# ABSORPTION SPECTRA OF RbCl:Yb2+ RbBr:Yb2+ AND RbI:Yb2+ CRYSTALS

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#### Abstract

Single crystals of rubidium chloride, bromide and iodide were doped with substitutional divalent ytterbium. Yb<sup>2</sup> ions, by heating them in ytterbium atmosphere. The absorption spectra of the Yb<sup>2</sup> doped crystals were measured at room and liquid nitrogen temperatures. The spectra were found to consist of intense broad absorption bands located mainly in the ultraviolet spectral region. They have been ascribed to the electric dipole allowed transition of the Yb<sup>2</sup> ions from the  $4f^4$  (S<sub>0</sub>) ground state to states of the first excited  $4f^4$ 5d configuration of the ions in the crystals. On the basis of the experimental data obtained from the study, an energy level structure has been derived for the  $4f^4$ 5d configuration of Yb<sup>2</sup> ions in rubidium chloride, bromide and iodide crystals.

**Keywords**: Rubidium halides, absorption spectra, divalent ytterbium ions and metal vapour phase diffusion.

#### Introduction

Ytterbium is one of the few rare earth metals that easily exist in the divalent state when combined with non-metallic elements to form inorganic compounds. This has motivated a number of studies on the spectral characteristics of transparent inorganic compound insulators such as alkaline earth fluorides and chlorides doped with divalent ytterbium, Yb<sup>2+</sup>, ions (Kaplyanskii and Feofilov, 1962, Piper, et al., 1967, Loh, 1968, 1969).

The doping method adopted in most of these studies is the conventional bulk doping technique. This consists in incorporating some quantities of a trivalent ytterbium halide into the melt of the desired host crystal. By some reduction process the trivalent ytterbium ions are reduced to the divalent state. Doped single crystals are then grown from melt by using any of the crystal growing methods such as the Czochralski (Hernandez, et al., 1979, 1980),

Kyropoulous (Aguilar, et al., 1974, Rubio, et al., 1976 and Eremin, 1970) and Bridgeman (Piper, et al., 1967) methods. The absorption spectra of Yb<sup>21</sup> ions in these crystals are usually found to consist of strong broad bands located in the visible and ultraviolet. A theoretical interpretation of the results of these studies reveals that the spectral bands could be ascribed to the Laporte allowed  $4f^{14}(^{1}S_{o}) \rightarrow 14f^{13}5d$  electronic transitions of Yb<sup>24</sup> ions in the crystals.

In their study of the absorption spectra of Yb<sup>2+</sup> ions in sodium and potassium halide crystals. Bland and Smith (1985) were able to dope the crystals with Yb<sup>2+</sup> ions by heating the pure crystals in ytterbium atmosphere. The absorption spectra of the Yb<sup>2+</sup> ions in the sodium and potassium halide crystals consist of groups of strong bands, which also are located in the visible and ultraviolet. The optical absorption spectrum of NaCl:Yb<sup>2+</sup> obtained by

Tsuboi, et al., 1981, has a structure similar to that obtained by Bland and Smith, 1985. There is one main difference between the spectra of Yb2+ - doped sodium and potassium halide crystals and those of Yb2+ - doped alkaline earth fluoride and chloride crystals, however. The absorption spectra of Yb<sup>2+</sup> - doped crystals of sodium and potassium halides have three broad bands in the lower energy part (spectral range 25 000 -33 333 cm<sup>-1</sup>) of the spectra. On the other hand, the spectra of Yb<sup>2+</sup> - doped alkaline earth fluorides and chlorides, contain only one broad band in the spectral range 25 000 -33 333 cm<sup>-1</sup>. Several theoretical studies (Piper, et al., 1967, Eremin, 1970, Bland and Smith, 1985, Mejeha and Smith, 1998a) clearly predict these experimental results.

This work, which is an extension of the study of Yb<sup>2+</sup> - doped alkali halide crystals, represents an attempt to study the spectral characteristics of Yb<sup>2+</sup> ions in rubidium chloride, bromide and iodide crystals.

## Theoretical Considerations

The strong absorption bands of the Yb<sup>2+</sup>-doped sodium and potassium halide crystals studied by Bland and Smith (1985) have been ascribed to the Laporte allowed transitions of the Yb<sup>2+</sup> ions from the 4f<sup>4+</sup>(<sup>1</sup>S0) grounded state to the states of the first excited 4f<sup>43</sup>5d configuration of the Yb<sup>2+</sup> ions in the crystals. It is considered that the states of the 4f<sup>13</sup>5d configuration of the Yb<sup>2+</sup> ions in the crystals are perturbed by a number of interactions, including:

1. The interelectronic interaction between pairs of electrons in the ion, represented by the operator H<sub>el</sub>(f,d). The 4f<sup>13</sup> core configuration is considered to be a 4f hole. Consequently, the 4f<sup>13</sup>5d configuration is equivalent to a configuration of two non-

equivalent electrons. Accordingly, the operator  $H_{\rm e}(f,d)$  simply represents the interaction between the 4f hole and the lone 5d electron.

ii. Spin-orbit interactions represented by the operator  $H_{so}$ . This consists of two components  $H_{so}(f)$  and  $H_{so}(d)$  which respectively act on the 4f and 5d subspaces of the electronic wave functions.

iii. Crystal field interactions, which exist between the ytterbium ions and the surrounding ligand ions. The interactions are represented by the operators  $H_{\rm cr}(d)$  and  $H_{\rm cr}(f)$ . They act in the d-electron and f-electron (hole) states respectively.

It has been pointed out that for the 4f135d configuration of the Yb<sup>2+</sup> ions in free space, spin-orbit coupling is indeed very strong [Bryant (1965)]. In crystal fields therefore, H<sub>so</sub>(f), H<sub>so</sub>(d), H<sub>cr</sub>(d) and H<sub>el</sub>(f,d) cause energy level splittings of the same order of magnitude, and are therefore treated on the same footing (Piper, *et al.*, 1967, Eremin, 1970, Bland and Smith 1985, Mejeha and Smith, 1998a).

## **Experimental Procedure**

The single crystals of rubidium chloride, bromide and iodide used in this study were obtained from BDH Chemicals Ltd. Poole, England. Ingots of ytterbium used were supplied by Rare-Earth Products Ltd. Cheshire, England. The certified purity level of the sublimed metal ingots was 99.99%.

A small disc of the crystal to be doped and a ytterbium metal ingot were placed in a specially designed device known as primary diffusion ampoule, (PDA), which was then evacuated to ultra-high vacuum by means of a diffusion pump. The PDA was then lowered into a secondary diffusion ampoule (SDA) pre-heated in an upright furnace. Details of the special features of the PDA, SDA, the upright furnace and the special procedures,

adopted during the doping can be found elsewhere (Bland and Smith 1985, and Mejeha and Smith, 1995). The doping temperature was set at about 25° C below the melting point of the host crystal to be doped. Doping times ranged from 4 hours to 6 hours for RbCl and RbBr crystals and 8 hours for RbI crystals. At the end of the doping time, the PDA was lowered into a dewar of liquid nitrogen to quench the doped crystal. During doping, atoms of ytterbium deposited on the crystal surface were oxidized to the divalent state. The resulting Yb24 ions diffuse into the crystal bulk from the surface. The doping technique just described is known as the metal vapour phase diffusion, MVPD, technique.

The Yb<sup>2+</sup> - doped rubidium halide crystals were found to be coloured as a result of the presence of colour defect centres, such as F-centres, F-aggregate centres, U-centres or some other light absorbing defect centres. In order to eliminate the colour centres or reduce their concentration, the doped crystals were thermally bleached using the procedure described by Mejeha and Smith (1995). The procedure also prevented the formation of Yb<sup>2+</sup> ion precipitates or the aggregation of Yb<sup>2+</sup>

ion cation-vacancy complexes.

The absorption spectra of the Yb<sup>2</sup> - doped crystals were measured at room temperature (RT) as well as at liquid nitrogen temperature (LNT) using a Varian D M S - 9 0 - U V - v i s i b l e - N I R spectrophotometer with wavelength range 190 nm - 900 nm. In addition, the second derivative absorption spectra of the doped crystals were measured at RT and LNT in order to locate the peak positions of the absorption bands more precisely.

#### Results and Discussion

Thermally bleached RbBr:Yb<sup>2</sup> and RbI:Yb<sup>2+</sup> crystals were found to be colourless indicating that colour defect centers whose absorption bands occur in the visible have been eliminated. However, RbCl:Yb<sup>2+</sup> crystals could not be thermally bleached completely and exhibit bluish colour.

The optical absorption spectra of RbCl:Yb<sup>2+</sup>, RbBr:Yb<sup>2+</sup> and RbI:Yb<sup>2+</sup> crystals obtained at room and liquid nitrogen temperatures are shown in Figs 1-3. Each absorption spectrum consists of a number of broad bands appearing partly in the visible but mostly in ultraviolet. The absorption bands have been categorized

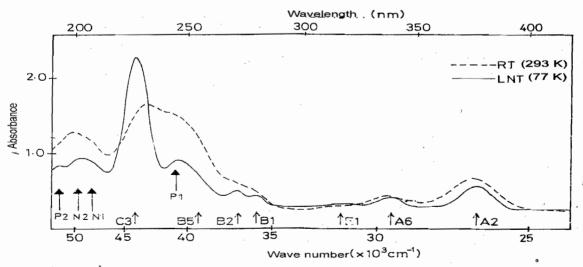


Fig. 1. Optical absorption spectra of  $Yb^{2+}$  ions in RbCl crystals at room and liquid nitrogen temperatures.

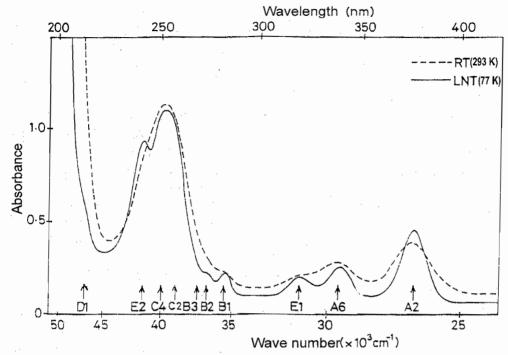


Fig. 2: Optical absorption spectra of Yb<sup>2+</sup> ions in RbBr crystals at room and liquid nitrogen temperatures.

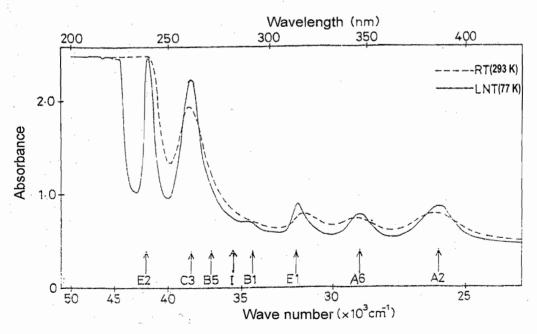


Fig. 3:Optical absorption spectra of  $Yb^{2^+}$  ions in RbI crystals at room and liquid nitrogen temperatures.

into three groups; namely A, B and C. The bands in each band group have been distinguished by attaching numeral labels on the letters identifying each band group. The choice of numeral will be explained later.

Table 1. Shows the peak positions and relative transition intensities of the major absorption bands in the spectra of the RbX:Yb<sup>2+</sup> (X = Cl, Br, I) crystals. In each LNT spectrum, the experimental transition intensify of a band is derived relative to the transition intensity of the

A2- band which has been normalized to 100. In all the spectra, the intensities of the A2 and A6 bands relative to each other follow the same trend, with the A2- band always more intense than the A6- band. Interestingly, the separation of the peak positions of the A2- and A6 bands remain fairly the same across the RbX:Yb<sup>2+</sup>, (X = Cl, Br, I) crystal series. The separations are 2989 cm<sup>-1</sup>, 2983 cm-1 in the LNT spectra of RbCl:Yb<sup>2+</sup>, RbBr:Yb<sup>2+</sup> and RbI:Yb<sup>2+</sup> crystals respectively.

Another interesting feature of the absorption spectra is that the peak position of a given absorption band tends to

Table 1: Spectral positions and relative transition intensities of main bands in the absorption spectra of RbX:Yb<sup>2+</sup>(X=Cl, Br, I) crystals at room and liquid nitrogen temperatures

Host Crystal	RbCl			RbBr			RbI		
	Spectral position (cm <sup>-1</sup> )		Relative Intensity at LNT	Spectral position (cm <sup>-1</sup> )		Relative Intensity at LNT	Spectral position (cm <sup>-1</sup> )		Relative Intensity
Band	RT	LNT	atLANI	RT	LNT		RT	LNT	at LNT
D1	28.			. •.	46 729	25	•	-	• .
E2	parenter 20	Same Saide		· -	41 494	223	-	41 667	493
C4	-			40 000	40 000	292		<b>→</b> \.	
C3	43 526	44 101	638			- M27	38 462	38 314	434
C2	_			39. <del>13</del> 9 -	<b>3</b> 9 063	141	-	-	-
Andrew State Control of the Control	a to distribute the control of the c			15		i,			
B5	39 216	39 139	106	-			36 697	36 765	85
		,		in the same		100		,	
B3	_		-		37313	25	<b>-</b> .	36 364	29
B2	36 866	36 900	81	36 364	36 430	40	• - /	. <b>.</b>	<u>.</u>
. ≥ 5 <b>B</b> 1	35 746	35 810	56	35 273	35 398	41		34 483	24
							١.		
El	31 056	31 898	28	30 912	31 348	36	31 496	31 771	100
7.49	and the same of th								
A6	29 630	29 532	50	29 542	29 477	57	28-902	28 860	78
Á2	26 649	26 543	100	26 560	26 473	100	26 042	25 907	100
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decrease in wavenumber (or energy) as the lattice parameter, d, of the host crystal increases. In this respect, ones notes that  $d_{RbCl} \le d_{RbBr} \le d_{Rbl}$ . When a Yb<sup>2+</sup> -doped rubidium halide crystal is cooled from RT to LNT, the absorption bands become sharper; the A-bands shift to lower energies. For the C-bands, the, matter is more complicated. In the absorption spectra of RbCl: Yb<sup>2+</sup> crystals, the C bands shift to higher energies while the in the RbBr:Yb2+ and RbI:Yb2+ crystals, the Cbands in general shift to lower energies when the crystals are cooled. In general, the B bands tend to be weaker than the A and C- bands while the C- bands are the most intense in all the spectra studied.

The structure of the absorption spectra of  $RbX:Yb^{2}$ , (X = Cl, Br, I) crystals as well as the various features of the A-. B- and Cbands already highlighted have striking similarities with corresponding bands in the absorption spectra of Yb24 -doped sodium and potassium halide crystals obtained in an earlier study (Bland and Smith, 1985). In that study, the investigators convincingly showed that the absorption spectra obtained could be ascribed to the  $4f^{14}(^{1}S_{0}) \rightarrow 4f^{13}5d$ electronic transitions of the Yb2+ ions in the crystals. Accordingly, the A-, B- and C- bands identified in the absorption spectra of RbX: $YB^{2+}$ , (X = Cl, Br, I) crystals obtained in this study are hereby attributed to the  $4f^{14}(^{1}S_{o}) \rightarrow 4f^{13}5d$ electronic transitions of the Yb2+ ions in the crystals.

Some theoretical studies of Yb2+ ions at substitutional sites in cubic crystals have predicted four groups of energy levels for the 4f<sup>13</sup>5d configuration of Yb<sup>2+</sup> ions in an octahedral crystal field (Piper, et al., 1967, Eremin, 1970, Bland and Smith, 1985, Mejeha and Smith, 1998a). It can be shown that the A -, B- and C-bands identified in the spectra of RbX:Yb<sup>2+</sup>, (X =

Cl. Br. D crystals in this study correspond to the lowest three of the four groups of energy levels predicted by Mejeha and Smith, 1998a, for Yb2+ ions in octahedral crystal field. The energy spectrum predicted by these authors is shown in Fig.4; in that figure, the numbers across the spectral lines of the spectrum at chosen values of Dq are transition intensities of the lines. It has already been pointed out that the separation of the peak positions of the A2- and- A6 bands remain fairly the same across the spectra of the RbX:Yb<sup>2+</sup>. (X = Cl. Br. I) crystal series. This fact, as well as the various features of the A2- and A6 bands already mentioned suggests that the A bands correspond to the lowest group of energy levels in the theoretical energy spectrum of the 4f<sup>13</sup>5d configuration of Yb<sup>2+</sup> ions in octahedral crystal fields.

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The lowest group of theoretical energy levels consists of six levels. The second lowest of these is the most intense while the sixth is the next in intensity in the region of the spectrum for which Dq, the crystal field parameter is larger than 800cm<sup>-1</sup>. It is therefore reasonable to assign the A2-band, the most prominent of the experimental A- bands to the most intense of the six energy levels in the lowest group of the theoretical energy levels. This happens to be the second lowest level. The A6- band, which is the next in intensity in the experimental A bands is assigned to the sixth energy levels, since the sixth theoretical energy is the next in intensity to the second theoretical energy level. It is remarkable to note that the separations between the theoretical energy level corresponding to the experimental A2- and A6- bands in the theoretical energy spectrum are practically constant as Dq increases within the crystal field regime for which Da > 800cm<sup>-1</sup>. This is consistent with the experimental observation that the separation between the peak positions of the A2- and A2bands remain fairly constant across the

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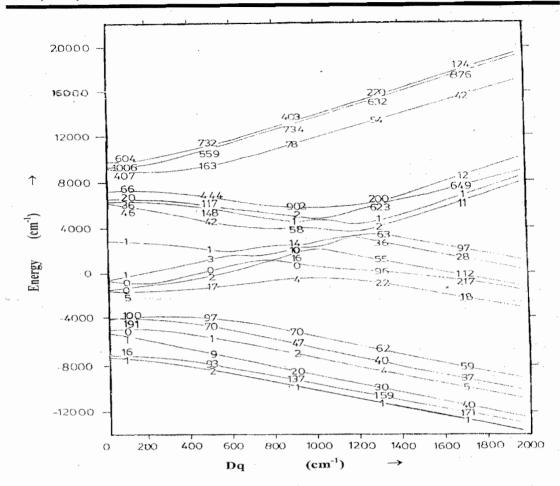


Fig. 4 Variation of  $\Gamma_{4u}$  energy levels of the  $4f^{13}5d$  configuration of  $Yb^{24}$  ions with crystal field parameter Dq in octahedral crystal field. The energy parameters  $F_2$ ,  $F_4$ ,  $G_1$ ,  $G_3$ ,  $G_5$ ,  $\zeta_{46}$ , and  $\zeta_{5d}$ , are set at free ion values [After Mejeha and Smith (1998a)].

rubidium halide series. In this respect, it is worth noting that the crystal field parameter, Dq =  $\Delta/10$ , where  $\Delta$  is a measure of the crystal field splitting of the 5d electron orbitals of the Yb<sup>2+</sup> ions in an octahedral environment. For RbCl:Yb<sup>2</sup> crystals, Dq = 1550cm<sup>-1</sup> while it has values 1057cm-1 and 931cm<sup>-1</sup> for RbBr:Yb2' and RbI:Yb2' crystals respectively (Mejeha and Smith, 1998a). A close scrutiny of the experimental energy spectra of Yb2+ ions in RbX:Yb2+. (X=Cl, Br, I) crystals and the theoretical energy spectrum (Fig.4) shows that the B and C bands correspond to the second and third group of theoretical energy levels respectively.

In the LNT absorption spectrum of RbBr:Yb<sup>2+</sup> crystal, a weak high energy band has been identified as the D1 band. It has been assigned to the lowest energy level in the fourth group of levels in the theoretical energy level spectrum. It is note worthy that in the absorption spectra of KCl:Yb2', KBr:Yb2', and NaBr:Yb2' crystals, some absorptions bands were labeled Dbands (Bland and Smith, 1985). These were found to correspond to the fourth group of theoretical energy levels computed by the investigators just cited. It is possible that the D-bands in the absorption spectra of RbCl:Yb<sup>2+</sup> and RbI:Yb2+ crystals have been masked by the onset of the intrinsic absorption edge of the

host crystals. It is also possible that their peak positions may be located in the conduction bands of the crystals and therefore outside the range of optical transparency of the host crystals.

The correspondence of the absorption bands identified in the spectra studied to the first three groups of the theoretical energy levels predicted for the 4f<sup>13</sup>5d configuration of Yb21 ions in an octahedral crystal field requires further comments. To start with, it has to be noted that the site symmetry of a substitutional Yb2 ion in a rubidium halide crystal is not truly octahedral, Oh, point symmetry. Rather, it is orthorhombic,  $C_{2v}$ , point symmetry. Nevertheless, it has been shown that when dealing with the first excited configurations of doubly ionized rareearth ions at substitutional sites in alkali halide crystals, it is a good approximation to regard the site symmetry of the substitutional divalent impurity ions as octahedral (Hernandez, et al., 1980, 1981. Tsuboi, et al., 1981, Bland and Smith, 1985, Mejcha and Smith, 1998b). The octahedral approximation will therefore be adopted in the analysis that follows.

The theoretical computer-based investigation of the effects of the interaction operators  $H_{si}(f)$ ,  $H_{si}(d)$ ,  $H_{c}(d)$ and H<sub>a</sub>(f,d) on the energy level structure of the 4f<sup>3</sup>5d configuration of Yb<sup>2</sup> ions in Oh crystal field (Mejeha and Smith, 1998a) led the investigators to purpose an interaction model depicted schematically in Fig.5. Basically, the model recognizes the strong influence of the spin-orbit interaction operator H<sub>s0</sub>(f) on the eigenstates of the 4f hole and of the crystal electron orbitals. There effects are however moderated by the actions of the spin-orbit interaction operator H<sub>si</sub>(d) and the direct Coulomb and exchange interactions operators  $H_{al}(f,d)$ . The rule of the latter operator is to couple the

multiplet states 2FJ, J = 7/2, 5/2 of the 4f hole (that is the 4f<sup>13</sup> core subconfiguration) to the crystal field split and spin-orbit perturbed 5d electron states. It also spreads the energy levels thereby closing the spectral gaps between the energy level groups resulting from the actions of the interaction operators  $H_{a0}(f)$ .  $H_{\infty}(d)$  and  $H_{\infty}(d)$  on the eigensystem of the 4f<sup>43</sup>5d configurations of the Yb<sup>2+</sup> ions in octahedral environment. In column d of Fig.5, only those energy levels associated with crystal field states which transform as the irreducible representations  $\Gamma$ 4u of the O<sub>b</sub> point group are shown for reasons to be explained shortly.

In free space, the  $4f^{13}5d$  configuration of  $Yb^{2^{12}}$  ions consists of 20 free energy levels. These are slit into 58 crystal field levels in  $O_b$  crystal field. These levels are associated with crystal field states spanning the irreducible representatives  $\Gamma$  iu (i=1, 2... 5) of  $O_b$  point group as follows:

6Γ1u ÷ 5Γ2u ÷ 12Γ3u ÷ 18Γ4u ÷ 18Γ5u The subscript u attached to the representations Γi shows that the associated crystal field states are of odd parity.

In the  $O_h$  crystal field, electric dipole transitions are allowed from the  $4f^4$  ( $^1S_0$ )  $\Gamma 1g$  ground state to only the  $18\Gamma 4u$  crystal field levels which can be categorized into four groups labeled as A', B', C' and D' from the lowest energy group in that order. Group theory predicts that there are  $6\Gamma 4u$  levels in the A: group,  $5\Gamma 4u$  levels in the B group while the C and D groups consist of  $4\Gamma 4u$  and  $3\Gamma 4u$  levels respectively. Clearly, the model correctly predicts the number of energy levels in each of the four groups of energy levels in the theoretical energy spectrum (see Fig. 4).

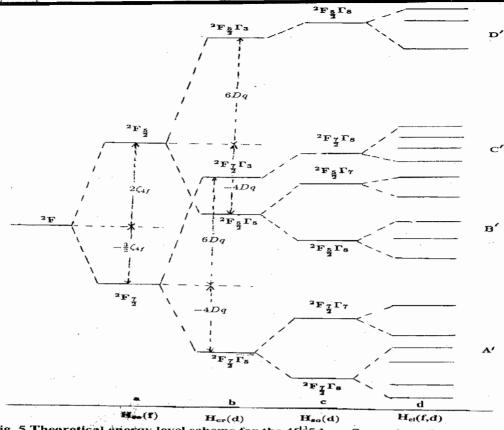


Fig. 5 Theoretical energy level scheme for the  $4f^{13}5d$  configuration of  $Yb^{24}$  ions in high octahedral crystal field. (a)  $H_{SO}(f)$ : Spin-orbit interaction within 4f subshell. (b)  $H_{cr}(d)$ : Crystal field interaction within 5d states. (c) Spin-orbit interaction within 5d subshell. (d)  $H_{cl}(f,d)$ : Direct Coulomb and exchange interactions between  $4f^{13}$  electrons and the 5d electron. Only  $\Gamma_{4n}$  levels are indicated [After Mejeha and Smith 1998a].

The model is quite valid if the 5d electron orbitals are strongly split into  $\Gamma 3(e_g)$  and  $\Gamma_3(t_{2g})$  components by the crystal field interaction operator  $H^{er}(d)$  as when Dq 1400 cm<sup>-1</sup>. This is case for RbCl:Yb<sup>2+1</sup> crystals for which Dq = 1550 cm<sup>-1</sup>. However, in the intermediate crystal fields (800 cm<sup>-1</sup> < Dq < 1400 cm<sup>-1</sup>), the 5d electron states can no longer be unambiguously described by using the crystal field quantum numbers  $\Gamma 3$  and  $\Gamma 5$ . This is the case applicable to the RbBr:Yb<sup>2+</sup> and RbI:Yb<sup>2+</sup> for which Dq has values of 1057 cm<sup>-1</sup> and 931 cm<sup>-1</sup> respectively.

On the basis of the above considerations, an energy level scheme is hereby proposed for the 41<sup>43</sup>5d configuration of

 $Yb^{2^{2}}$  ions in RbX (X = Cl. Br. I) crystals. The scheme is illustrated in Fig.6. Column (a) in the figure shows the calculated  $18\Gamma 4u$  energy levels of the  $4f^{13}5d$ configuration of Yb2+ ions in RbBr crystal with Dq = 1057 cm<sup>-1</sup> (Mejeha and Smith, 1998a). In column b, the calculated 4u levels were merely assigned to the free ion states of the 4f<sup>13</sup>5d configuration from which they were genealogically derived. The last three column show the experimental energy level structure of Yb<sup>2</sup> ions in the RbX (X = Cl, Br,  $\bar{I}$ ) crystals. The experimental energy level structure shows that the B- and C- bands in the absorption spectra of RbBr: Yb2 and Rb1:Yb2 crystals are genealogically derived from the admized  ${}^{2}F_{so}5d_{so}$  and  ${}^{2}F_{so}5d_{so}$  free ion states in the crystalline matrix. However, in the spectra of RbCI: Yb2+ crystals, the B- bands are derived from  $^2F_{s/2}5d_{s/2}$  free ion states which in the strong crystal field correspond to the  $^2F_{s/2}\Gamma_s$  and  $^2F_{s/2}\Gamma_r$  crystal field states, while the C-bands are derived from the  $^2F_{7/2}5d_{3/2}$  free ions states which correspond to the  $^2F_{7/2}\Gamma_8$  crystal field states.

Mention has not been made of the absorption bands labeled EI and E2. These have been identified as due to electronic transitions of Yb<sup>2+</sup> ions but of different nature from those giving rise to the A-, B- and C-bands. They show similar features as the E1 and E2 bands identified by Bland and Smith (1985) in the spectra of Yb<sup>2+</sup> - doped spectra of sodium and potassium halides crystals.

They have since been ascribed to the forbidden  $4f^{14}(^{1}S_{0}) \oplus 4f^{13}6s$  transitions of the Yb<sup>2+</sup> ions in the crystals (Bland, *et. al* (1996)].

The bands labeled I in the LNT spectrum of RbI:Yb²+ crystal and the P1 and P2 bands in the LNT spectrum of RbCl:Yb²+ crystals were identified to be due to unknown impurities present in the nominally pure crystals. Their transition intensities relative to the A2 -band vary from sample to sample. The absorption bands labeled N1 and N2 on the high energy side of the LNT spectrum of the RbCl:Yb²+ crystals are not due to Yb²+ ion transitions. Their intensities relative to the A2-band also vary from sample to sample. They probably are colour centre bands

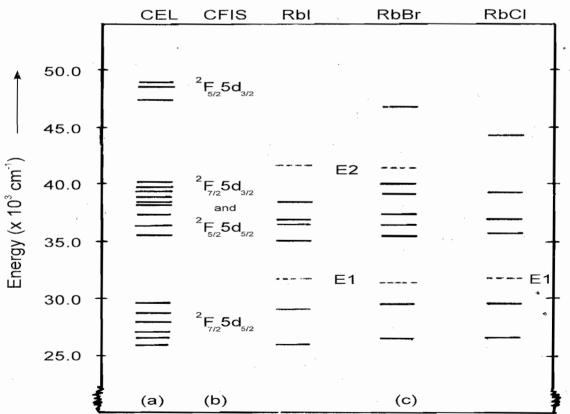


Fig. 6: Theoretical and experimental energy levels of Yb<sup>2+</sup> ions in rubidium halide crystals; (a) Calculated energy levels (CEL) in RbBr crystals, values of which were obtained from Mejeha and Smith, 1998a; (b) Corresponding free - ion states (CFIS); (c) Last three columns show the experimental energy levels of Yb<sup>2+</sup> ions in the crystal hosts indicated.

since they become prominent mostly in heavily coloured RbCl:Yb<sup>2+</sup> crystal samples which could not be appreciably bleached thermally. Their true origin is the subject of another investigation to be reported soon.

## **Summary and Conclusions**

In this study, single crystals of rubidium chloride, bromide and iodide have successfully been doped with Yb<sup>2</sup> ions by heating the crystals in ytterbium vapour. The absorption spectra of the doped crystals consist of strong broad bands located in the visible and ultraviolet spectral region. These absorption bands have been shown to be due to the electric dipole allowed transitions of the Yb<sup>24</sup> ions from the 4f<sup>4</sup>(<sup>1</sup>S<sub>0</sub>) ground state to the states of the 4f<sup>3</sup>5d configuration of the ions in the crystals.

The experimental bands can be categorized into three groups which correspond to the lower three of the four groups of the theoretically predicted energy levels of the 4f<sup>43</sup>5d configuration of Yb<sup>21</sup> ions in an octahedral crystal field. The experimental energy level scheme derived from the study shows a very close similarity with the theoretically calculated energy levels of the Yb<sup>21</sup> ions in an RbBr crystal.

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