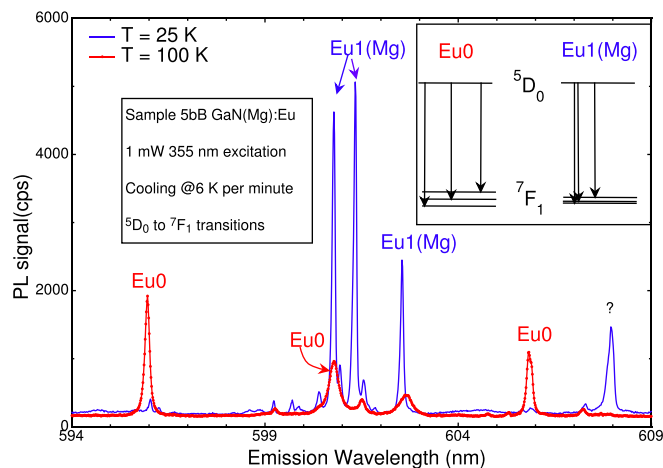

FIG. 1. Showing emission at room temperature of a GaN(Mg):Eu sample excited above the bandgap of GaN. Phonon assisted transitions are separated by ∼90 cm^{-1} (10.5 meV) from the main line (586.7 nm). The small emission line marked nu0 will be described in a later publication.

FIG. 2. Showing spectra obtained while cooling down a GaN(Mg):Eu sample from RT towards 10 K. In a narrow temperature range below 30 K, the spectrum *switches* from Eu0-dominated to one featuring a new spectrum, denoted here as Eu1(Mg). The inset shows the corresponding splittings of the receiving $^7F_1$ states of Eu0 and Eu1(Mg) centers (not to scale).
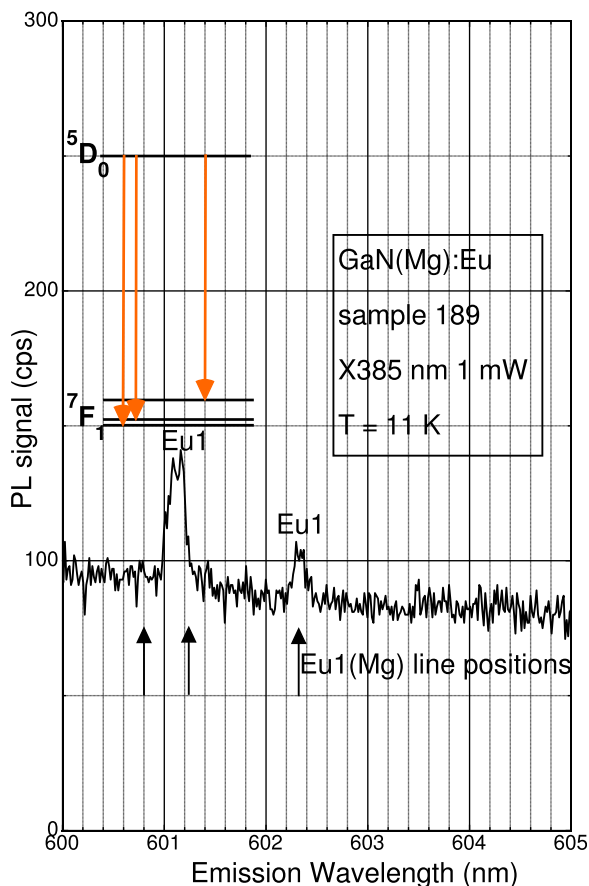
FIG. 3. Showing emission at low temperature of a GaN(Mg):Eu sample excited below the bandgap of GaN. Black arrows indicate Eu1(Mg) line positions in this spectral region.

shows a prominent sub-gap feature with a peak near 385 nm in addition to the GaN bandedge above ~350 nm.[19] Neither Eu0 nor Eu1(Mg) can be excited efficiently below the GaN gap in this way. However, we do observe, as shown in Figure 3, a weak emission from Mg-doped samples excited below the bandgap at low temperature, which we ascribe to residual Eu1 centers: the observed close-doublet and singlet lines match those of transitions of Eu1 in undoped samples (not shown); the rather different line positions of the $^5D_0$ to

$^7F_1$ transitions of Eu1(Mg), indicated by arrows in Figure 3, further distinguish Eu1 from Eu1(Mg).

Although the $^5D_0$ to $^7F_2$ transitions of Eu^{3+} are by far the brightest, and therefore the ones most intensively studied in the literature, their relative complexity compromises their use in determining the symmetry of the associated luminescent centers. Both Eu0 and Eu1(Mg) show 5 spectral components, including the unexpected "split-off" lines, in the ~620 nm and ~635 nm ROI. Remarkably, the $^5D_0$ to $^7F_2$ transitions of Eu1(Mg) exactly *match those reported for Eu1* within experimental error; this spectral coincidence is the main cause of previous misidentifications of the Eu1(Mg) center as Eu1 (e.g., Refs. 5–9, 11, and 12). It is also worth noting that transitions of the "prime" Eu2 center, an unassociated Eu atom on a Ga lattice site,[5] are completely absent from our GaN(Mg):Eu samples at all temperatures.

Figure 4 compares all $^5D_0$ to $^7F_{0,1,2}$ transitions of Eu0 and Eu1(Mg) centers in GaN(Mg):Eu. It is quite clear that the Eu0 center is of lower symmetry, while Eu1(Mg) is nearly axial, the splittings of the $^7F_1$ level indicate this fact most directly. In line with the Judd-Ofelt model, the higher symmetry of Eu1(Mg) accounts for the weakness, nearly to the point of extinction, of its sensitive transition near 587 nm (Fig. 4). By the same token, the "real" Eu1 center is even closer to axial than Eu1(Mg), with an unresolved $^7F_1$ doublet splitting that is comparable in magnitude to the spectral line-width (Figure 3). Consequently, its sensitive line is found to be even weaker than that of Eu1(Mg).

We now consider the energy splitting of the $^7F_1$ multiplets of Eu0 (non-axial), Eu1 and Eu1(Mg) (nearly axial) centers according to CF theory.[20,21] Neglecting terms of 6th order, the equivalent operator Hamiltonian for C_{3v} symmetry is given by[18]

$$H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 (O_4^{-3} - O_4^3). \qquad (1)$$

The crystal field operator appropriate to a non-axial distortion adds a perturbative term
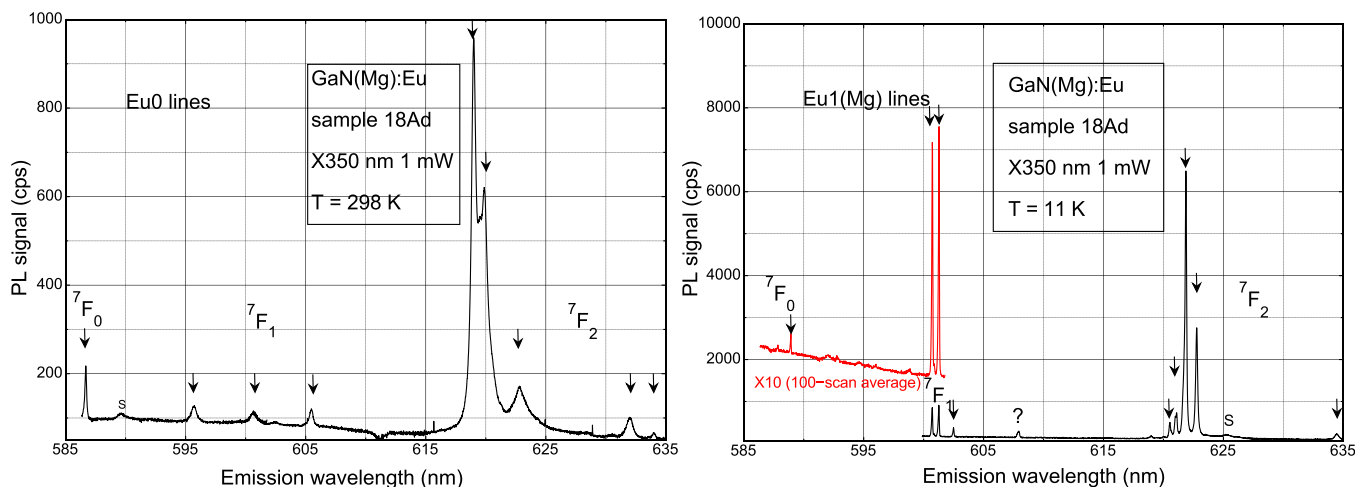
$$H_1 = B_2^2 O_2^2. \qquad (2)$$

FIG. 4. Comparing emission spectra of a GaN(Mg):Eu sample excited above the bandgap of GaN at high and low temperature. Arrows indicate Eu0 and Eu1(Mg) line positions at 298 K and 11 K, respectively, while S shows a phonon-assisted Stokes' line.

TABLE I. Comparing axial and non-axial distortion parameters of Eu^{3+} centers in GaN. All values are $\pm 1 \, cm^{-1}$.

|	Eu0	Eu1(Mg)	Eu1
B_2^0 (cm^{-1})	69	14	15
B_2^2 (cm^{-1})	37	8	<2

The observed energy splitting of the $^7F_1$ multiplets ($|0\rangle$, $|\pm1\rangle$) for Eu0 and Eu1(Mg) allow us to calculate directly the axial and non-axial components of the interaction, B_2^0 and B_2^2, respectively. In a co-ordinate frame where z coincides with the trigonal axis

$$H = 3B_2^0 J_z^2 + 2B_2^2 (J_x^2 - J_y^2). \qquad (3)$$

Hence, the doublet splitting $2B_2^2$ is expected to be zero for purely axial defects, while $3B_2^0$, the energy separation of the doublet's center of gravity from the singlet, quantifies the axial distortion of the center. The experimentally determined values are listed in Table I.

The calculated energy distortions are indeed small compared to the term differences of $\sim 17\,000 \, cm^{-1}$ but are decisive for symmetry assignment. While the distortion energies for Eu1 and Eu1(Mg) centers are similar, and small, those of Eu0 show a strong non-axial component. The random variation of its larger distortion parameter values, caused by inhomogeneous strain, accounts very well for the excess line broadening of the Eu0 centers, compared with those of Eu1(Mg) and Eu1.

The results of the calculation suggest that Eu is strongly affected by the presence of Mg in the lattice, particularly in the Eu0 center and rather less so in Eu1(Mg). Figure 5 shows the simplest composite defect model with both Eu and Mg substitutional. The absence of Eu2 from GaN(Mg):Eu samples further suggests that this is a *preferred* configuration for Eu^{3+} ions in the presence of Mg acceptors in GaN. On the other hand, the Eu1(Mg) center, with symmetry close to C_{3v}, is assigned to an Eu^{3+} ion in an Eu1-type center, but with Mg_{Ga} displaced to a relatively long distance in a nearly axial direction. All of these observations support the HPS model,[11,12] which ascribes the observed hysteretic
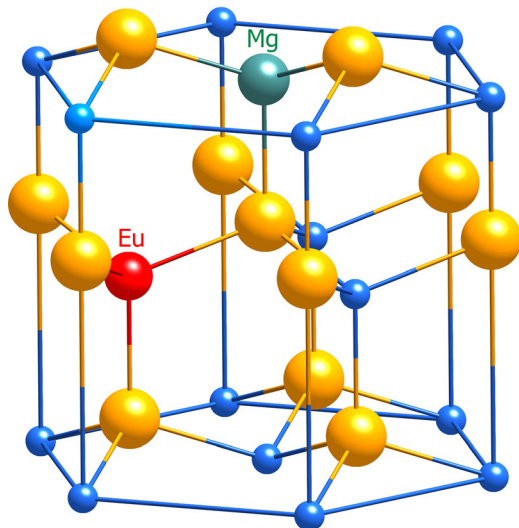
FIG. 5. A model of the Eu0 centre, Eu0 = Eu2 + Mg_{Ga}.

photochromism to the theoretically predicted shallow-deep instability of the Mg acceptor.[22,23]

While the $^7F_1$ splittings provide a rough and ready guide to site symmetry, more information can be extracted from an analysis of the $^5D_0$ to $^7F_2$ line patterns.[18] Considering Eqs. (1) and (2), we see that a trigonal field splits the $^7F_2$ multiplet into a doublet, singlet and doublet according to the magnitudes of B_2^0 and B_4^0, while B_2^2 further splits the level into 5 singlets, as observed experimentally. The results of the more complex calculations required to determine these distortion parameters will be discussed in full elsewhere.

In summary, the symmetry of composite Eu^{3+} centers (sites) in GaN is most clearly made evident in the crystal field splitting of the $^7F_1$ state as revealed by the line pattern of the $^5D_0$ to $^7F_1$ spectra near 600 nm. Eu0 and Eu1-type centers are clearly distinguished as non-axial and near-axial, respectively. The axial and non-axial distortions of different composite centers are characterised by their relative magnitude, allowing a simple differentiation of centers, which promises to solve, at least partially, the long-standing site multiplicity problem. Informed structural assignments are a key for producing and controlling luminescence centers in future optical communication and quantum information applications.

[1]P. N. Favennec, H. L'Haridon, M. Salvi, D. Moutonnet, and Y. Le Gillou, Electron. Lett. **25**, 718 (1989); see also K. P. O'Donnell, Phys. Status Solidi C **12**, 466 (2015).
[2]*Topics in Applied Physics*, edited by K. P. O'Donnell and V. Dierolf (Springer, Dordrecht, 2010), Chaps 1, 4, and 8, Vol. 124.
[3]A. Nishikawa, T. Kawasaki, N. Furukawa, Y. Terai, and Y. Fujiwara, Appl. Phys. Express **2**, 071004 (2009).
[4]K. Lorenz, E. Alves, I. S. Roqan, K. P. O'Donnell, A. Nishikawa, Y. Fujiwara, and M. Boćkowski, Appl. Phys. Lett. **97**, 111911 (2010).
[5]I. S. Roqan, K. P. O'Donnell, R. W. Martin, P. R. Edwards, S. F. Song, A. Vantomme, K. Lorenz, E. Alves, and M. Boćkowski, Phys. Rev. B **81**, 85209 (2010).
[6]D.-G. Lee, A. Nishikawa, Y. Terai, and Y. Fujiwara, Appl. Phys. Lett. **100**, 171904 (2012).
[7]R. Wakamatsu, D. Lee, A. Koizumi, V. Dierolf, and Y. Fujiwara, J. Appl. Phys. **114**, 043501 (2013).
[8]B. Mitchell, J. Poplawsky, D. Lee, A. Koizumi, Y. Fujiwara, and V. Dierolf, J. Appl. Phys. **115**, 204501 (2014).
[9]M. Ishii, A. Koizumi, and Y. Fujiwara, Appl. Phys. Lett. **107**, 082106 (2015).
[10]V. Kachkanov, M. J. Wallace, G. van der Laan, S. S. Dhesi, S. A. Cavill, Y. Fujiwara, and K. P. O'Donnell, Sci. Rep. **2**, 969 (2012).
[11]K. P. O'Donnell, R. W. Martin, P. R. Edwards, K. Lorenz, E. Alves, and M. Boćkowski, AIP Conf. Proc. **1566**, 63 (2013).
[12]K. P. O'Donnell, P. R. Edwards, M. J. Kappers, K. Lorenz, E. Alves, and M. Boćkowski, Phys. Status Solidi C **11**, 662 (2014).
[13]D. Timmerman, R. Wakamatsu, K. Tanaka, D.-G. Lee, A. Koizumi, and Y. Fujiwara, Appl. Phys. Lett. **107**, 151107 (2015).
[14]B. Judd, Phys. Rev. **127**, 750 (1962).
[15]G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).
[16]J. B. Gruber, U. Vetter, T. Taniguchi, G. W. Burdick, H. Hofsass, S. Chandra, and D. K. Sardar, J. Appl. Phys. **110**, 023104 (2011).

[17]K. Wang, K. P. O'Donnell, B. Hourahine, R. W. Martin, I. M. Watson, K. Lorenz, and E. Alves, Phys. Rev. B **80**, 125206 (2009).

[18]M. Yamaga, H. Watanabe, M. Kurahashi, K. P. O'Donnell, K. Lorenz, and M. Boćkowski, J. Phys.: Conf. Ser. **619**, 012025 (2015).

[19]K. Wang, R. W. Martin, K. P. O'Donnell, V. Katchkanov, E. Nogales, K. Lorenz, E. Alves, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **87**, 112107 (2005).

[20]B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids* (Clarendon Press, Oxford, 1989), Chap. 8.

[21]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford,1970), pp 209 and 338.

[22]S. Lany and A. Zunger, Appl. Phys. Lett. **96**, 142114 (2010).

[23]J. L. Lyons, A. Janotti, and C. G. Van de Walle, Phys. Rev. Lett. **108**, 156403 (2012); see also J. J. Davies, Phys. Rev. B **87**, 235208 (2013).