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Optical absorption spectra of Pr³⁺ doped in yttrium pyrogermanate (Y₂Ge₂O₇) crystal

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Abstract. This paper reports the low temperature absorption and Zeeman spectra of Pr³⁺ doped in yttrium pyrogermanate (YPG), which were studied for the first time. In this compound the site symmetry of Pr³⁺, or the crystal field (CF) symmetry, was found to be D_{5h}, as present in other rare earth pyrogermanates, and not C₁. The spectral results were analysed by diagonalizing the total Hamiltonian consisting of the atomic (electrostatic, spin–orbit and configuration interactions) and the CF interactions, in a basis of 91|*SLJM_J*⟩ states spanning the entire 4f² ground configuration of Pr³⁺ in the intermediate coupling formalism, including *J*-mixing under CF. The best fitted free ion and CF parameters obtained were $E^1 = 4335.0$, $E^2 = 23.1$, $E^3 = 464.0$, $\zeta = 775.0$, $\alpha = 22.9$, $\beta = -674.0$, $\gamma = 1520.0$, $B_{20} = -100$, $B_{40} = 1650$, $B_{60} = -1600$ and $B_{65} = -1000$ (all in cm⁻¹). Using these parameters the thermal characteristics of molar magnetic susceptibilities (K_{\parallel} , K_{\perp}), their anisotropy $\Delta K = \pm(K_{\parallel} - K_{\perp})$ and the Schottky specific heat (C_{Sch}) of Pr³⁺ in YPG were calculated. It was found that the calculated values of $K_{\parallel} > K_{\perp}$ between 300 and 152 K (T_i) but on cooling further $K_{\perp} > K_{\parallel}$ was observed, i.e. the sign of ΔK was reversed below T_i . The calculated values of C_{Sch} exhibited a sharp peak at 24 K and a broad maximum at 156 K. These characteristics were similar to other Pr³⁺ compounds studied earlier.

1. Introduction

The rare earth pyrogermanates (RPG), have a general formula R₂Ge₂O₇ in which the R³⁺ ion has a sevenfold coordination, which is very rare. Single crystals of the heavy RPG (R = Gd–Lu and Y) belong to an interesting isomorphous series, having a tetragonal space group symmetry $P4_12_12$ (D₄⁴) and a unique D_{5h} point group symmetry [1–8]. The seven oxygens from the pyro group are coordinated to the R³⁺ ion in the form of a slightly distorted pentagonal bipyramid, having a common base, and the R atoms lie nearly in the basal plane [1]. Consequently the crystal field (CF) produced by the anionic oxygens at the R³⁺ cationic site has D_{5h} point symmetry, the axis of which nearly coincides (~5° off) with the tetragonal (D₄⁴) *c*-axis. For this reason experimental studies and CF analysis of the data of the spectral and magnetic properties of these RPG crystals are quite convenient and accurate, as was demonstrated earlier from the studies of (i) circular dichroism (CD) spectra of ErPG [9], TmPG and TbPG [10] and GdPG [11]; (ii) optical absorption spectra of ErPG and DyPG [12, 13], GdPG [14] and TmPG [15]; (iii) magnetic susceptibilities and anisotropies of TmPG [16], DyPG [17], HoPG [18], ErPG [19] and GdPG [14]; (iv) nuclear hyperfine effects in TmPG [20] and DyPG [21].

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It is relevant to mention here that, from the study of the Mössbauer spectra (MS) of TmPG between 740 and 4.2 K, Stewart *et al* [22] observed only a quadrupole splitting due to a doublet pattern of the first excited nuclear level of ^{169}Tm . From such an observation they suggested that the lowest CF level from the ground $^3\text{H}_6$ term of TmPG was a singlet and not a doublet because, in the latter case, a sextet pattern would have appeared in the MS at low temperatures. Prior to this study, we reported [20] a doublet level lowest in TmPG from the analysis of the magnetic susceptibility and anisotropy results of this crystal [15]. Stewart *et al* [22] also studied the XRD of the TmPG crystal and noted that when viewed along the tetragonal *c*-axis the molecular polyhedron of TmPG appeared to have a pentagonal $\text{D}_{5\text{h}}$ symmetry, but when looked at along the perpendicular direction a small deviation from this symmetry was noted because the R atom was slightly displaced from the basal plane. In view of this, they considered the CF in TmPG to have triclinic C_1 symmetry, in which case all CF levels of each of the multiplets are singlet levels. In order to analyse their MS results, they used two types of point charge model (PCM) calculation, employing a semi-empirical method of analysis to characterize the C_1 symmetry, and expressed the associated 27 CF parameters in terms of only four independent ones. However Stewart *et al* failed to obtain reasonably consistent values especially for the rank $n = 2$ of the CF ratio calculations [22]. It is well known that PCM calculations 'are notoriously unsuccessful for predicting absolute values of CF parameters', as was acknowledged by Stewart *et al* [22] themselves and others [23, 24]. Saxe *et al* [25] also observed that CF values obtained from PCM calculations and from optical studies differed, even by five- to tenfold in case of the B_{20} parameter because of strong shielding effect on the $\langle r^2 \rangle$ values.

In view of such contradictions, we later studied the optical absorption spectra of TmPG at 80 and 10 K and the level patterns of the different multiplets in the visible region, details of which did not indicate C_1 symmetry [15]. Furthermore, on remeasurement of the magnetic anisotropy of TmPG, we detected a simple mistake in our records of our earlier results, which led to the wrong assignment of the sign of the anisotropy. Considering these findings, we were able to explain the optical, magnetic and MS results of TmPG consistently using $\text{D}_{5\text{h}}$ symmetry [15]. This motivated the present study of the low temperature absorption and Zeeman spectra of Pr^{3+} doped (2%) in YPG, in order to determine the CF symmetry at the Pr^{3+} site in YPG, which developed as a tetragonal (D_4) crystal and has a CF with $\text{D}_{5\text{h}}$ symmetry [8].

To date a considerable amount of spectroscopic work has been reported involving interpretation of the optical spectra of Pr^{3+} ion embedded in different crystalline solids, as have been reviewed in research books [24, 26–28] and published in research papers by experimentalists [29–36] and theoretical workers [37–39]. This is because the spectra of Pr compounds are reasonably simple, arising from fewer widely spaced multiplets compared to the spectra of heavier R ions, so that spectral analysis is easy. To date, there has been no report on the optical absorption spectra or the magnetic properties of $\text{Pr}_2\text{Ge}_2\text{O}_7$ or on Pr^{3+} doped in other germanate lattices or on any compounds of Pr^{3+} having $\text{D}_{5\text{h}}$ CF symmetry. All these facts provided further motivation for the present study on $\text{Pr}^{3+}:\text{YPG}$ (or PrYPG).

In case of lighter RPGs ($\text{R} = \text{La, Pr, Nd, Gd}$) [8], the crystals have $P1$ or $P\bar{1}$ space group symmetry depending on the ionic radius. It is well known that in the case of paramagnetic crystals belonging to the triclinic class, determinations of the principal magnetic susceptibility tensors of the crystalline or the molecular ellipsoid from direct measurements are extremely laborious [40, 41]. For such a reason, studies of the magnetic susceptibilities as well as the optical properties of triclinic crystals for evaluating CF effects are generally avoided. However by doping Pr^{3+} (2%) in the tetragonal YPG crystal, experimental work becomes easier and at the same time allows study of the spectra of Pr^{3+} in the PG host with greater accuracy. The analysis of the spectral results of PrYPG is expected to provide accurate values of the CF energy values

and wavefunctions of the ground and excited multiplets which can be utilized for comparison with the corresponding results of other Pr³⁺ crystals in different hosts. Furthermore, using the CF level patterns and the corresponding wavefunctions of the ground ³H₄ multiplet of PrYPG, it was further aimed to calculate the thermal characteristics of the molar magnetic susceptibilities, their anisotropies and the paramagnetic Schottky specific heat, and then to find out whether these properties resemble those of other Pr³⁺ compounds.

2. Theoretical considerations

The analysis of the PrYPG spectral results was done by diagonalizing a total Hamiltonian, describing the free ion interactions H_{FI} together with the CF interaction H_{CF} , in 91 $|SLJM_J\rangle$ basis states spanning the entire 4f² electronic ground configuration of Pr³⁺. Full J -mixing under CF was considered for a realistic approach.

The free ion Hamiltonian H_{FI} considered has the standard form, i.e.,

$$H_{FI} = E^1 e^1 + E^2 e^2 + E^3 e^3 + \zeta \sum_i l_i \cdot s_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(G_7)$$

where the symbols have their usual meanings as discussed elsewhere [42].

The CF Hamiltonian appropriate for D_{5h} symmetry was defined as

$$H_{CF} = B_{20}U_{20} + B_{40}U_{40} + B_{60}U_{60} + \text{Re } B_{65}(U_{65} - U_{6-5})$$

where U_{kq} are unit irreducible tensors and B_{kq} ($=\bar{B}_{kq}$ of table 4 of [24]) are the even parity CF parameters [42, 43]. Since the FI level patterns do not vary much from host to host, we used the 13 intermediately coupled (IC) free ion states of Pr³⁺ in LaCl₃, for calculating the reduced matrix elements of U^2 , U^4 and U^6 , following standard procedures [26, 42, 44] using a computer program developed by us. For fitting the spectra of PrYPG as closely as possible, the FI parameters were slightly varied and the CF parameters were exhaustively varied.

The energy values E_i and wavefunctions ψ_i obtained from best fitted parameters were then used to calculate the splitting factors g_{\parallel} and g_{\perp} for all the CF doublet levels. Next using Van Vleck's formula [45], expressions were derived for the molar magnetic susceptibilities K_{\parallel} and K_{\perp} , which are respectively in the directions parallel and perpendicular to the D_{5h} axis, the anisotropy $\Delta K = \pm(K_{\parallel} - K_{\perp})$ and the mean magnetic susceptibility $\bar{K} = (K_{\parallel} + 2K_{\perp})/3$, as functions of temperature. Also the thermal characteristic of the Schottky component (C_{Sch}) of the electronic specific heat was calculated using the following standard formula [46].

$$C_{Sch} = \frac{R}{Z^2} \left[Z \sum_{i=1}^n x_i^2 \exp(-x_i) - \left\{ \sum_{i=1}^n x_i \exp(-x_i) \right\}^2 \right]$$

x_i being the n CF energy values divided by kT ; Z and R are the partition function and gas constant respectively.

3. Results and discussion

3.1. Optical absorption spectra

Single crystals of Pr³⁺ (2%) in YPG were grown from flux growth at the Clarendon Laboratory, Oxford University. The pale green coloured crystals developed as thin platelets with a well developed c -plane. Crystal selection and mounting were done under a polarizing microscope. The crystal was mounted on a small hole on a copper sheet which was bolted to the cold tip of an optical shroud of a helium cryocooler (Air Products 202). The crystal was mounted by means of apiezon grease impregnated with copper powder to make it a better heat conductor.

The absorption spectra of PrYPG at 10 K were taken photographically on film (ORWO NP77) in a Carl Zeiss plane grating spectrograph (PGS-2), having dispersion $3.38\text{--}3.55 \text{ \AA mm}^{-1}$ in the second order. The microphotometric tracings of the spectra were taken with a Kipp and Zomen microphotometer, modified to trace the spectra in an XY-recorder (Rikadenki RW 201). The absolute accuracy is 2 cm^{-1} and relative accuracy for some lines is 1 cm^{-1} and results obtained in this manner are reproducible to less than 0.5 \AA over the entire range. Suitable Corning filters were used to reduce the effect of the scattered light and to avoid unnecessary heating of the crystal. Spectral lines were calibrated by mercury lines [15]. Zeeman spectra of the crystal placed in a pulsed magnetic field of $49 \pm 0.5 \text{ kG}$, applied along the c -axis of the crystal, were recorded at 15 K and experimental details have been given elsewhere [46].

Most of the transition lines observed were of low intensity and some were quite weak which is due to the low concentration of Pr^{3+} in YPG, for which reason transitions from the first or second CF levels of the $^3\text{H}_4$ ground term could not be resolved meaningfully in the 80 and 10 K spectra. Thus the spectral lines corresponded to transitions from only the lowest level to the excited multiplets so that the values of the energy levels of the excited multiplets were directly obtained from the spectra. The spectra of PrYPG did not show polarization as in other RPG crystals [10, 12, 13, 15].

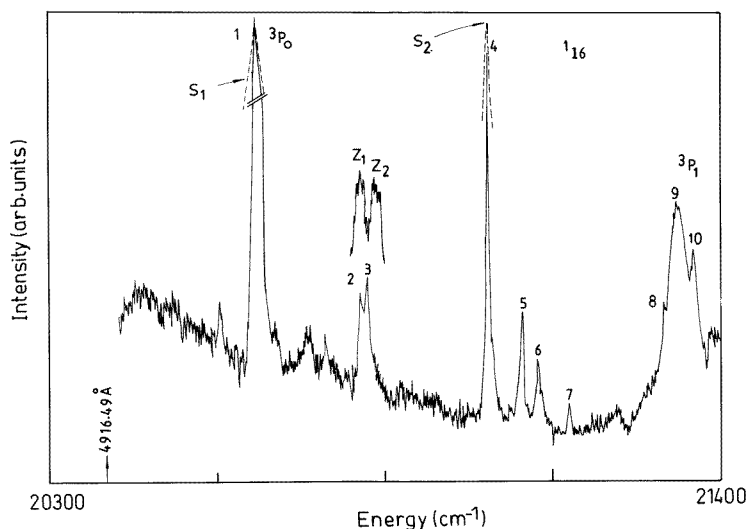


Figure 1. Optical absorption spectra of $^3\text{P}_{0,1}$ and $^1\text{I}_6$ multiplets of $\text{Pr}^{3+}:\text{YPG}$ at 10 K. The arrow shows the mercury line (used as standard in this region of spectra). Z_1 and Z_2 are the Zeeman peaks for the doublets at 20772 and 20782 cm^{-1} . S_1 and S_2 (—) are the singlet levels (intensity scale different) unaffected under Zeeman field.

Figures 1 and 2 show the microphotometric traces of the absorption spectra of $^1\text{D}_2$, $^3\text{P}_{0,1,2}$, and $^1\text{I}_6$ multiplets of PrYPG. The IC states of Pr^{3+} , used in the present CF calculation, and the calculated values along with the observed values of the CF energy levels of different multiplets are given respectively in tables 1 and 2. In the transitions $^3\text{H}_4 \rightarrow ^1\text{D}_2$, $^3\text{P}_2$ and $^1\text{I}_6$, we observed respectively three, two and seven lines and there were two lines in the $^3\text{H}_4 \rightarrow ^3\text{P}_1$ transition, which indicated that the CF symmetry in the PrYPG is not C_1 . Furthermore, Zeeman splittings of two doublet levels of $^1\text{I}_6$ multiplet were noted as discussed below.

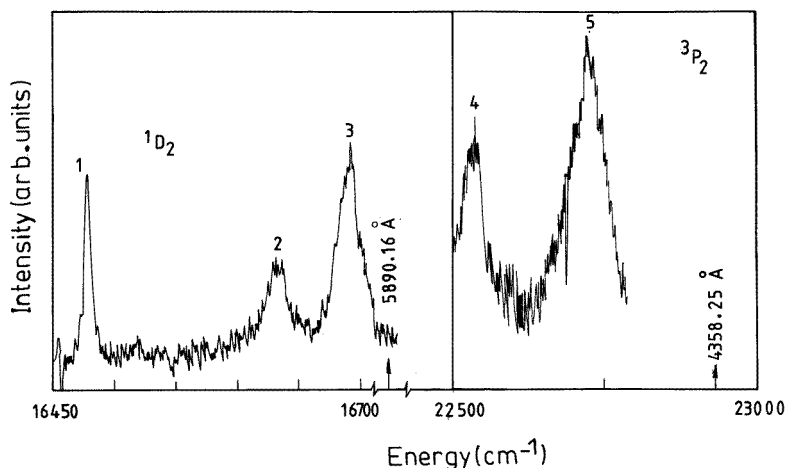


Figure 2. Optical absorption spectra of 3P_2 and 1D_2 multiplets of Pr³⁺:YPG at 10 K. The arrows show the mercury lines (used as standards in the regions of spectra).

Table 1. IC states of Pr³⁺ used in CF calculation of Pr³⁺:YPG.

Multiplets	IC states
3P_0	$0.994 ^3P_0 + 0.112 ^1S_0$
3P_1	$1.0 ^3P_1$
3P_2	$0.958 ^3P_2 + 0.285 ^1D_2 - 0.032 ^3F_2$
3F_2	$-0.986 ^3F_2 - 0.164 ^1D_2 + 0.016 ^3P_2$
3F_3	$1.0 ^3F_3$
3F_4	$-0.707 ^3F_4 + 0.689 ^1G_4 - 0.160 ^3H_4$
3H_4	$0.981 ^3H_4 + 0.191 ^1G_4 - 0.036 ^3F_4$
3H_5	$1.0 ^3H_5$
3H_6	$-0.998 ^3H_6 + 0.059 ^1I_6$
1S_0	$0.994 ^1S_0 - 0.112 ^3P_0$
1D_2	$0.944 ^1D_2 - 0.286 ^3P_2 - 0.162 ^3F_2$
1G_4	$0.699 ^1G_4 + 0.707 ^3F_4 - 0.110 ^3H_4$
1I_6	$0.998 ^1I_6 + 0.059 ^3H_6$

$^3H_4 \rightarrow ^3P_0$. The transition $^3H_4 \rightarrow ^3P_0$ was observed at $20\,595\text{ cm}^{-1}$ (peak 1 of figure 1). The line being quite isolated and sharp, it was very easy to identify this transition.

$^3H_4 \rightarrow ^3P_1$. Inspection of figure 1 showed that there are two comparatively intense lines at $21\,303$ and $21\,325\text{ cm}^{-1}$ (peaks 8, 9 respectively of figure 1) which were assigned as 3H_4 ($\mu = 0$) \rightarrow 3P_1 ($\mu = \pm 1, 0$) transitions. Overlap of 3P_1 with 1I_6 was also observed in PrVO₄ and Pr(OH)₃ [46, 47]. The total splitting of 3P_1 was found to be $23 \pm 1\text{ cm}^{-1}$ and our calculated value is $25 \pm 1\text{ cm}^{-1}$. The corresponding splitting of 3P_1 or Pr³⁺ in LaCl₃ [30, 32], LaBr₃ [48, 49] and La³⁺ ethylsulphate (LaES) [35, 36] are 30, 29 and 9 cm^{-1} respectively.

$^3H_4 \rightarrow ^1I_6$. From figure 1 it is found that there are seven lines (peaks 2–7 and 10) lying between $20\,772$ and $21\,352\text{ cm}^{-1}$, which were assigned as 3H_4 ($\mu = 0$) \rightarrow 1I_6 ($\mu = \pm 1, \pm 2, 5, \pm 2', \pm 1', \pm 1'', 0'$) transitions. All lines, except the singlet line at $20\,988\text{ cm}^{-1}$, were of low intensity. This is a very common feature of Pr³⁺ compounds and in some cases some of the transitions of 1I_6 cannot be observed [26]. The total observed splitting was 578 cm^{-1} and the corresponding calculated value is 598 cm^{-1} . Zeeman splittings were observed only

Table 2. Observed (E_O) and calculated (E_C) energies in cm^{-1} for the multiplets of Pr^{3+} :YPG. g_{\parallel} values (g_{\perp} being 0 for the doublets) and magnetic quantum number μ [26] for the multiplets are also given. The best fitted FI and CF parameters obtained are $E^1 = 4335.0$, $E^2 = 23.1$, $E^3 = 464.0$, $\zeta = 775$, $\alpha = 22.9$, $\beta = -674.0$, $\gamma = 1520.0$, $B_{20} = -100$, $B_{40} = 1650$, $B_{60} = -1600$ and $B_{65} = -1000$ (all in cm^{-1}).

Multi-plets	Atomic parentages	μ	E_O (in cm^{-1})	E_C (in cm^{-1})	g_{\parallel}
$^3\text{H}_4$	96% $^3\text{H}_4 + 3.4\%$ $^1\text{G}_4 + 0.4\%$ $^3\text{H}_5$	0		0	
	95.6% $^3\text{H}_4 + 3.4\%$ $^1\text{G}_4 + 0.7\%$ $^3\text{H}_5$	± 1		44	3.28
	95.6% $^3\text{H}_4 + 3.9\%$ $^1\text{G}_4 + 0.4\%$ $^3\text{H}_5$	$\pm 1'$		216	0.93
	95.6% $^3\text{H}_4 + 3.4\%$ $^1\text{G}_4 + 0.5\%$ $^3\text{H}_5 + 0.4\%$ $^3\text{F}_4$	± 2		295	3.51
	95.4% $^3\text{H}_4 + 3.9\%$ $^1\text{G}_4 + 0.3\%$ $^3\text{F}_3$	$\pm 2'$		418	2.16
$^1\text{D}_2$	90% $^1\text{D}_2 + 7.2\%$ $^3\text{P}_2 + 2.3\%$ $^3\text{F}_2 + 0.4\%$ $^1\text{I}_6$	± 1	16 476	16 467	1.83
	88.8% $^1\text{D}_2 + 8.1\%$ $^3\text{P}_2 + 2.6\%$ $^3\text{F}_2 + 0.4\%$ $^1\text{I}_6$	± 2	16 640	16 661	4.04
	87.3% $^1\text{D}_2 + 8.9\%$ $^3\text{P}_2 + 2.9\%$ $^3\text{F}_2 + 0.9\%$ $^1\text{I}_6$	0	16 690	16 773	
$^3\text{P}_0$	94.5% $^3\text{P}_0 + 4.2\%$ $^1\text{I}_6 + 1.3\%$ $^1\text{S}_0$	0	20 595	20 601	
$^3\text{P}_1$	95.1% $^3\text{P}_1 + 4.8\%$ $^1\text{I}_6$	± 1	21 303	21 301	2.56
	99.9% $^3\text{P}_1$	0	21 325	21 325	
$^1\text{I}_6$	98.8% $^1\text{I}_6 + 0.8\%$ $^3\text{P}_2 + 0.3\%$ $^3\text{H}_6$	± 1	20 772	20 770	1.94
	99.3% $^1\text{I}_6 + 0.3\%$ $^3\text{H}_6 + 0.2\%$ $^3\text{P}_2$	± 2	20 782	20 866	2.91
	95.7% $^1\text{I}_6 + 2.8\%$ $^3\text{P}_0 + 1.1\%$ $^3\text{P}_2 + 0.3\%$ $^3\text{H}_6$	0		20 913	
	99.7% $^1\text{I}_6 + 0.3\%$ $^3\text{H}_6$	5	20 988	20 914	
	98.2% $^1\text{I}_6 + 1.4\%$ $^3\text{P}_2 + 0.3\%$ $^3\text{H}_6$	$\pm 2'$	21 047	21 067	3.96
	99.3% $^1\text{I}_6 + 0.3\%$ $^3\text{H}_6 + 0.3\%$ $^3\text{P}_2$	$\pm 1'$	21 074	21 217	10.20
	93.6% $^1\text{I}_6 + 4.9\%$ $^3\text{P}_1 + 1.2\%$ $^3\text{P}_2 + 0.3\%$ $^3\text{H}_6$	$\pm 1''$	21 134	21 289	2.18
	94.6% $^1\text{I}_6 + 3.5\%$ $^3\text{P}_2 + 1.4\%$ $^3\text{P}_0 + 0.4\%$ $^3\text{H}_6$	$0'$	21 352	21 367	
$^3\text{P}_2$	90.5% $^3\text{P}_2 + 7.5\%$ $^1\text{D}_2 + 1.9\%$ $^1\text{I}_6$	± 1	22 527	22 521	2.96
	90.2% $^3\text{P}_2 + 8.4\%$ $^1\text{D}_2 + 1.3\%$ $^1\text{I}_6$	± 2		22 622	5.77
	86.5% $^3\text{P}_2 + 9.7\%$ $^1\text{D}_2 + 3.8\%$ $^1\text{I}_6$	0	22 720	22 712	

for the two doublets at 20 772 and 20 782 cm^{-1} (table 2) which have been shown in figure 1. Under the pulsed field, the separation between these two adjacent doublets increased by about 5 cm^{-1} and showed some unresolved components, suggesting Zeeman splitting of the levels. Using the wavefunctions corresponding to these doublets, the values of the splitting factors were found to be respectively 1.94 and 2.91 (table 2) so the Zeeman levels are expected at 20 769.8, 20 774.2 and at 20 778.7, 20 785.3 cm^{-1} . Thus the calculated separation between the two extreme levels was $15.5 \pm 0.3 \text{ cm}^{-1}$ which is close to the observed value (between Z_1 and Z_2) of $16.5 \pm 0.2 \text{ cm}^{-1}$.

$^3\text{H}_4 \rightarrow ^3\text{P}_2$. Two lines, separated by 193 cm^{-1} , were observed in the $^3\text{P}_2$ multiplet (peaks 4 and 5 of figure 2) which are respectively due to $^3\text{H}_4 (\mu = 0) \rightarrow ^3\text{P}_2 (\mu = \pm 1, \pm 2, 0)$ transitions. The corresponding calculated value of the splitting of $^3\text{P}_2$ is 191 cm^{-1} , which is quite close to the observed value. The splitting of Pr^{3+} in LaCl_3 [30, 32], LaBr_3 [48, 49] and LaES [35, 36] are 39, 37 and 23 cm^{-1} respectively, all of which are much smaller than that in PrYPG . A very weak line was observed around 22 600 cm^{-1} which may be due to $^3\text{H}_4 (\mu = 0) \rightarrow ^3\text{P}_2 (\mu = \pm 2)$, the corresponding calculated value of which is 22 622 cm^{-1} . It may be remarked here that in order to match the centroid of $^3\text{P}_2$ multiplet, the value of ζ had to be increased from the corresponding value in Pr^{3+} in LaCl_3 [27].

$^3H_4 \rightarrow ^1D_2$. In the transitions $^3H_4 (\mu = 0) \rightarrow ^1D_2 (\mu = \pm 1, \pm 2, 0)$, only three lines were observed (peaks 1–3 of figure 2) and the total splitting was found to be 224 cm^{-1} . The corresponding splittings of Pr³⁺ in LaCl₃ [30, 32], LaBr₃ [48, 49] and LaES [35, 36] are respectively 150, 132 and 246 cm^{-1} . However, the calculated value of the total splitting of 1D_2 is 306 cm^{-1} in PrYPG, which is rather higher than the observed value. This type of discrepancy for this multiplet is very common in Pr³⁺ compounds [37, 38, 42, 46]. From table 2 it is seen that the overall matching between the observed and calculated values of energy levels is quite good except for one of the levels at $16\,690 \text{ cm}^{-1}$ in the 1D_2 multiplet. In the case of the 1D_2 multiplet of Pr³⁺ compounds, a similar type of ‘anomalous CF splittings’ has been observed and was explained by considering spin correlated CF effects (SCCFs) [37, 38, 50]. Thus there is scope for applying SCCF theory for closer fitting of the multiplet levels of PrYPG.

The large splittings in almost all the observed excited multiplets indicated a stronger CF perturbation in PrYPG compared to Pr³⁺ in LaCl₃, LaBr₃ and LaES [22]. This is also consistent with the findings in other RPG crystals in which CF was also found to be strong. Also the multiplet patterns of PrYPG did not indicate C₁ symmetry, but were closely fitted considering the CF with D_{5h} symmetry.

3.2. Magnetic susceptibilities

Magnetic susceptibilities K_{\parallel} , K_{\perp} are ground term properties due to the Boltzmann term in the Van Vleck formula [45]. Table 3 shows that only the 1G_4 multiplet is appreciably mixed with the ground 3H_4 multiplet of PrYPG by the CF interaction. The table further shows that the lowest singlet level of the 3H_4 term is followed by a doublet at 44 cm^{-1} and the total splitting of the multiplet is 418 cm^{-1} .

Table 3. Energy values and wavefunctions of CF levels of the ground multiplet 3H_4 of Pr³⁺:YPG.

Energy values (E_i) in cm^{-1}	Magnetic quantum	
	No μ	Wavefunction (ψ_i)
0	0	$0.979 ^3H_4, 0\rangle + 0.183 ^1G_4, 0\rangle$
44	± 1	$\pm 0.776 ^3H_4, \pm 4\rangle \mp 0.050 ^3H_4, \pm 1\rangle + 0.588 ^3H_4, \mp 1\rangle + 0.067 ^3H_4, \mp 4\rangle$ $\pm 0.148 ^1G_4, \pm 4\rangle + 0.111 ^1G_4, \mp 1\rangle$
216	$\pm 1'$	$0.199 ^3H_4, \pm 4\rangle + 0.732 ^3H_4, \pm 1\rangle \pm 0.262 ^3H_4, \mp 1\rangle \pm 557 ^3H_4, \mp 4\rangle$ $+ 0.146 ^1G_4, \pm 1\rangle \pm 0.116 ^1G_4, \mp 4\rangle$
295	± 2	$-0.905 ^3H_4, \pm 3\rangle \mp 0.369 ^3H_4, \mp 2\rangle - 0.168 ^1G_4, \pm 3\rangle$ $\mp 0.072 ^1G_4, \mp 2\rangle$
418	$\pm 2'$	$-0.372 ^3H_4, \pm 3\rangle \pm 0.903 ^3H_4, \mp 2\rangle \pm 0.074 ^3H_4, \pm 3\rangle$ $\pm 0.184 ^1G_4, \mp 2\rangle$

The energy values and wavefunctions of CF levels of the ground 3H_4 term (table 3), corresponding to the best fitted parameters determined from the optical work, were used to calculate the thermal characteristics of K_{\parallel} , K_{\perp} and $\Delta K = \pm(K_{\parallel} - K_{\perp})$. Inspection of figure 3 shows that on cooling down from 300 to 245 K, $\Delta K = K_{\parallel} - K_{\perp}$ increased from 183×10^{-6} to $201 \times 10^{-6} \text{ emu mol}^{-1}$ ($=3.6\% - 3.3\%$ of \bar{K}). However on further cooling, ΔK decreased to zero value at 152 K ($\equiv T_i$) and then on further cooling the sign of ΔK reversed indicating that $K_{\perp} > K_{\parallel}$ for $T < T_i$ and $K_{\perp} - K_{\parallel}$ increased sharply, becoming equal to $34\,180 \times 10^{-6} \text{ emu mol}^{-1}$ at 10 K. Inspection of figure 3 reveals that K_{\parallel} and K_{\perp} increased on cooling as expected; however below 60 K the former decreased on cooling. Between 300 and 60 K, the value of K_{\parallel} increased from $57\,153 \times 10^{-6} \text{ emu mol}^{-1}$ to a maximum value of

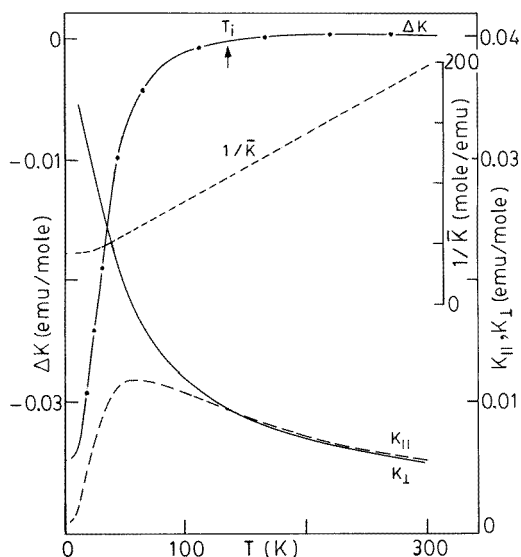


Figure 3. Calculated thermal characteristics of ΔK (— · —), $1/\bar{K}$ (---), K_{\parallel} (— — —) and K_{\perp} (—) Pr^{3+} : YPG. T_i denotes the inversion temperature.

$11858 \times 10^{-6} \text{ emu mol}^{-1}$ but decreased on cooling and was only $392 \times 10^{-6} \text{ emu mol}^{-1}$ at 10 K. On the other hand, K_{\perp} increased from 4969×10^{-6} to $34570 \times 10^{-6} \text{ emu mol}^{-1}$ between 300 and 10 K.

It is relevant to mention here that similar type of inversion of sign of ΔK at a particular low temperature T_i had been also observed while measuring the magnetic anisotropy in single crystals of other Pr^{3+} compounds [42, 46, 47]. In such cases it was noted that on cooling at and below T_i , the freely suspended crystal rotated sharply by 90° because K_{\perp} , being greater than K_{\parallel} , aligned along the magnetic field below T_i . Thus T_i could be accurately determined and it was found that the value of T_i was almost the same for all batches of the crystal and under reversible temperature cycles in each of these compounds. While fitting such experimental results, we found that only few sets of CFPs would produce such inversion characteristics and among these sets the one that closely matched the observed thermal characteristics of ΔK , K_{\perp} and K_{\parallel} was chosen as the best fitted one. Thus the T_i value can be treated as an important experimental observable while determining CF parameters from fitting of magnetic results on PrYPG or PrPG, that can be done in future.

The calculated value of the effective magnetic moment P_{eff} of PrYPG was 3.47 Bohr magnetons (μ_B) at 300 K, which is slightly lower than the free ion value of $3.58 \mu_B$. The corresponding values obtained for PrVO_4 [46] and Pr^{3+} diglycollate or PrDG ($\text{Na}_3\text{Pr}(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$) [42] are respectively 3.53 and $3.33 \mu_B$. The value of P_{eff} decreased gradually from the value of $3.02 \mu_B$ at 100 K until 20 K but sharply thereafter, since the lowest state is an isolated singlet level as was also observed experimentally in the case of HoPG [18] and TmPG [15].

3.3. Schottky contributions to electronic specific heat

Using the energy pattern of the ground $^3\text{H}_4$ multiplet of PrYPG, obtained from best fitted CF parameters, the thermal characteristic of the Schottky contribution C_{Sch} of the electronic

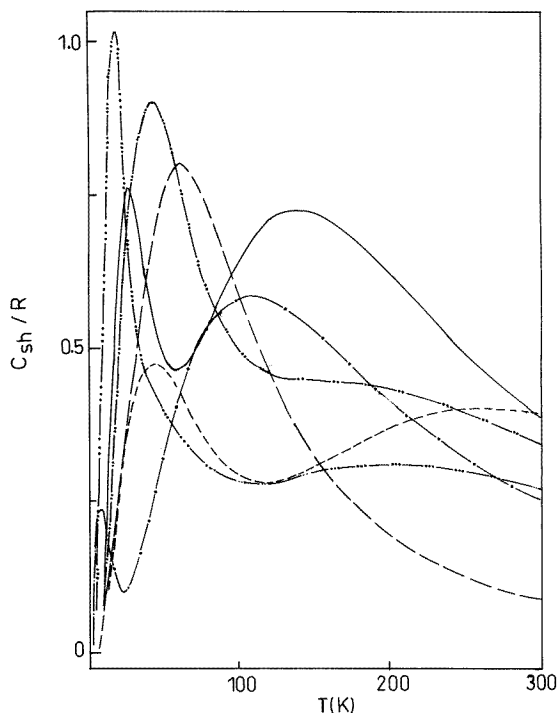


Figure 4. Calculated thermal variations of Schottky component of electronic specific heat (C_{Sch}) of Pr^{3+} :YPG (—), PrDN (---), PrVO₄ (- · - · -), PrDG (— · — · —) and the observed characteristics of C_{Sch} of Pr^{3+} :LaCl₃ (— · —) and Pr(OH)₃ (- · · -).

specific heat was calculated between 300 and 2 K, and is shown in figure 4. For comparison, figure 4 also includes the $C_{Sch}-T$ curves, observed experimentally or calculated using CFP values of few other Pr^{3+} compounds e.g. Pr^{3+} :LaCl₃ [30, 32, 33, 51], Pr(OH)₃ [34, 47], PrDG [42], PrVO₄ [46], Pr₂Mg₃(NO₃)₁₂·24H₂O [52–54] and Pr₂(SO₄)₃·8H₂O [55]. In the case of PrYPG, the calculated $C_{Sch}-T$ curve showed a sharp peak at 24 K and a broad maximum at about 136 K. A similar type of sharp peak was found in Pr(OH)₃ [34], Pr₂(SO₄)₃·8H₂O, Pr₂Mg₃(NO₃)₁₂·24H₂O and PrDG at 8, 4, 42 and 14 K respectively, followed by a broad maximum at 156, 126, 264 and 200 K respectively. Sometimes only one peak had been observed, viz., in Pr^{3+} :LaCl₃ [51] and expected in PrVO₄ at 58 and 40 K respectively [46].

Such characteristics arise due to the CF pattern of the ground $^3\text{H}_4$ term and the temperature where the maximum occurs depends predominantly on the positions of the first few low lying levels. For such reasons it is often possible to determine the CF pattern and CFP values from fitting of experimental results of the total specific heat C_p as demonstrated in the case of R(OH)₃, especially when the maximum occurred at a low temperature where the lattice component (C_L) of specific heat is small. Similarly in the case of ErPG, using the ground level pattern obtained from the spectral study [13], the calculated $C_{Sch}-T$ curve was expected to show a sharp peak at 8 K, whereas the ground pattern obtained by us from fitting the magnetic results on ErPG indicated the maximum to be at 110 K [19]. A recent study of the C_p-T curve of ErPG between 0.5 and 30 K [19] showed that there was no peak at 8 K. It was found that $C_L = 0.33 \pm 2 \times 10^{-4} T^3 R$ [19], so that at 110 K C_L is much larger than C_{Sch} for which reason the peak of C_{Sch} at 110 K was masked. The high temperature tail due to magnetic ordering at 0.95 K was also estimated by us using our CF energy pattern [19].

It is relevant to mention here that a change in the sign of B_{65} does not change the CF pattern of the multiplets [43] but the wavefunctions vary. Thus while fitting the g_{\parallel} values of the doublets Z_1 , Z_2 of the Zeeman spectra, shown in figure 1, we noted that a change in the sign of B_{65} alters the g_{\parallel} values appreciably. As expected, the thermal variations of C_{Sch} do not depend on the sign of B_{65} and that of the susceptibilities in Pr^{3+} compounds at some higher temperature region change only by small amounts due to the population of few levels, the wavefunctions of which are similarly affected by variation of the sign of B_{65} .

4. Conclusions

(1) The absorption and Zeeman spectra of the Pr^{3+} :YPG crystal did not indicate C_1 symmetry and the transition lines were quite well matched considering D_{5h} symmetry at the Pr^{3+} ion site.

(2) Using the optically derived best fitted CF parameters, thermal characteristics of the magnetic susceptibilities, their anisotropy and the Schottky component of the electronic specific heat of PrYPG were calculated. These properties were found to be quite consistent with those observed in other Pr^{3+} compounds.

(3) It is well known that the CF parameters and the energy patterns of Ln compounds do not change appreciably on doping for which reason it is expected that the molecular magnetic susceptibilities and Schottky specific heat properties of PrPG will be same as in PrYPG, which may be verified by future experiments.

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