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Strong-Field Assignment on $4f^{13}\ 5d$ Levels of Yb^{2+} in SrCl$_2$

Eugene Loh[*]
Laboratoire de Chimie Physique "Matière et Rayonnement" Associé au,
Centre National de la Recherche Scientifique, Université de Paris VI, 75 005-*Paris-France*

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The $4f^{14} \rightarrow 4f^{13}\,5d$ absorption spectrum of an Yb^{2+} ion in cubic crystals is demonstrated to have four peaks, which correspond to the four $5d$ (e_g or t_{2g}) $4f^{13}$ ($^2F_{7/2}$ or $^2F_{5/2}$) final states.

The $4f^{n-1}\,5d$ configuration of most of the divalent and trivalent rare-earth ions in solids is known[1,2] to be formed by weak interaction between the $5d$ orbitals, which are split strongly in the crystal field, with the $4f^{n-1}$ core. For example, the $4f^{14} \rightarrow 4f^{13}\,5d$ absorption spectrum[3] of Yb^{2+} in CaF$_2$ consists of e_g and t_{2g} components of the $5d$ electron with a separation of 16 700 cm^{-1}. Each of these $5d$ orbitals has a high-energy partner,[3] which corresponds to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ($4f^{13}$) at ~10 000 cm^{-1}. For each Yb^{2+} ion in the cubic crystal there are therefore four $4f^{14} \rightarrow 4f^{13}\,5d$ ab-

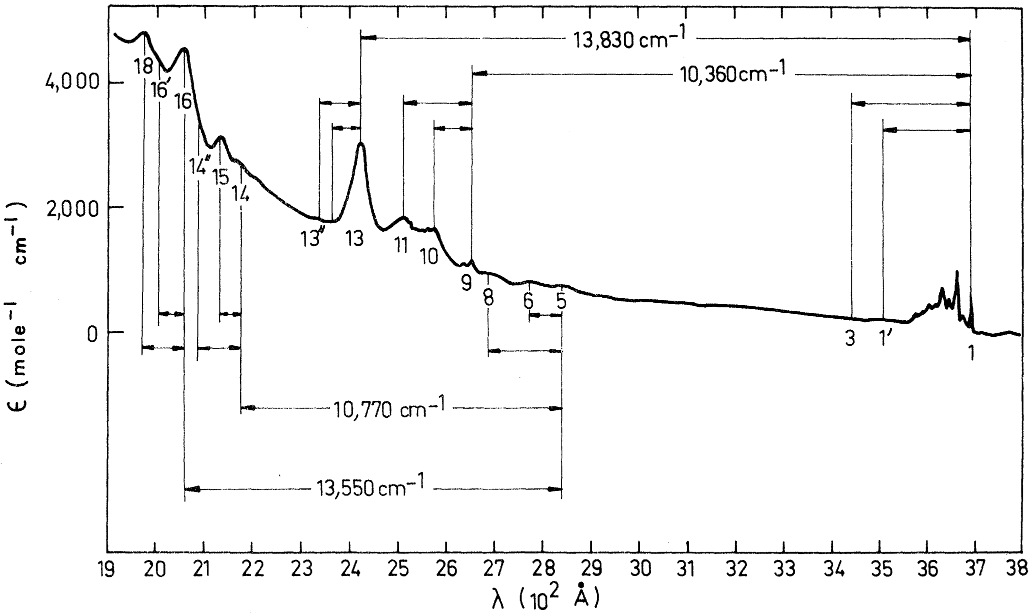

FIG. 1. $4f^{14} \rightarrow 4f^{13}$ $5d$ absorption spectrum of Yb^{3+} in $SrCl_2$ at 4.2 °K.

sorption peaks,[3] which correspond to the final states $5d(e_g$ or $t_{2g})4f^{13}(^2F_{7/2}$ or $^2F_{5/2})$ with e_g lower than t_{2g} in fluorite structure and $^2F_{7/2}$ lower than $^2F_{5/2}$. The energy difference between the e_g and t_{2g} components is $10Dq \approx 13\,000$ to $17\,000$ cm^{-1} in alkaline-earth fluorides[4] and that between $^2F_{7/2} - {}^2F_{5/2}$ should be that of Yb^{3+} $(4f^{13}) \sim 10\,000$ cm^{-1}.[5]

In this paper we shall demonstrate that the seemingly complicated spectrum[6] of Yb^{2+} in $SrCl_2$, which has the same fluorite structure as other alkaline-earth fluorides, can and should be simply interpreted as in CaF_2.[3] The apparent complexity of the $4f^{14} \rightarrow 4f^{13}\,5d$ absorption spectrum[6] of Yb^{2+} in $SrCl_2$ is possibly due to the presence of (a) three types of "isolated" Yb^{2+} ions and (b) three types of Yb^{2+} sites with Yb^{3+} neighbors. In CaF_2, there seems to be only (a) one type of "isolated" Yb^{2+} ion and (b) one type of Yb^{2+}-Yb^{3+} site as suggested by the ultraviolet absorption spectrum[3,4] of Yb^{2+} in CaF_2.

Figure 1 reproduces the $4f^{14} \rightarrow 4f^{13}\,5d$ absorption spectrum[6] of Yb^{2+} in $SrCl_2$. Starting at the long-wavelength end, we assign the structure at 1, 1', and 3 as the $5d(e_g)4f^{13}(^2F_{7/2})$ state of three types of "isolated" Yb^{2+}. Their corresponding $5d(e_g)4f^{13}\,(^2F_{5/2})$ states are at 9, 10, and 11, respectively, and the $5d(t_{2g})4f^{13}(^2F_{7/2})$ states are at 13, 13', and 13'', respectively. The $5d(t_{2g})4f^{13}\,(^2F_{5/2})$ states will be in the vacuum-ultraviolet region.[3] This assignment yields $^2F_{5/2}$-$^2F_{7/2} \approx 10\,360$ cm^{-1} and crystal field strength $10Dq \approx 13\,830$ cm^{-1} as indicated in Fig. 1 by the separation between peaks 9 to 1 and 13 to 1, respectively. Similarily, we assign the structures at 5, 6, and 8 in Fig. 1 as $5d(e_g)4f^{13}\,(^2F_{7/2})$ states of Yb^{2+} with Yb^{3+} neighbors. Again, their corresponding $5d(e_g)4f^{13}\,(^2F_{5/2})$ states are at 14, 15, and 14'', respectively, and the $5d(t_{2g})4f^{13}\,(^2F_{7/2})$ states are at 16, 16', and 18, respectively. The $5d(t_{2g})4f^{13}\,(^2F_{5/2})$ states of Yb^{2+} with Yb^{3+} neighbors, again, will be in the vacuum-ultraviolet region.[3] Figure 1 shows that $^2F_{5/2}$-$^2F_{7/2} \approx 10\,770$ cm^{-1} and $10Dq \approx 13\,550$ cm^{-1} are the energy separations between 14 to 5 and 16 to 5, respectively.

Table I summarizes the values of $^2F_{5/2}$-$^2F_{7/2}$ and $10Dq$ of $5d$ electron as deduced by subtracting the frequencies between corresponding peaks. The averaged value of $^2F_{5/2}$-$^2F_{7/2} \approx 10\,500$ cm^{-1} agrees well with the direct measurement[7] on Yb^{3+} in $SrCl_2$. The averaged value of the crystal field strength $10Dq \approx 13\,600$ cm^{-1} on the $5d$ electron in $SrCl_2$ is also in line with the values in other alkaline-earth fluorides,[4] e.g., 16 350 cm^{-1} in CaF_2, 14 750 cm^{-1} in SrF_2, and 13 300 cm^{-1} in BaF_2.

In order to demonstrate that the spectrum of $SrCl_2 : Yb^{2+}$ in Fig. 1 is not due to only one type of Yb^{2+} ion, we present the spectrum of another crystal in Fig. 2 at 8 °K. The Yb^{2+} in this sample was converted from Yb^{3+} in the single crystal $SrCl_2 : 0.1$-mole% Yb^{3+} by backing it with ytterbium metal chips in a sealed quartz capsule at 450 °C for a $\frac{1}{2}$ h. Figure 2 shows that the absorption due to Yb^{2+}-Yb^{3+}, peaks 5, 6, and 8, is of the same order of magnitude as that due to peaks 1 of isolated Yb^{2+} ions, while Fig. 1 shows that the former is about one order of magnitude lower than the latter due to low Yb^{3+} concentration. Apparently, the Yb^{3+}-Yb^{2+} conversion by vapor-baking reduction at 450

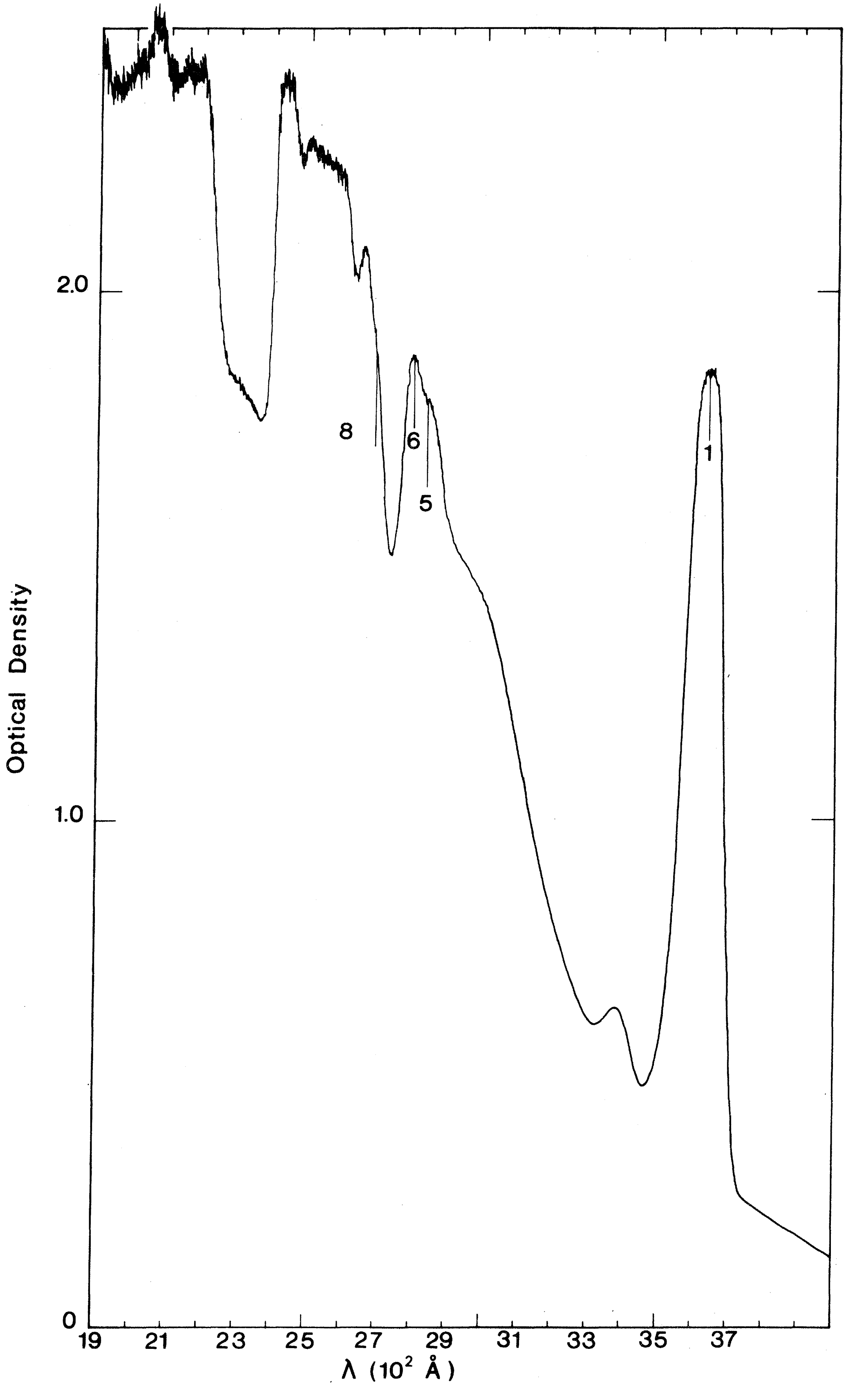

FIG. 2. $4f^{14} \rightarrow 4f^{13}$ $5d$ absorption spectrum of Yb^{3+} - rich $SrCl_2 : Yb^{2+}$ at 8 °K.

TABLE I. $4f^{14}\rightarrow 4f^{13}\,5d$ absorption peaks of Yb^{2+} in $SrCl_2$, their assignments, the deduced values of spin-orbit splitting of Yb^{3+}, and the crystal-field strength. (i) Experimental location of peaks, (ii) their assignments, (iii) the possible types of Yb^{2+} ions in $SrCl_2$, and (iv) spin-orbit splitting, $^2F_{5/2}-{}^2F_{7/2}$, of Yb^{3+} ($4f^{13}$) and the crystal field strength, $10Dq$, on the $5d$ electron as deduced by taking the difference in frequencies between the corresponding peaks.

(i) Experimental peaks (cm^{-1})		(ii) Assignment	(iii) Type of Yb^{2+}	(iv) Frequency $^2F_{5/2}-{}^2F_{7/2}$	Difference (cm^{-1}) $10Dq$
E_1	27 262	$5d(e_g)$ $4f^{13}$ ($^2F_{7/2}$)	"isolated" Yb^{2+}		
$E_{1'}$	28 500				
E_3	29 272				
E_5	35 028		Yb^{2+} with Yb^{3+} "neighbors"		
E_6	36 100				
E_8	37 219				
E_9	37 625	$5d(e_g)$ $4f^{13}$ ($^2F_{5/2}$)	"isolated" Yb^{2+}	10 360	
E_{10}	38 748			10 250	
E_{11}	39 749			10 480	
E_{13}	41 089	$5d(t_{2g})$ $4f^{13}$ ($^2F_{7/2}$)			13 830
$E_{13'}$	42 200				13 700
$E_{13''}$	42 750				13 480
E_{14}	45 794	$5d(e_g)$ $4f^{13}$ ($^2F_{5/2}$)	Yb^{2+} with Yb^{3+} "neighbors"	10 770	
E_{15}	46 649			10 550	
$E_{14''}$	47 900			10 680	
E_{16}	48 575	$5d(t_{2g})$ $4f^{13}$ ($^2F_{7/2}$)			13 550
$E_{16'}$	49 700				13 600
E_{18}	50 403				13 180

°C for $\frac{1}{2}$ h is not as efficient as the method, which was applied[6] to the sample in Fig. 1, of passing hydrogen through the mixture of $SrCl_2+0.05$-mole% $YbCl_3$ just below its melting point. The possible presence of the absorption due to Yb^{2+}-Yb^{3+} may also be deduced from the published spectra in Refs. 6 and 4:

(i) The absorption spectrum of $SrCl_2:Yb^{3+}$ in Fig. 2 of Ref. 6 shows two humps, one in the region 2650 to 2950 Å and the other 2000 to 2200 Å, which are in the absorption region of Yb^{2+}-Yb^{3+}. This suggests that there was a minute amount of Yb^{2+} in the $SrCl_2:Yb^{3+}$ sample used in the Fig. 2 of Ref. 6.

(ii) The strength of peaks 5 and 6 increases[4] as the lattice parameter decreases from BaF_2 toward CaF_2 as shown in Fig. 5 of Ref. 4. This enhancement of peaks 5 and 6 in a small lattice suggests that the Yb^{2+} ion, being of larger size, prefers to associated with smaller ions Yb^{3+} in a tight lattice.

We wish to emphasize that before a detailed fitting between a theoretical calculation and the experimental spectra it is useful to examine whether the experimental spectra are due to a single type or many types of ions in solids. Eremin[8] has recently compared his $4f^{n-1}\,5d$ calculation of Yb^{2+} in solids with the experimental spectra. Unfortunately, he tacitly assumed that all the peaks of Yb^{2+} in fluorides and chloride are due to one type of ion.

In conclusion, we have demonstrated that the $4f^{14}\rightarrow 4f^{13}\,5d$ transition of an Yb^{2+} ion in cubic solids, e.g., alkaline-earth fluorides and $SrCl_2$, simply has four peaks. Piper, Brown, and McClure,[6] in their analysis on the $4f^{14}\rightarrow 4f^{13}\,5d$ absorption spectrum[6] of Yb^{2+} in $SrCl_2$, have treated the complicated spectrum as due to one type of Yb^2 ion instead of several types as we illustrate here.

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[*] Present address: Instituto de Energia Atôinica, Caixa Postal 11.049, Pinheiros, São Paulo, Brasil.

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Positron Annihilation in the Wigner Crystal

Chanchal K. Majumdar
Tata Institute of Fundamental Research, Bombay-5, India

T. V. Ramakrishnan
Indian Institute of Technology, Kanpur, India

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The positron annihilation rate is calculated in the Wigner crystal and shown to approach the positronium value continuously from above as r_s becomes large. For $r_s \approx 15$, the numerical value is roughly in agreement with what is expected from the knowledge of the rate in low-density metals.

I. INTRODUCTION

Positron annihilation in metals has been studied by many workers with the computational methods of many-body theory. Up to about $r_s \approx 4$ in sodium, the conventional electron-gas theory yields fair results, but beyond this point for the low-density situation more sophisticated calculations become necessary. (r_S is the interelectron spacing measured in units of the Bohr radius.) In this region, the calculations of Kahana, Carbotte, and Salvadori[1] or of Bergersen and Terrell[2] give too low a value. Crowell *et al.*[3] find that their calculated rates diverge to $+\infty$ around $r_s = 6$; difficulties stem from those associated with the calculation of the dielectric constant of the electron gas. Sjöllander and Stott[4] also find that their rates are too high. Following Sjöllander and Stott's approach, Bhattacharyya and Singwi[5] have shown that a more refined self-consistent consideration of rell[2] give too low a value. Crowell *et al.*[3] find that their calculated rates diverge to $+\infty$ around $r_s \approx 6$; difficulties stem from those associated with the calculation of the dielectric constant of the electron electron correlations, including in particular three-body correlations, leads to good agreement with experiment in the region $r_s = 5$ to 6. Their rates tend to the free-positronium value as r_s becomes larger.

Going beyond the region around $r_s \approx 5$, Arponen[6] has published a calculation in which the annihilation rate drops well below the positronium value around $r_s = 8$, but approaches this value from below. It is well known that all the experimentally measured values are above the positronium value and approach this smoothly from above. Arponen's calculation uses the Thomas–Fermi screening for large r_s, obviously outside its range of validity, and ignores the fact that the electron gas undergoes drastic transformation in this region.

We shall restrict ourselves to this extreme low-density region and consider the annihilation of a positron in the Wigner crystal[7] into which the electron gas transforms at large r_s. Of course, there are many uncertainties connected with this crystal.[8-13] Therefore we shall try only for a qualitatively correct behavior. Our main aim is to show that if this crystallization is taken into account, the positron annihilation rate approaches that of positronium from *above*, not from below.

Since the calculation involves considerable algebra, it is perhaps worthwhile to motivate the final equation by simple arguments. Consider first the bcc lattice of the Wigner crystal as broken up into the Wigner–Seitz spheres. One electron sits at the center of each sphere, and there is enough uniformly distributed positive charge in it to make it neutral. The potential experienced by the positron is made up of the Coulomb interaction of the electron and that of the distributed positive charge:

$$\begin{aligned} \phi(r) &= -\frac{e^2}{r} + \frac{3e^2}{2r_{\text{WS}}} - \frac{e^2 r^2}{2r_{\text{WS}}^3}, \qquad & r \le r_{\text{WS}} \\ &= 0, & r \ge r_{\text{WS}}\ . \qquad (1.1) \end{aligned}$$

The wave function ψ for the lowest state satisfies the equation

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} + \frac{2\mu_{\text{red}}}{\hbar^2}\left[E - \phi(r)\right]\psi = 0\ , \qquad (1.2)$$

with the boundary condition $d\psi/dr|_{r=r_{\text{WS}}} = 0$.