

Zeeman measurements of Pr^{3+} centres in CaO and CaF_2

Tosporn Boonyarith^a, John P.D. Martin^a, Boazhu Luo^b and Neil B. Manson^a

^a Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 2601, Australia

^b Changchun Institute of Physics, Academia Sinica, Changchun, PR China

Received 22 July 1991

Revised 4 November 1991

Accepted 6 November 1991

Three Pr^{3+} centres in two different crystal hosts have been studied by site selective laser spectroscopy and Zeeman spectroscopy with attention directed at the $^3\text{P}_0$, $^3\text{P}_1$ and $^1\text{I}_6$ crystal field level assignments. The $^3\text{H}_4 \rightarrow ^3\text{P}_0$ excitation line is readily identified in each case. For a tetragonal and a trigonal centre in CaF_2 there is, in each case, a further weak excitation line higher in energy which exhibits a large Zeeman splitting. The associated excited levels are attributed to $^1\text{I}_6$ states. For the Pr^{3+} centre in CaO there are two lines adjacent to that associated with the $^3\text{P}_0$ state and although they do not exhibit linear Zeeman splittings, there are quadratic Zeeman shifts due to large off-diagonal terms. Again the related levels are attributed to $^1\text{I}_6$ states. The centre is shown to have orthorhombic symmetry and the energy levels for this centre are determined.

1. Introduction

Porter and Wright [1] have reported the excitation and emission of $\text{CaO}:\text{Pr}^{3+}$. The crystal was shown to exhibit efficient up-conversion and with the current interest in up-conversion for laser applications it is worthwhile to identify the nature of the active centre or centres. Porter and Wright [1] have established that the centre giving the up-conversion is the dominant centre in CaO . The spectroscopy of the centre has several interesting features. In particular there are three excitation lines in the region of the $^3\text{H}_4 \rightarrow ^3\text{P}_0$ wavelength region where, if it is a single Pr^{3+} ion centre, only one line is expected. From various considerations such as the temperature dependence of the excitation and emission and the concentration dependence of the energy transfer between the $^3\text{P}_0$ and $^1\text{D}_2$ states, Porter and Wright [1] concluded that the centre was associated with a single Pr^{3+} ion. Thus the two additional excitation lines are associated with excited state levels adjacent to the $^3\text{P}_0$ level. This paper

is concerned primarily with the origin of these lines and the geometric nature of the centre. The Zeeman effect of the levels is investigated and compared with that of two other Pr^{3+} centres; one of tetragonal symmetry and one of trigonal symmetry in CaF_2 . The analysis of the Zeeman splittings gives strong support for Porter and Wright's [1] conclusions both regarding the single ion nature of the $\text{CaO}:\text{Pr}^{3+}$ centre and their model of the centre.

The two high symmetry centres investigated in CaF_2 are both centres where the Pr^{3+} ion substitutes for Ca^{2+} but charge compensation arises in two different ways. One is by an interstitial F^- ion in an adjacent location along the $\langle 100 \rangle$ direction forming the centre of C_{4v} symmetry. This is the predominant Pr^{3+} centre in $\text{CaF}_2:\text{Pr}^{3+}$ and has been extensively discussed in the literature including Zeeman measurements [2,3]. When oxygen is present in the growth of the CaF_2 crystal another common mechanism for charge compensation is by the substitution of an O^{2-} ion for a nearest-neighbour F^- ion giving in this

instance a centre with C_{3v} symmetry. Some aspects of this centre have been given before by Gustafson and Wright [4] and by Hasan and Manson [5]. Masui and Ibuki [6] have also identified a trigonal centre in $\text{CaF}_2:\text{Pr}^{3+}$ but the excitation wavelengths are different from those reported here or those given by Gustafson and Wright [4] and, hence, involves a different centre. It is not clear that their crystal was grown in the presence of oxygen and, hence, may not involve O^{2-} charge compensation.

2. Experimental

The crystals were all grown in the Laser Physics Centre. The CaO was grown by the arc fusion process and pieces $\sim 2 \text{ mm}^3$ were cleaved from the crystalline mass. The $\text{CaF}_2:\text{Pr}^{3+}$ was grown by the Bridgman technique with the oxygen centres formed subsequently by heating crystals in moist air at 800°C .

Excitation spectra were performed using a N_2 pumped dye laser and the emission was dispersed by a monochromator and detected by a photomultiplier. The samples were either cooled by (i) a flow of helium gas (10 K), or (ii) a Oxford Instruments cryomagnetic dewar (4.2 K) which included a split pair superconducting magnet (0–5 T).

3. Excitation of $\text{CaO}:\text{Pr}^{3+}$

The low temperature $\sim 4.2 \text{ K}$ excitation of $\text{CaO}:\text{Pr}^{3+}$ in the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ spectral region shows, as mentioned earlier, three lines at 486.2, 484.9 and 484.5 nm. The excitation spectrum obtained by monitoring the emission at 486.2 nm which coincides with the lowest energy excitation line, is shown in fig. 1(a). Non-selective excitation gives the same spectrum with only weak additional features indicating that the excitation spectrum is associated with the dominant centre in

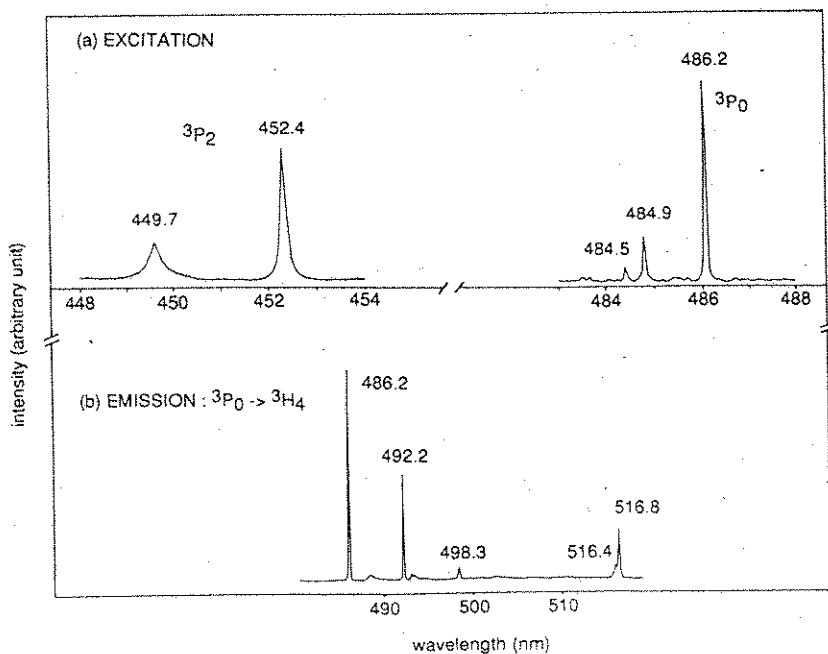


Fig. 1. (a) Low temperature (10 K) excitation spectrum of the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transitions of $\text{CaO}:\text{Pr}^{3+}$ obtained by monitoring fluorescence at 486.2 and 619.0 nm, respectively. (b) ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ fluorescence spectrum when exciting at 486.2 nm.

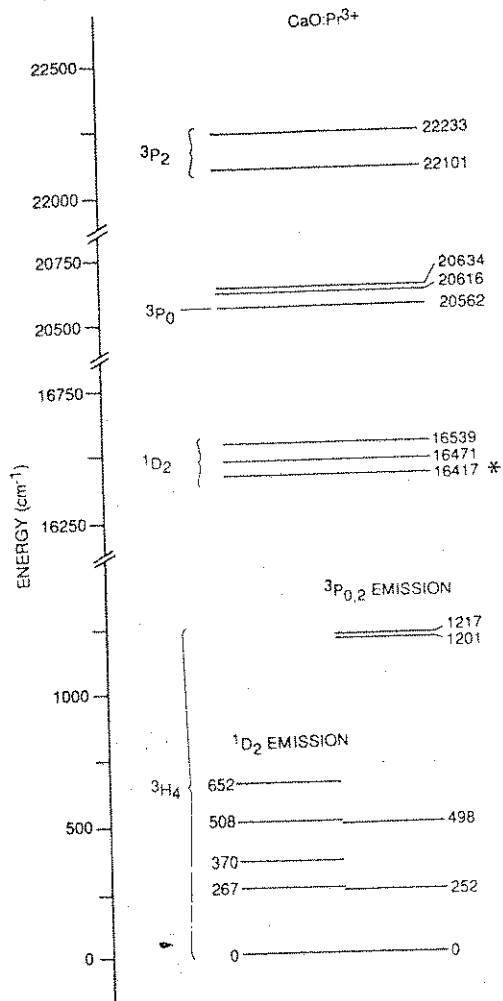


Fig. 2. Energy level diagram for the principal Pr^{3+} centre in CaO . The energy of nine $^3\text{H}_4$ levels have been established some from $^1\text{D}_2$ emission and some from $^3\text{P}_{0,2}$ emission and these are shown separately. The position of the lowest $^1\text{D}_2$ level indicated by an asterisk has been determined from the temperature dependence of the $^1\text{D}_2$ emission (fig. 3).

the crystal. Exciting any of the three lines gives the same emission as shown in fig. 1(b) with four sharp lines and some broad features. The energy levels associated with these transitions are summarised in fig. 2. The strongest transition at 486.2 nm, observed in both excitation and emission, is considered to be associated with the $^3\text{P}_0$ excited state.

The $^3\text{H}_4 \rightarrow ^1\text{D}_2$ excitation and emission has also been recorded and is shown in fig. 3. In this case there were no coincidences in the low temperature spectrum between excitation and emission lines. However, by plotting the temperature dependence of the emission from two emitting levels the energy separation between the levels was determined and hence the relative position of the levels of $^1\text{D}_2$ and $^3\text{H}_4$ states (fig. 2) has also been established.

In addition, no excitation lines consistent with the $^3\text{P}_1$ state could be detected whereas the two lines at 22101 and 22233 cm^{-1} are assigned to the $^3\text{P}_2$ state (fig. 1(a)).

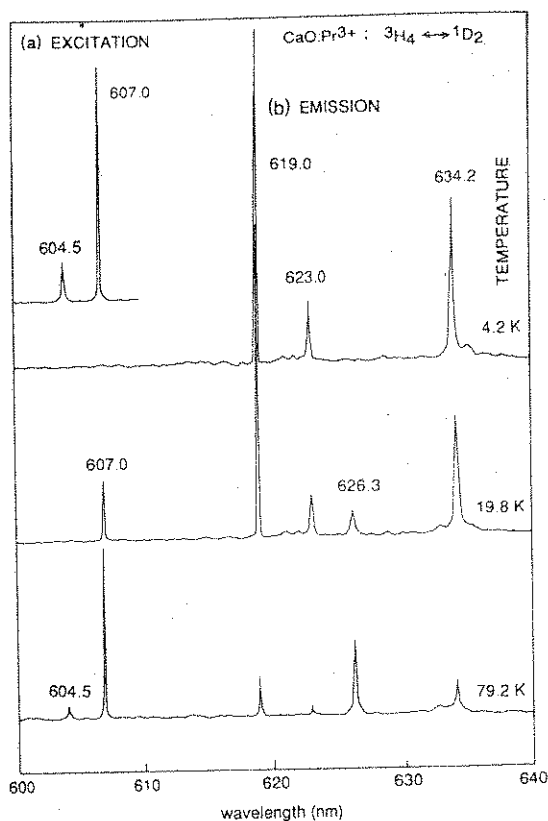


Fig. 3. $^1\text{D}_2 \rightarrow ^3\text{H}_4$ emission spectra at 4.2, 19.8, 79.2 K, during excitation at 607 nm and the $^3\text{H}_4 \rightarrow ^1\text{D}_2$ excitation spectrum at 4.2 K observed by monitoring the emission at 619 nm. No extra lines are seen in the excitation spectra recorded at temperatures up to room temperature.

4. Excitation of $CaF_2:Pr^{3+}:F^-$ and $CaF_2:Pr^{3+}:O^{2-}$

As the origin of the three lines in the $CaO:Pr^{3+}$ excitation spectrum in the neighbourhood of the $^3H_4 \rightarrow ^3P_0$ transition is of some concern, it is advantageous to investigate the analogous excitation of other centres. The excitation of two such centres is shown in fig. 4. It is noteworthy that in both cases there are lines to the high energy side of the $^3H_4 \rightarrow ^3P_0$ excitation line. The lines in the three centres presumably have a common physical origin and this can be substantiated by the Zeeman data presented below.

In axial symmetry the 3P_1 state is split into a doublet and a singlet and from a knowledge of the free ion energies it can be anticipated that there will be two levels $\sim 500 \text{ cm}^{-1}$ above the 3P_0 state. The fluorine compensated centre is the only one that gives such lines in the appropriate spectral region and Reeves [7] has made assignments of these lines based on a crystal field analysis. The oxygen compensated centre has spectral features to both lower and higher energy but none that can be readily attributed to 3P_1

states. As mentioned earlier there are no lines in this spectral region in $CaO:Pr^{3+}$.

5. Magnetic field measurements and discussion

5.1. $CaF_2:Pr^{3+}:F^-$

The $CaF_2:Pr^{3+}:F^-$ centre has tetragonal symmetry and, thus, an external magnetic field along a $\langle 001 \rangle$ axis will be aligned along the principal axis for one crystallographic orientation and at right angles for the other two orientations. Now, since a non-Kramers ion in a crystal field of axial symmetry exhibits no transverse Zeeman splitting ($g_{\perp} = 0$), the transitions associated with the centres whose axes are perpendicular to the field will be unaffected by the field. The shifted lines in fig. 5, therefore, are all associated with the axial centre.

The Zeeman splitting of the $^3H_4 \rightarrow ^3P_0$ transition at 477.1 nm in a field of 5 T is consistent with transitions from a ground state split by 8.8 cm^{-1} to a nondegenerate excited state. At 4.2 K one of the Zeeman components of the ground

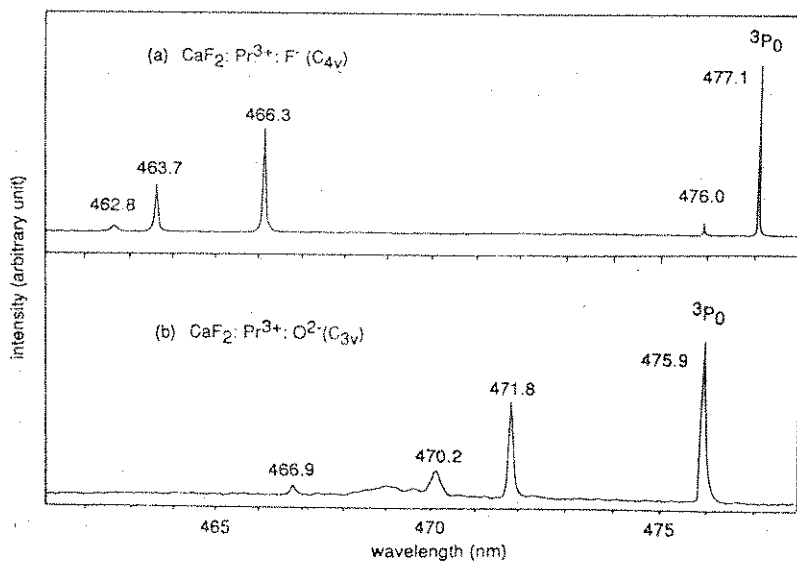


Fig. 4. Excitation spectra of the $^3H_4 \rightarrow ^3P_0$ transition for: (a) $CaF_2:Pr^{3+}:F^-$ obtained by monitoring the fluorescence at 642.3 nm. (b) $CaF_2:Pr^{3+}:O^{2-}$ obtained by monitoring the fluorescence at 656.1 nm.

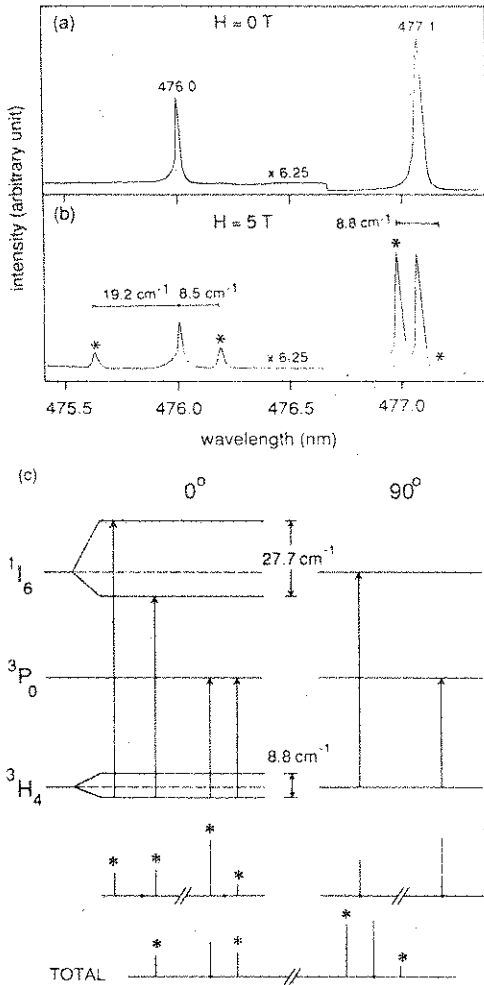


Fig. 5. Zeeman splittings of $CaF_2:Pr^{3+}:F^- (C_{4v})$ at 4.2 K in (a) zero magnetic field, (b) a magnetic field of 5 T, $H \parallel \langle 001 \rangle$, and (c) a schematic representation of the assignments of the Zeeman splittings for the $^3H_4 \rightarrow ^1I_6$ and $^3H_4 \rightarrow ^3P_0$ transitions. The angle between the principal symmetry axis of a site and the magnetic field direction is given above the corresponding Zeeman energy level diagram. Asterisks are used to distinguish lines from different site orientations.

state is thermally depopulated causing loss in the intensity of the Zeeman components displaced to lower energy.

The 476.0 nm line likewise has undisplaced components associated with centres whose symmetry axis is transverse to the field. The magnetic field in this case causes large splittings of the

aligned centres and the pattern corresponds to that for an $E \rightarrow E$ transition with an excited state g -value of 11.9 ± 0.3 and the ground state g -value of 3.8 ± 0.2 . These values and the Zeeman patterns are in agreement with previous measurements on this Pr^{3+} centre [2,3].

5.2. $CaF_2:Pr^{3+}:O^{2-}$

The excitation spectrum of the O^{2-} compensated site shows a strong sharp line at 475.9 nm which is considered to be associated with the 3P_0 level. In addition, there are other lines 183, 257 and 407 cm^{-1} higher in energy (fig. 4) and the Zeeman splitting or shifts of all four lines have been measured.

The site symmetry of the $CaF_2:Pr^{3+}:O^{2-}$ centre is C_{3v} , and when the magnetic field is along the $\langle 100 \rangle$ direction the various trigonal axes all subtend the same angle (54.70°) with the external magnetic field. The 475.9 nm line splits into two components consistent with a transition from an E ground state to a non-degenerate excited state. The 471.8 nm line gives an entirely different splitting pattern, indicating that the associated excited state must also be split. The lines at 470.2 and 466.9 nm exhibit displacements to higher energy in a field of 5 T consistent with transitions to excited states of A symmetry. The Zeeman shifts are less than the line widths ($\sim 4\text{ cm}^{-1}$) and, hence these assignments are not conclusive.

In C_{3v} symmetry the g -values of the ground and excited states for an $E \rightarrow E$ transition can be determined directly by applying the magnetic field along the $\langle 111 \rangle$ crystal direction. The observed splittings shown in fig. 6(b) were obtained in a field of 5 T. The field is along the axis of one centre and it is this centre that gives the largest splittings. The other centres all have their axis at an angle of 70.5° to the field and the associated Zeeman splittings will be subsequently $\frac{1}{3}$ smaller than those for the axial case. The Zeeman spectrum is then readily assigned as shown in fig. 6(c). The ground state g -value is determined to be 5.9 ± 0.2 whereas that of the excited state giving rise to the 471.8 nm line is larger at 9.4 ± 0.3 .

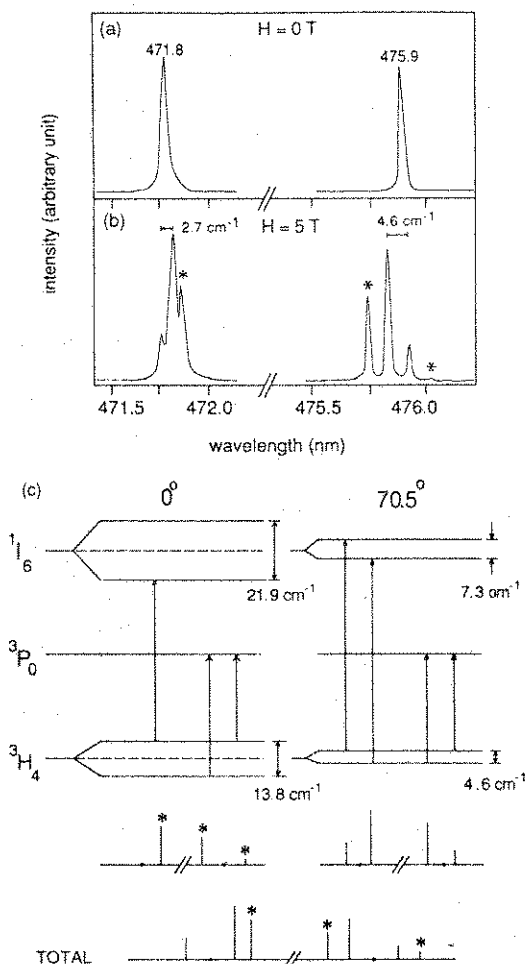


Fig. 6. Zeeman splittings of $\text{CaF}_2:\text{Pr}^{3+}:\text{O}^{2-}$ (C_{3v}) at 4.2 K in (a) zero magnetic field, (b) a magnetic field of 5 T, $H \parallel \langle 111 \rangle$ and (c) a schematic representation of the assignments of Zeeman splittings for the ${}^3\text{H}_4 \rightarrow {}^1\text{I}_6$ and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ transitions. Notation is the same as for fig. 5.

5.3. $\text{CaO}:\text{Pr}^{3+}$

Unlike the former two centres the nature of the $\text{CaO}:\text{Pr}^{3+}$ centre has not been reliably established.

As discussed earlier there are three excitation lines in the blue spectral region. The lowest energy line at 486.2 nm has been assigned to the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ transition and it exhibits no splitting or shift in magnetic fields up to 5 T. Thus in this

case the ground state is not split by a magnetic field. This behavior is consistent with optical transitions of non-Kramers ions in low symmetry sites where all degeneracy has been lifted. Supporting this claim is the observation that with the exception of the two excitation lines at 484.5 and 484.9 nm none of the other excitation or emission lines shown in fig. 1 give splittings or shifts in a magnetic field of 5 T.

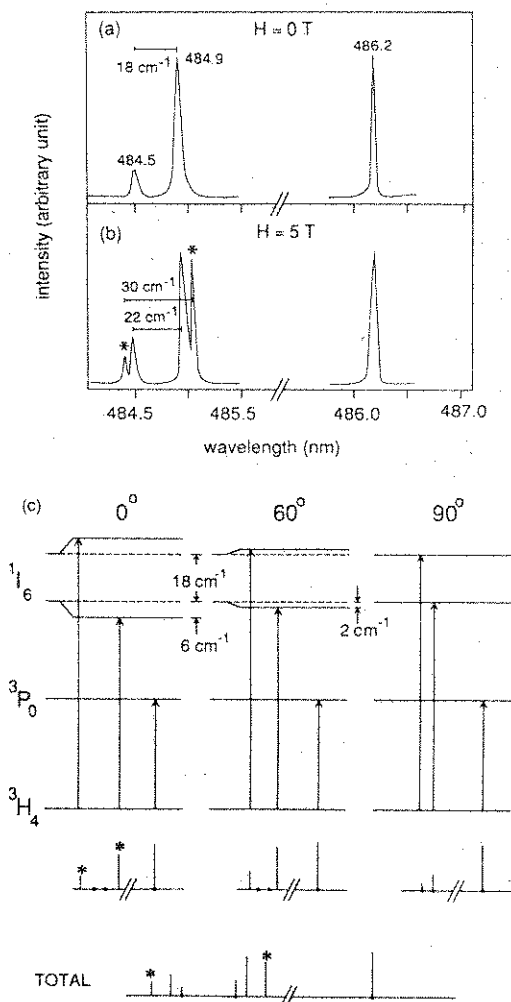


Fig. 7. Zeeman splittings of $\text{CaO}:\text{Pr}^{3+}$ (C_{2v}) at 4.2 K (a) zero magnetic field, (b) a magnetic field of 5 T, $H \parallel \langle 110 \rangle$, and (c) a schematic representation of the assignments of the quadratic Zeeman shifts for the ${}^3\text{H}_4 \rightarrow {}^1\text{I}_6$ and the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ transitions. Notation is the same as for fig. 5.

Table 1
Magnetic splitting (g) factors for the lowest crystal field levels of the $^3\text{H}_4$ ground multiplet and the $^1\text{I}_6$ multiplet, as determined from low temperature Zeeman measurements in a magnetic field of 5 T.

	$^3\text{H}_4$	$^1\text{I}_6$
$\text{CaF}_2:\text{Pr}^{3+}:\text{F}^-$	3.8 ± 0.2 3.89 ^{a)} 3.71 ^{b)}	11.9 ± 0.3 11.87
$\text{CaF}_2:\text{Pr}^{3+}:\text{O}^{2-}$	5.9 ± 0.2	9.4 ± 0.3
$\text{CaO}:\text{Pr}^{3+}$	0	10.3 ± 0.3 (effective)

^{a)} Macfarlane et al. [2].

^{b)} Tissue and Wright [3].

As shown in fig. 7, however, the lines at 484.9 and 484.5 nm split in the presence of a magnetic field. This can be readily understood as a consequence of a shifting of the levels, rather than a splitting of levels. It is observed that only the lower energy transition has components displaced to lower energy and the higher energy line components to higher energy. In addition, the magnitude of the Zeeman shifts depended on the square of the field strength. The pseudo-Zeeman splitting is a consequence of field mixing between the two excited state levels separated by 18 cm^{-1} .

For a field along the $\langle 100 \rangle$ direction, each line splits into two components and, for a field along the $\langle 110 \rangle$ direction, into three components (two of which are not fully resolved). In addition for both lines a component remains unshifted. The patterns are what would be expected for two interacting levels of a centre with its axis along a $\langle 110 \rangle$ direction. In C_{2v} symmetry all irreducible representations are non-degenerate and, hence, two levels can only interact via a perturbation of appropriate symmetry. Magnetic fields aligned along the separate axes of the C_{2v} site each transform according to a different irreducible representation (A_2 , B_1 or B_2) and, hence, only one can give rise to the interaction. The maximum shifts occur when the external magnetic field is along a $\langle 110 \rangle$ direction and this indicates it to be the major axis of one of the C_{2v} centres. The equivalent axis of the other C_{2v} centres will correspond to the other $\langle 110 \rangle$ crystallographic directions and it is the component of the field

along such axes that gives rise to the interaction between levels. The Zeeman patterns can, therefore, be predicted and the strength of the interaction determined from the experiment (fig. 7). The magnitude of the Zeeman interaction is found to be equivalent to a $g_{\text{effective}} = 10.3 \pm 0.3$ had the two levels been degenerate.

6. Discussion

In each of the three Pr^{3+} centres investigated, the transition from the ground state to the $^3\text{P}_0$ level has been identified and the magnetic field measurements confirm that the excited state level in all cases is, indeed, non-degenerate. To higher energy there are additional levels and in all three cases it has been shown that the first of these levels has associated with it a large g -value. In the axial centres the g -value is that associated with a linear splitting of a two-fold degenerate state. In CaO the states are non-degenerate and the effective g -value was determined from the repulsion of two levels by an off-diagonal Zeeman interaction. These two levels would be degenerate in higher symmetry (cubic or axial) and the distortion which produces the C_{2v} symmetry is what causes the splitting of 18 cm^{-1} . Once the magnetic field is large enough to make the Zeeman interaction comparable with the zero field splitting the levels are repelled from one another and the magnitude of the interaction can be expressed in terms of an effective g -value that would appropriate if there was no zero field splitting.

The magnitude of the excited state g -value in all three centres (9.4, 11.9 and 10.3) is much larger than that which is possible for a $^3\text{P}_1$ level (3 in first order) but compatible with that expected for a $^1\text{I}_6$ state. Spectroscopic g -values of similar magnitude have been established for $^1\text{I}_6$ states in $\text{LaCl}_3:\text{Pr}^{3+}$ [8]. The extra levels can, therefore, be clearly assigned to crystal field $^1\text{I}_6$ states. For the $\text{CaF}_2:\text{Pr}^{3+}:\text{F}^-$ centre this is consistent with the assignment of Tissue and Wright [3].

Charge compensation for the trivalent ions in the alkaline-earth oxides is generally achieved through the incorporation of cation vacancies in

the ratio one vacancy for every two trivalent cations. There is, therefore, a binding energy between the ion substituting for the Ca^{2+} ions in the O_h site and the vacancy. This encourages an association between the species and results in lower symmetry sites. With a nearest neighbour vacancy the Pr^{3+} centre will have C_{2v} symmetry and the Zeeman measurements have established that this is the symmetry of the dominant centre. It is clear that this is the major centre in CaO but there also exists a significant number of non-compensated cubic Pr^{3+} ions [1].

7. Conclusions

In these studies it has been found that Pr^{3+} doped crystals have crystal field energy level patterns which frequently exhibit $^1\text{I}_6$ states lying close in energy to the $^3\text{P}_0$ state. This behaviour is found for both six-fold and eight-fold co-ordinated systems. In particular, from the Zeeman measurements, it is shown that the two levels at 54 and 72 cm^{-1} above the $^3\text{P}_0$ level in CaO are

single Pr^{3+} site ion levels associated with the $^1\text{I}_6$ state.

Porter and Wright [1] have proposed that the predominant Pr^{3+} ion centre in CaO is formed by a substitutional Pr^{3+} ion with an adjacent charge compensating Ca^{2+} vacancy giving an orthorhombic site of C_{2v} symmetry. An analysis of the quadratic Zeeman effect reported here gives convincing support for this model of the centre.

References

- [1] L.C. Porter and J.C. Wright, *J. Chem. Phys.* 77 (1982) 2322.
- [2] R.M. Macfarlane, D.P. Burum and R.M. Shelby, *Phys. Rev. B* 29 (1984) 2390.
- [3] B.M. Tissue and J.C. Wright, *Phys. Rev. B* 36 (1987) 9781.
- [4] F.G. Gustafson and J.C. Wright, *Anal. Chem.* 51 (1979) 1762.
- [5] Z. Hasan and N.B. Manson, *J. Lumin.* 38 (1987) 40.
- [6] H. Masui and S. Ibuki, *J. Phys. Soc. Jpn.* 22 (1967) 1387.
- [7] R.J. Reeves, Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand (1987).
- [8] R. Sarup and M.H. Crozier, *J. Chem. Phys.* 42 (1965) 371.