Spectroscopic properties of Cr^{3+} In $RbCdF_3$

Spectroscopic properties of Cr^{3+} in $RbCdF_3$

B Villacampa, J Casas González, R Alcalá and P J Alonso

Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza–CSIC, Plaza S Francisco, 50009 Zaragoza, Spain

Abstract. A spectroscopic study of chromium-doped $RbCdF_3$ crystals has been performed. Cubic, tetragonal and trigonal Cr^{3+} centres have been detected by EPR measurements. The spin Hamiltonian parameters of trigonal and one type of tetragonal Cr^{3+} ions, not previously reported, have been found to be: $g_\parallel = 1.969$, $g_\perp = 1.971$ and $|D| = 0.1576$ cm^{-1} for the trigonal centre and $g_\parallel = 1.970$, $g_\perp = 1.972$ and $|D| = 0.0722$ cm^{-1} for the tetragonal one. Crystal field and Racah parameters of cubic Cr^{3+} derived from the optical absorption spectrum are: $D_q = 1420$ cm^{-1}, $B = 800$ cm^{-1} and $C = 3290$ cm^{-1}. Photoluminescence has been measured at different temperatures and the phonon structure observed at 15 K has been associated with different Cr^{3+} centres. The lifetimes of the emitting levels of cubic and trigonal Cr^{3+} ions measured at 15 K have been found to be 470 μs and 220 μs respectively. At 300 K the lifetime of cubic centres decreases to about 180 μs. No direct influence of the phase transition on the optical properties of Cr^{3+} ions, when we go through the transition temperature, has been detected.

1. Introduction

The search of active media for tunable solid state lasers has renewed the interest in the spectroscopic properties of Cr^{3+}-doped fluoroperovskites [1]. $KZnF_3$:Cr has proved to be a good laser material with a broad tunability range and room temperature operation [2, 3] and because of this its spectroscopic properties have been extensively investigated using optical and magnetic resonance techniques [2–8].

Other crystals of the same family such as $RbCdF_3$:Cr which also have good qualities for laser applications [4] have received less attention. Only two types of Cr^{3+} centres (cubic and tetragonal) have been studied in these crytals by magnetic resonance techniques [9–11] while at least four different centres were found in $KZnF_3$ and, although some optical properties have been reported [4], a detailed analysis of the emissions associated with the different Cr^{3+} centres has not been performed.

Furthermore, $RdCdF_3$ crystals undergo a structural phase transition at 124 K that has been investigated by different techniques [9–14]. In particular, magnetic resonance spectra of Cr^{3+} centres [9–11] have been shown to be very sensitive to the phase transition and it is interesting to find out if a similar influence appears in the optical properties of these centres.

In this paper we report our results on EPR, optical absorption, photoluminecence, lifetime measurements and phonon structure of Cr^{3+} ions in $RbCdF_3$. The results are discussed and compared with those in $KZnF_3$.

2. Experiment

The Cr-doped fluoroperovskite crystals used in this work were grown by the Bridg-mann technique using a RF heated furnace and vitreous carbon crucibles. Some of the samples were kindly provided by Professor Dr J M Spaeth (University of Paderborn, Germany), and the others were grown in our laboratory. The nominal CrF_3 content was 0.5 mol%.

Optical absorption measurements were taken with a Hitachi U3400 spectropho-tometer. Photoluminescence spectra were obtained by exciting the samples with light from a 150 W Xe arc lamp passed through a 0.25 m Bausch and Lomb monochroma-tor. Most of the measurements were performed exciting in the 470 nm region which corresponds to one of the main absorptions of Cr^{3+} ions but similar results were ob-tained exciting with 700 nm light in the transition between the ground state and the first excited level of Cr^{3+}. Fluorescence was detected through a 0.5 m Jarrel–Ash monochromator with either a Hamamatsu R-928 photomultiplier or a Si avalanche photodiode. Lifetime measurements were performed exciting with a pulsed dye laser (pulse width 2 ns) and using a Tektronik 2430 digital oscilloscope controlled by an IBM PC microcomputer. Sample temperatues between 15 K and 300 K were achieved with a CTi–Cryogenics close-cycle cryo-refrigerator.

EPR spectra were obtained in a Varian E-112 spectrometer working in the X-band. Magnetic field values were determined with an NMR gaussmeter, model ER035M from Bruker. The diphenylpirrylhydrazyl (DPPH) resonance signal ($g = 2.0037 \pm 0.0002$) was used as a standard to determine the microwave frequency.

3. Experimental results and discussion

The EPR spectrum of a $RbCdF_3$:Cr single crystal measured at room temperature (RT) with the magnetic field parallel to one of the $\langle 100 \rangle$ directions is shown in figure 1. This spectrum is very similar to the one reported by Vaills *et al* [6], for Cr^{3+}-doped $KZnF_3$ and different kinds of defects associated with Cr^{3+} ions can be identified. In all the cases Cr^{3+} enters the $RbCdF_3$ lattice in a Cd^{2+} site. The line marked with C in the figure corresponds to cubic Cr^{3+} ions already reported in [11]. The lines marked with □ are due to tetragonal centres. They have been studied by several authors [5–7] and a model consisting of a Cd^{2+} vacancy nearest neighbour to a Cr^{3+} ion has been proposed for them. The lines marked with Δ correspond to trigonal centres. To our knowledge no EPR study of these centres has been reported previously in $RbCdF_3$. We have measured the angular evolution of the signal when the static magnetic field B rotates in a (110) plane. The line positions are given in figure 2 together with the positions calculated using the spin Hamiltonian.

$$H = g_{\parallel}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + D\left[S_z^2 - \tfrac{1}{3}S(S+1)\right] \tag{1}$$

with the z-axis along a $\langle 111 \rangle$ direction and the following values for the parameters: $g_{\parallel} = 1.969 \pm 0.001$, $g_{\perp} = 1.971 \pm 0.001$ and $|D| = 0.1576$ cm^{-1}. These values correspond to the best fitting between calculated and experimental line positions. The parameters found for similar trigonal Cr^{3+} centres in $KZnF_3$ are [6]: $g_{\parallel} = 1.9716$, $g_{\perp} = 1.9725$ and $|D| = 0.1613$ cm^{-1}. It can be seen that the spin Hamiltonian parameters are very similar in the two matrices. Because of this we propose for the trigonal Cr^{3+} centre in

$RbCdF_3$ the same model as in $KZnF_3$: a Rb^+ vacancy nearest neighbour to the Cr^{3+} ion. The slightly bigger g-shifts with respect to the free electron value ($g = 2.0023$) observed in $RbCdF_3$ as compared with $KZnF_3$ can be understood in the following way. In low crystal fields such as those found in fluoroperovskites the ground state of the cubic Cr^{3+} ions is the $^4A_{2g}(^4F)$ and the first excited level is the $^4T_{2g}(^4T)$. A trigonal distortion splits the $^4T_{2g}$ triplet into a singlet and a doublet. Using a crystal field approximation up to second order it is found that [15]:

$$g_{\parallel} = 2.0023 - 8\xi_0/3\Delta_1 \qquad \text{and} \qquad g_{\perp} = 2.0023 - 8\xi_0/3\Delta_2 \qquad (2)$$

where ξ_0 is the spin–orbit coupling constant for a single d-electron and Δ_1 and Δ_2 are the singlet and doublet energies with respect to the $^4A_2$ ground state. Since the lattice parameter of $RbCdF_3$ is bigger than that of $KZnF_3$, lower values of the crystal field splittings Δ_1 and Δ_2 can be expected and consequently bigger g-shifts.
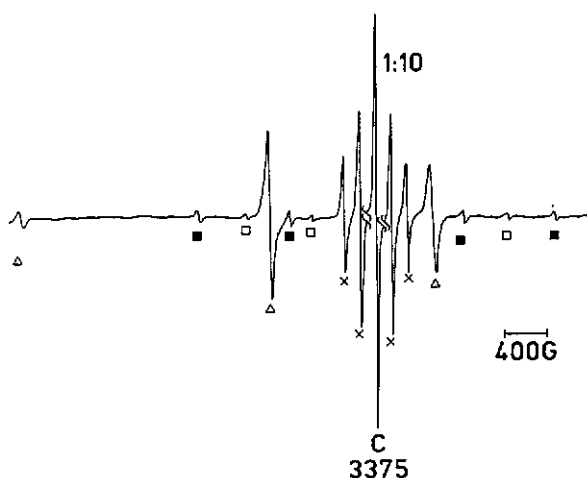

Figure 1. EPR spectrum of a $RbCdF_3$:Cr crystal. $H_0\|\langle 100\rangle$, $\nu \approx 9.3$ GHz. Measured at RT.

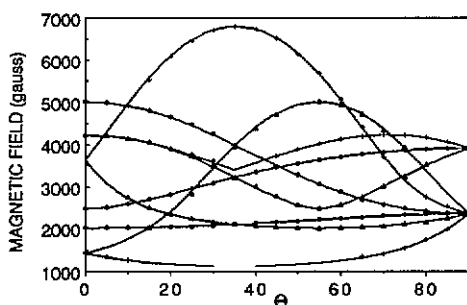**Figure 2.** Rotational diagram of trigonal Cr^{3+} centres in $RbCdF_3$ with the magnetic field rotating in a (110) plane. +, $\triangle$, $\blacklozenge$ correspond to centres with the z-axis along different $\langle 111\rangle$ directions. Θ is the angle between H_0 and the [110] direction. The solid curves give the calculated positions.

Besides the lines corresponding to these three types of Cr^{3+} centres another signal marked with (■) in figure 1 has been observed in our crystals. This signal for $B\|$ to a $\langle 100 \rangle$ direction is very similar to one reported in $KZnF_3$ [4, 9] that has been associated with some kind of tetragonal centres but without giving a definite model for them. Because of the low intensity of this signal we have not been able to measure its angular evolution. However using the spin Hamiltonian [1] with the z-axis along a $\langle 100 \rangle$ direction and the position of the lines for $B\| \langle 100 \rangle$ we have derived the following approximate values of the spin Hamiltonian parameters: $g_\| = 1.970 \pm 0.005$ and $g_\perp = 1.972 \pm 0.005$ and $|D| = 0.078$ cm^{-1}, which are close to those reported in $KZnF_3$ [7] ($g_\| = 1.9708$ and $g_\perp = 1.9766$ and $|D| = 0.09$ cm^{-1}).

Finally we want to mention that in the region close to the cubic Cr^{3+} pattern there is another group of lines marked with × in figure 1. A similar four-line pattern is also seen in $KZnF_3$ [6] although in our samples the relative intensity of this signal with respect to the trigonal one is slightly higher than in the case of $KZnF_3$. No assignment of these lines has previously been made. We have tried to measure their angular evolution but unfortunately the line positions can only be determined for magnetic field orientations very close to the $\langle 100 \rangle$ directions due to overlapping problems. Although the signal for B parallel to $\langle 100 \rangle$ is similar to the one expected for tetragonal centres (with another line hidden under the strong cubic signal) with a small value of the crystal field parameter ($|D| \approx 0.0135$ cm^{-1}) the splittings observed in the lines when the magnetic field is rotated in the (001) plane are not compatible with this model.

The presence of all these different types of Cr^{3+} centres makes it difficult to analyse the optical properties of our crystals. However as in other similar cases the RT optical absorption spectrum can be explained using an octahedral crystal field description for Cr^{3+} ions [16]. This spectrum is given in figure 3. Three main bands at about 33 300 cm^{-1} (300 nm), 21 300 cm^{-1} (470 nm), and 14 180 cm^{-1} (705 nm) and a structure at 15 550 cm^{-1} (643 nm) are observed. The bands correspond to the electronic transitions from the $^4A_{2g}(^4F)$ ground state to the levels given in the figure while the structure is associated with the Fano antiresonance [17] due to spin–orbit interactions between the $^2E_g(^2G)$ and the $^4T_{2g}(^4F)$ levels. This absorption spectrum can be associated with Cr^{3+} in an octahedral environment with the following crystal field and Racah parameters:

$$D_q = 1420 \text{ cm}^{-1} \qquad B = 800 \text{ cm}^{-1} \qquad C = 3290 \text{ cm}^{-1}.$$

These results are slightly different from those given in [4] mainly in the case of B ($B = 757$ cm^{-1} in [4]).

Photoluminescence measurements have also been performed at different temperatures. At RT a broad band with the peak at about 11 500 cm^{-1} is observed. It corresponds to the phonon side band of the $^4T_2(^4F) \rightarrow {}^4A_2(^4F)$ electronic transition. The contributions of the different centres cannot be resolved in this RT spectrum. At low temperatures sharp lines appear superimposed on the broad band emission (see figure 4). They are associated with the zero-phonon lines and the vibronic replicas of the different types of Cr^{3+} centres. We will compare this spectrum with the one observed in $KZnF_3$ that is also shown in figure 4.

It is interesting to point out that the EPR spectra of the two crystals indicate that the same types of Cr^{3+} defects are present in both of them and with similar intensities. On the other hand it has been shown [9] that the main phonon frequencies involved in the structure in the case of $KZnF_3$ are those associated with some normal
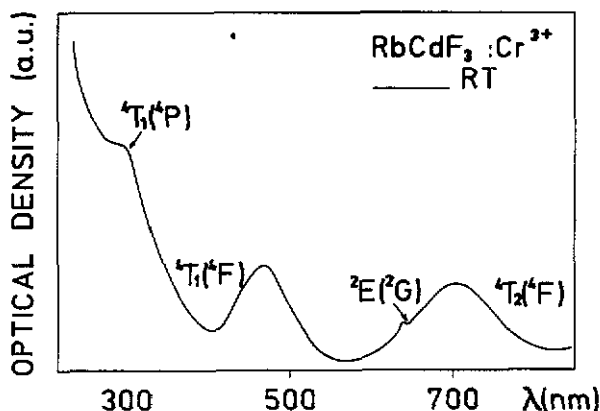
Figure 3. Optical absorption spectrum of RbCdF₃:Cr measured at RT. The bands correspond to transitions from the $^4A_2(^4F)$ ground state to the levels given in the figure.

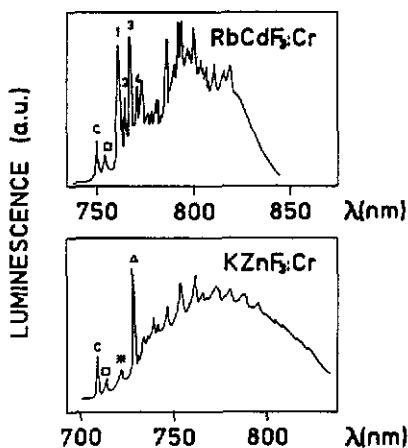**Figure 4.** Photoluminescence spectra of RbCdF₃:Cr and KZnF₃:Cr measured at 15 K.

modes of the $(CrF_6)^{3-}$ cluster which are expected not to change much from one matrix to another. Consequently we expect some similarities among the two phonon structures. An assignment of the phonon lines to different Cr^{3+} centres has been performed in KZnF₃ by several authors [4-6]. According to them the line at higher energy (14 091 cm⁻¹) marked with C in the figure, is the zero-phonon line of the cubic Cr^{3+} centres. The next one (at 14 016 cm⁻¹) marked with (□) has been assigned to the zero-phonon line of the tetragonal centres and the most intense one (at 13 765 cm⁻¹) marked with (△) is the zero-phonon line of the trigonal centres. The intermediate line marked with a (∗) in figure 4 has been tentatively associated with the coupling between the electronic states of cubic Cr^{3+} and some phonon modes of the matrix while the other lines at energies lower than 13 765 cm⁻¹ are the phonon replicas of the three zero-phonon lines. As we have already said the phonons involved in these lines correspond to local modes of the $(CrF_6)^{3-}$ octahedral complex having energies of 437 and 574 cm⁻¹ in the case of KZnF₃ [6]. These energies are close to those for

the vibrational modes e_g and a_{1g} of that complex in other fluorides [18–20].

By comparison with KZnF$_3$ the line (C) at the highest energy (13 303 cm^{-1} in RbCdF$_3$) can be assigned to the zero-phonon line of cubic centres because it has been found [4] that tetragonal and trigonal distortions split the $^4T_{2g}$ level of the cubic centres and give a decrease of the transition energy between the first excited state and the ground level $^4A_2$ in such a way that the transition to the first excited level appears at higher energies in the cubic centres than in the other ones. This assignment will be confirmed by lifetime measurements (see below).

Continuing the comparison we assign the next line (□) to zero-phonon transition of tetragonal centres. It appears at about 60 cm^{-1} of the cubic line in RbCdF$_3$ while this energy difference is about 75 cm^{-1} in KZnF$_3$.

It is worth mentioning that the structural phase transition which appears at 124 K in RbCdF$_3$ [12] could produce a splitting of that line. The phase transition causes an alternate rotation of the fluorine octahedra around a ⟨100⟩ direction as well as an elongation of the octahedra along the rotation axis. Of course different centres whose rotation axes are each of the three equivalent ⟨100⟩ directions appear. In the case of tetragonal Cr^{3+} ions the phase transition will produce two different types of centres depending on the relative orientation of the distortion axis with respect to the Cr^{3+}–Cd^{2+} vacancy direction (that is the tetragonal axis of the centre at temperatures above the phase transition). This splitting is not seen in our measurements (probably because it is too small as suggested by the small splitting of the EPR lines induced by the transition) [10].

Going down in energies we found some problems assigning the following lines in RbCdF$_3$. When we consider the spectral region at energy differences between 200 and 350 cm^{-1} with respect to the cubic zero-phonon transition, only two lines are observed in KZnF$_3$: the small and broad one-phonon replica of cubic centres (∗) and the sharp and intense zero-phonon line of the trigonal centres (Δ). On the other hand, the same spectral region in RbCdF$_3$ shows four narrow lines (1 to 4 in figure 4) at 13 107, 13 043, 13 004 and 12 945 cm^{-1}. Of course one of them is likely to be due to the zero-phonon transition of trigonal Cr^{3+} ions, but it is difficult to associate the presence of more phonon lines in RbCdF$_3$ than in KZnF$_3$ with other Cr^{3+} centres because, as we have said, the EPR spectra show the same types of Cr^{3+} and with similar intensity ratios in the two compounds. The structural phase transition that occurs in RbCdF$_3$ could be the reason for these extra lines because different perturbed centres could appear. However this is not the case either for the cubic Cr^{3+} ions or for the trigonal ones. The elongations and rotations of the fluorine octahedra associated with the phase transition are along the ⟨100⟩ axes and so only one type of distorted cubic or trigonal centre is expected in the low temperature phase. In the case of the tetragonal ions we have already mentioned that two different types of distorted centre appear. However, because of the low intensity of the zero-phonon line assigned to these centres and the small changes expected in the transition, it is not likely that the extra lines are due to perturbed tetragonal Cr^{3+}. Another possibility is that those lines are phonon replicas of the cubic zero-phonon lines since although the frequences of the phonons involved (200–350 cm^{-1}) are much smaller than those found in KZnF$_3$, other vibrational modes of the (CrF$_6$)$^{3-}$ complex have been found in that frequency range in several fluoride matrices [18–20].

In order to get more information about the origin of the phonon structure we also have performed some measurements at 15 K of the decay of the light emitted in the cubic zero-phonon line and the lines 1 and 3 in figure 4 after switching the

excitation off. The resolution used in the monochromator of the detection system was about 5 cm^{-1} for these measurements. When the detection was performed in the 13 303 cm^{-1} line an exponential decay was observed corresponding to a lifetime of about 470 μs, which is the lifetime reported for cubic Cr^{3+} centres in this compound [4] at low temperature.

At either 13 107 cm^{-1} or 13 004 cm^{-1} non-exponential decays are observed. We have tried to fit these decays to the sum of two single exponentials and a good fit as been found for decay times of about 470 μs and 220 μs. This can be understood if our decay measurements have contributions coming from two different types of Cr^{3+} centre with these lifetimes. As we have just said the lifetime corresponding to cubic Cr^{3+} is 470 μs and by comparison with the results given in [4] the other centres can be the trigonal ones with a lifetime of about 220 μs. Consequently we assign the 13 107 cm^{-1} line to the zero-phonon transition of trigonal Cr^{3+} ions. The 470 μs component can come from the phonon side band of cubic centres that appears superimposed on the zero-phonon line of the trigonal centres.

In the case of the 13 004 cm^{-1} emission it is not clear which is the contribution from the line and which is due to the background associated with the phonon side band. Trying to correlate this line with either the cubic or the trigonal centres we have measured the relative intensities (with respect to the broad band background) of the three lines (13 303, 13 107 and 13 004 cm^{-1}) at two different times (50 μs and 1 ms) after switching the exciting light off. It has been found that the relative intensities of the 13 303 and 13 004 cm^{-1} lines are the same in both measurements while the intensity of the 13 107 cm^{-1} line decreases more rapidly with time. Because of this we associate the 13 004 cm^{-1} line with a phonon replica of the 13 303 cm^{-1} line due to the cubic Cr^{3+} ions. For the lines at 13 043 and 12 945 cm^{-1} similar measurements have been attempted but no reliable results are obtained because of the low signal/noise ratio in these measurements.

As we have already said the vibrational structure of Cr^{3+} emissions in the $(CrF_6)^{3-}$ complex has been analysed in different compounds. Sharp lines at 235, 296, 309, 321, 340 and 359 cm^{-1} have been reported for example in $LiCaAlF_6$:Cr^{3+} [20], and have been assigned to different vibrational modes of the complex. In a similar way we propose that the lines 2 to 4 in figure 4 whose energy differences with the cubic zero-phonon line range from 260 to 360 cm^{-1} are phonon replicas of the cubic Cr^{3+} centres emission, associated with vibrations of the $(CrF_6)^{3-}$ octahedron. An assignment of each of the lines to a definitive mode cannot be made with our present results.

It is not clear why in $KZnF_3$:Cr only the vibrational lines corresponding to the e_g and a_{1g} modes are observed while in $RbCdF_3$:Cr more lines, probably due to the interaction with other modes of the $(CrF_6)^{3-}$ complex are seen. The main difference between the two compounds besides the change in the Cr–F distance is the structural phase transition that appears in $RbCdF_3$ and not in $KZnF_3$. The intensity of the lines associated with t_{1u} and t_{2u} vibrational modes comes from the 3d–4p mixing and this could be stronger in $RbCdF_3$ if the energy difference between the 3d and 4p states were smaller in this compound. It is also possible that the lattice distortion associated with the 124 K phase transition could provide the mechanism to increase the coupling of the Cr^{3+} electronic states with the vibrational modes. To unravel this problem a more detailed study involving other chromium-doped fluoroperovskites seems to be necessary.

We have also performed decay measurements with low resolution (2 nm) and with the detection centred at 810 nm at different temperatures between 15 K and 300 K.

Non-exponential decays have been observed as expected because of the contribution of the different types of Cr^{3+} centres. To get some idea about the temperature dependence of the lifetime of cubic ions that seem to give the dominant contribution to the light emitted at 810 nm we have tried to fit the decay to a single exponential using only the data for $t > 400$ μs after switching the excitation off. The measured decay times decrease from 470 μs at 15 K to about 180 μs at 300 K in reasonable agreement with the results reported in [4]. This behaviour is due to the increase of the non-radiative multiphonon relaxation rate.

Finally we want to mention that careful photoluminescence and decay measurements have been performed at temperatures above and below 124 K in order to detect any possible influence of phase transition on the optical properties of our samples, but in agreement with [4] no significant changes have been found within our experimental accuracy. This is not unexpected because the distortion induced by the phase transition is small. Besides, since the transition has a dominant second-order character [10], smooth changes of the crystal field parameters are expected at the transition temperature and it is difficult to detect their influence. So we can conclude that the only detectable effect (if any) of the phase transition on the optical properties of Cr^{3+} in our crystals could be the new phonon lines observed in the low temperature spectrum when we compare it with that of $KZnF_3$.

Acknowledgments

References

[1]   Durr U, Brauch U, Knierim W and Schillar C 1985 *Tunable Solid State Lasers* ed P Hammerling, A G Budgor and A Pinto (Berlin: Springer) p 20
[2]   Brauch U and Durr U 1984 *Opt. Commun.* **49** 61
[3]   Brauch U and Durr U 1984 *Opt. Lett.* **9** 441
[4]   Brauch U 1986 *PhD Thesis* University of Stuttgart, unpublished
[5]   Pilla O, Galvanetto E, Montagna M and Viliani G 1988 *Phys. Rev.* B **38** 3477
[6]   Vaills Y, Buzaré J Y and Rousseau M 1990 *J. Phys.: Condens. Matter* **2** 3997
[7]   Binois M, Leblé A, Rousseau J J and Fayet J 1973 *J. Physique Coll.* **34** C9 285
[8]   Pattel J L, Davies J J, Cavenette B C, Takeuchi H and Horai K 1976 *J. Phys. C: Solid State Phys.* **9** 129
[9]   Rousseau J J, Gesland J Y, Binois M and Fayet J 1974 *C R Acad. Sci. Paris* **279** B 103
[10] Arakawa M 1979 *J. Phys. Soc. Japan* **46** 1245
[11] Studzinski P and Spaeth J M *Phys. Status Solidi* b **136** 735
[12] Rousseau M, Gesland J Y, Julliard J, Nouet J, Zarembowitch J and Zarembiwitch A 1975 *Phys. Rev.* B **12** 1579
[13] Rousseau J J, Rousseau M and Fayet J C 1976 *Phys. Status Solidi* b **73** 625
[14] Studzinsky P and Spaeth J M 1986 *J. Phys. C: Solid State Phys.* **19** 6441
[15] Abragam A and Bleaney B 1970 *Electron Paramagnetic resonance of transition ions* (Oxford: Clarendon) p 431
[16] McClure D S 1959 *Solid State Physics* vol 9, ed F Seitz and D Turnbull (New York: Academic) p 400
[17] Fano U 1961 *Phys. Rev.* **124** 1866
[18] Wannemacher R and Meltzer R S 1989 *J. Lumin.* **43** 251
[19] Dubicki L, Ferguson J and von Oosterhout B 1980 *J. Phys. C: Solid State Phys.* **13** 2791
[20] Payne S A, Chase L L and Wilke G D 1989 *J. Lumin.* **44** 167