The J-mixing effect in Ln\textsuperscript{3+} ions crystal field levels

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The J-mixing effect in the 2\textsuperscript{S+1}L\textsubscript{J} level barycentre energy and splitting of trivalent lanthanide ions is analysed. The main predictions are that the maximum 2\textsuperscript{S+1}L\textsubscript{J} level splitting (\(\Delta E\)) is reduced and the barycentre energy can become lower with increasing \(\Delta E\). This effect is particularly important in low symmetries. Satisfactory agreement between the predictions and experimental data was obtained to all analysed systems, namely, the maximum \(F\textsubscript{1}\) level splitting of the Eu\textsuperscript{3+} ion and its barycentre energy in crystals and glasses.

1. Introduction

The crystal field effect on tripositive lanthanide ions (Ln\textsuperscript{3+}) is still an attractive theme of study in theoretical physics and chemistry. The recent interest for this study is stimulated by necessity of the luminescent materials with Ln\textsuperscript{3+} used in telecommunication, lighting, electroluminescent devices, (bio-) analytical sensors and bio-imaging set-ups [1,2]. The Eu\textsuperscript{3+} ions in several structures have been analysed by various techniques, and has been often used as a luminescent structural probe [3,4]. However, the splitting of levels and its barycentre energy position are very important and some aspects are still in study [4-6]. In a crystal field (CF) the states may be completely defined by a (JM) basis, J being the total angular momentum and M its projection [7]. However, states with different J can be mixed due to the CF; this effect is known as J-mixing effect and can lead to change in the energy level positions. This Letter aims to discuss how the J-mixing effect affects the barycentre position and the nonlinear behaviour of the maximum splitting of the \(^7F\textsubscript{1}\) energy level of the Eu\textsuperscript{3+} ion as a function of the crystal field parameters.

The CF Hamiltonian can be obtained by phenomenological simulation, but the CF parameters (\(B_{k}\)) depend on the base functions used to describe the 4f electronic configuration [8]. However if J-mixing is considered the problem of finding the \(B_{k}\) becomes more complex due to the nonlinear terms in \(B_{k}\). In the case of a strong CF, the J-mixing contribution cannot be neglected in predicting the energy level scheme [9]. Two effects are frequently attributed to the J-mixing: the change in the barycentre energy position and the nonlinear maximum splitting of the 2\textsuperscript{S+1}L\textsubscript{J} manifold versus CF strength parameters [10,11].

2. The 2\textsuperscript{S+1}L\textsubscript{J} levels barycentre energy position shift

The standard form of the Hamiltonian acting within the 4f\textsuperscript{m} configuration of trivalent lanthanides in any host is commonly written with 19 free ion parameters [3,7]. When a lanthanide ion is incorporated into a crystal host, the Slater parameter, \(F\), and the spin-orbit parameter, \(\zeta\), change with respect to their free-ion value. This changing is usually attributed to the nephelauxetic effect and cause a change in the barycentre of the 2\textsuperscript{S+1}L\textsubscript{J} energy level. However, this shift depends only on the type and distance of the nearest neighbour and not on the angular part of the CF.

For each 2\textsuperscript{S+1}L\textsubscript{J} manifold, the J-splitting depends on the \(B_{k}\) only for \(k \leq J\). Neglecting J-mixing, the relation between the maximum Stark splitting of the 2\textsuperscript{S+1}L\textsubscript{J} manifold and \(B_{k}\) is found in Ref. [10]. In the case that the degeneracy of the \(^5D\) and \(^7F\textsubscript{1}\) level is removed the \(B_{k}\) values are nonzero. For the \(^7F\textsubscript{1}\) level splitting, \(\Delta E\), there is an expression for the maximum splitting as a function of the \(B_{k}\). This has been discussed for some crystals in Refs. [11,12]. The discrepancy in the predictions of \(\Delta E\) is attributed to the J-mixing effect. However, the calculations have not yet been discussed without approximations.

The shift in barycentre of the level J through of the non spherical part occurs due to the J-mixing effect and depends on the symmetry of the CF. The CF states are written as \(|J\Gamma\rangle = \sum_{M |JM\rangle } |JM\rangle |J\Gamma\rangle\). |JM\rangle are states of the free ion and all others quantum number are implicit. The perturbation that removes the degeneracy in J also causes mixing of states with different J. By using perturbation theory as found in text books [14], to describe the corrections due to the J-mixing, the energy level is given by:

\[
E_{J'} = (|J\Gamma\rangle \langle J\Gamma|) + \sum_{J''} \frac{(|J\Gamma\rangle H_{el}|J\Gamma|)^2}{E(J) - E(J'')},
\]

where

\[
E(J) = \sum_{\alpha} \frac{E_{\alpha}}{Z} - \sum_{\alpha \beta} \frac{H_{\alpha \beta}}{Z^2} \langle \alpha | Z | \beta \rangle
\]
H_{CF} is the non-spherical part of the crystal field Hamiltonian, $H_{CF} = \sum_{\mathbf{k}} B_{\mathbf{k}}^{b} C_{\mathbf{k}}^{b}$, $k = 2.4.6$ and $|q| \leq k$ [2,7]. The CF states and energy level are $|J\Gamma\rangle$ and $E(J\Gamma)$ respectively and $\sum_{J} g_{J} |J\Gamma\rangle H_{CF} |J\Gamma\rangle = 0$. Therefore, the shift in barycentre due J-mixing effect is given by:

$$\Delta E_{\Gamma}[J] = (2J + 1)^{-1} \sum_{J} \frac{|\langle J\Gamma|H_{CF}|J\Gamma\rangle|^{2}}{E(J) - E(J\Gamma)}$$

(2)

The summation over the $\Gamma$ and $\Gamma$ quantum numbers can be converted to a sum in $M$ and $M'$ through the projection operator $P_{0} = \sum_{\Gamma} |\Gamma\rangle \langle \Gamma\Gamma|$, onto the subspace of the free-ion state acts in $|\Gamma\rangle$ and $|\Gamma\Gamma\rangle$ one gets:

$$\Delta E_{\Gamma}[J] = (2J + 1)^{-1} \sum_{J} \frac{1}{E(J) - E(J\Gamma)} \sum_{M,-J} |\langle J|H_{CF}|J'M\rangle|^2$$

(3)

By using the Wigner–Eckart theorem and the 3-j symbol orthogonal proprieties, the sum over $M$ and $M'$ can be readily performed [10,13]. Therefore, an exact analytical formula for the change of the barycentre of the CF levels is:

$$\Delta E_{\Gamma}[J] = (2J + 1)^{-1} \sum_{J} \frac{|\langle J|C\rangle|^{2}}{E(J) - E(J\Gamma)} S^{k}$$

(4)

$S^{k} = (2k + 1)^{-1} \sum_{\mathbf{k}} |B_{\mathbf{k}}^{b} C_{\mathbf{k}}^{b}|^{2}$ is the CF strength parameter [10] and $|\langle J|C\rangle|^{2}$ is the reduced matrix elements, which can be rewritten in terms of the unit tensor $U^{b}$ [7,15]. Eq. (4) has been already obtained through an effective Hamiltonian that includes J-mixing [9]. In weak CF or high symmetry $\Delta E_{\Gamma}[J]$ is negligible because the $S^{k}$ parameters are small. The composition of the wave functions now contains different J values. The appropriate wave functions can be obtained through perturbation theory [14].

3. The maximum splitting of the $^{2S+1}L_{J}$ manifold

The relation between the maximum splitting of the $^{2S+1}L_{J}$ manifold, $(\Delta E[J])^{2}$, is linear with the root-mean-square of $\Delta E[J]$ [10]:

$$(\Delta E[J])^{2} = \frac{1}{g} \sum_{i} g(E_{i}) \propto (\Delta E[J])^{2}$$

(5)

$E_{i}$ is the energy of the $i$th level with respect to the free ion position and $g_{i}$ is its degeneracy. The $(\Delta E[J])^{2}$ of the $E_{i}$ levels of a 2J+1 degenerate level after the CF perturbation is given by [14]:

$$\Delta E[J]^{2} = (2J + 1)^{-1} Tr_{0}(V - \Delta E[J]) P_{0}(V - \Delta E[J])$$

$$= (2J + 1)^{-1} Tr_{0} V_{0} P_{0} V_{0} - (2J + 1)^{-1} \Delta E[J] Tr_{0} P_{0} (V + \Delta E[J])^{2}$$

(6)

In related literature it is assumed that $\Delta E[J] = 0$ [6,10,11]. However, because of the J-mixing effect, the term in $\Delta E[J]$ in Eq. (6) can be no more neglected. Therefore, in order to consider the J-mixing effect, the CF potential is now expressed by [16]: $V = H_{CF} + H_{corr}$ and

$$H_{corr} = \sum_{M,-J} \frac{H_{CM}}{E(J) - E(J\Gamma)}$$

(7)

The $Tr_{0} P_{0}(V)$ in Eq. (6) is obtained using both Eq. (4) and $Tr_{0} P_{0}(H_{CF}) = 0$ [3]. This leads to $Tr_{0} P_{0}(V) = (2J + 1) \Delta E[J]$. Eq. (6) then becomes

$$(\Delta E[J])^{2} = (2J + 1)^{-1} Tr_{0} P_{0} V_{0} - (\Delta E[J])^{2}$$

(8)

For the phenomenological $B_{\mathbf{k}}^{b}$ values obtained through the functions without J-mixing it is assumed that the effective CF can be written as $V = \sum_{\mathbf{k}} B_{\mathbf{k}}^{b} C_{\mathbf{k}}^{b}$ and that $\Delta E[J] = 0$. Considering the corrected Eq. (7), the first term in Eq. (8) can be clearly explained by the following expression:

$$Tr_{0} P_{0} V_{0} = Tr_{0} P_{0} H_{CF} P_{0} H_{CF} + Tr_{0} P_{0} H_{CF} P_{0} H_{corr} + Tr_{0} P_{0} H_{corr} P_{0} H_{corr}$$

The last term in Eq. (9) can be obtained from Eq. (8) by entering $V = H_{corr}$ and using that $(\Delta E[J])^{2} = (2J + 1)^{-1} \sum_{J} g_{J} (\Delta E[J])^{2}$, which is the root-mean-square of the $\Delta E[J]$ correction. Then,

$$Tr_{0} P_{0} H_{corr} P_{0} H_{corr} = \sum_{J} g_{J} (\Delta E[J])^{2} + (2J + 1)(\Delta E[J])^{2}$$

(10)

$\Delta E[J]$ is the corrections due J-mixing and $g_{J}$ is the degeneracy. The second and three terms can be obtained through the project operator and the proprieties that the $H_{CF}$ is orthogonal in relations to functions $|\Gamma\rangle = \sum_{\Gamma} |\Gamma\rangle \langle \Gamma\Gamma|$ thus the trace is given as:

$$Tr_{0} P_{0} H_{corr} = \sum_{J} |\Gamma\rangle H_{corr} |\Gamma\rangle$$

$$= \sum_{J} g_{J} (\Delta E[J])^{2}$$

(11)

$E_{0}$ is the energy level of the CF without J-mixing, $Tr_{0} P_{0} H_{CF} P_{0} H_{CF}$ have the same results. Therefore, the $(\Delta E[J])^{2}$ is found using the Eqs. (11) and (10) in the Eq. (9) and substitute in Eq. (8). Thus has:

$$(\Delta E[J])^{2} = \frac{1}{2J + 1} \sum_{J} |\langle J|C\rangle|^{2} S^{k} + \frac{1}{2J + 1} \sum_{J} g_{J} E_{0}^{b} \Delta E[J] + \frac{1}{2J + 1} \sum_{J} g_{J} (\Delta E[J])^{2}$$

(12)

From Eq. (1) $\Delta E[J]$ have the same signal for all $\Gamma$ if the mixing is only with one J. Using the propriety of the energy level without J-mixing $\sum_{J} g_{J} E_{0}^{b} = 0$ and the approximation $E_{0}^{b} = \Delta E[J]/(2J + 1)$, one has

$$(\Delta E[J])^{2} \propto \frac{1}{2J + 1} \sum_{J} |\langle J|C\rangle|^{2} S^{k} + \left(\frac{\Delta E[J]}{2J + 1}\right)^{2}$$

(13)

In this case the J-mixing effect can lead to a decrease or increase in $(\Delta E[J])^{2}$, and then in $\Delta E[J]$, depending on if J-mixing decreases or increases the magnitude of $\Delta E[J]$. 4. Applications to the Eu$^{3+}$ ion

The Eq. (8) predicts that the theoretical value of the $(\Delta E[J])^{2}$ from $B_{\mathbf{k}}^{b}$ without J-mixing $(B_{\mathbf{k}}^{b})$ is smaller than the experimental value due the value $\Delta E[J]$. This prediction is confirmed in Figure 1 for the $^{7}F_{2}$ of the Eu$^{3+}$ ion for different crystals. One has just shown that the shift in the barycentre of the energy of the $^{7}F_{2}$ level in a CF is due to two effects: J-mixing and changing in the spin–orbit interaction parameter. Considering these effects, the correction in the energy of the $^{7}F_{2}$ and $^{7}F_{1}$ levels are given by the Eq. (4). Thus, the position of the $^{7}F_{1}$ level in relation the $^{7}F_{2}$ level can be written as:

$$E_{0}^{b}[F_{1}] = E_{0}^{b}[F_{2}] + \delta(S^{2}) + \delta(S^{2} \times P)$$

(14)

$E_{0}^{b}[F_{1}]$ is the free ion energy position. $\delta(S^{2})$ and $\delta(S^{2} \times P)$ are obtained by expanding the right side of Eq. (4). This leads to:

$$\delta(S^{2}) = \frac{1}{3} \left(\frac{|(\langle F_{2}|C^{2}|F_{1}\rangle)^{2}|}{E_{F_{2}}^{2}} + \frac{|(\langle F_{2}|C^{2}|F_{1}\rangle)^{2}|}{E_{F_{1}}^{2}} + \frac{3|(\langle F_{1}|C^{2}|F_{2}\rangle)^{2}|}{E_{F_{2}}^{2}}\right) S^{2}$$

(15)

Then, $\delta(S^{2}) > 0$ and $\delta(S^{2} \times P) < 0$, this latter because the denominator in Eq. (4) is negative. Therefore, three cases in Eq. (14) can be analysed: firstly, for $\delta(S^{2} \times P)$ small in comparison to $\delta(S^{2})$. This can be found in sites with high symmetry, due to the fact that several $B_{\mathbf{k}}^{b}$ components are zero, or for high values of $E_{0}^{b}[F_{1}]$. 139
Here is a new relation between $S_2$ and the maximum due to $J$-mixing effect. The value of $S_2$ can be obtained through of $\Delta E_b$ is given by:

$$\Delta E_b = \frac{1}{2} \frac{\Delta E^2 - (2/3)(\Delta E_b)^2}{|\langle 7F_1 | C^2 | 7F_1 \rangle|^2}$$

Therefore, in the case of $\delta(S^{k+4})$ negligible, and using the Eq. (18) in Eq. (15), and then in Eq. (14), one has

$$\Delta E_b = E_c(|\langle 7F_1 | U^2 | 7F_2 \rangle|^2 E_c 2F_1) - E_c 2F_1 | U^2 | 7F_2 |^2 + \sum |\langle 7F_0 | U^2 | 7F_1 \rangle|^2$$

$\Delta E_b$ is also equal to the difference $\Delta E_b = \Delta E_{bb} - \Delta E_{ab}$. From Eq. (4) only in the first term ($k = 2$) $\Delta E_b$ is proportional to $\Delta E_{bb}$. Thus $\Delta E_b$ can be written in terms of $\Delta E_b$ as follows:

$$\Delta E_b = \left(1 - \frac{1}{2} \frac{\langle 7F_1 | U^2 | 7F_2 \rangle^2 + \langle 7F_2 | U^2 | 7F_1 \rangle^2 + \sum \langle 7F_0 | U^2 | 7F_1 \rangle^2}{|\langle 7F_1 | C^2 | 7F_1 \rangle|^2}\right) \Delta E_b$$

Using the value of $|\langle 7F_1 | U^2 | 7F_2 \rangle|^2$, $E_c 2F_1 - E_c 2F_2$ is $1024 \text{ cm}^{-1}$, and $E_c 2F_2 - E_c 2F_1 = 1800 \text{ cm}^{-1}$ given in Ref. [15], as the barycentre energy positions of each respective manifold, the Eq. (20) leads to $\Delta E_b = 2.4 \Delta E_b$ and the Eq. (19) can be written as:

$$\Delta E = 2 \cdot 10^{-4} \left[ \Delta E^2 + (2.4 \times (2/3)(\Delta E_b)^2 \right]$$

Solving for $\Delta E$ with $\Delta E_b$ the solution with physical meaningful is

$$\Delta E = \left(\frac{2}{5}\right) \left[ 31250(\Delta E_b) - 10(\Delta E_b)^2 \right]$$

In order to test this prediction, one enters the hypothetical values $E_c 2F_1 = 360 \text{ cm}^{-1}$ (in the case of the Eu$^{3+}$: KYF$_4$ and Eu$^{3+}$: KLuF$_4$ crystals and $E_c 2F_1 = 356 \text{ cm}^{-1}$ (in the case of Eu$^{3+}$ doped calcium diborate glass) lead to very satisfactory predictions (Figures 2 and 3).

The second case is for $\delta(S^2)$ small compared to $\delta(S^{k+4})$. This occurs when $E_c 2F_1$, $S^4$, and $S^6$ are large. Therefore, the change in $\Delta E_b$ [Eq. (12)] due to $S^2$ is small. So, the $J$-mixing contributes to a decrease in the barycentre energy position. For instance, in Figure 3 it is shown that $E_c 2F_1 = 447 \text{ cm}^{-1}$ while $\Delta E(7F_1) = 0$ for Eu$^{3+}$ in zinc oxyfluorotellurite glass [19]. This is being predicted for the first time. In Ref. [19], as a function of excitation energy, it is observed repulsion between neighbouring levels. Figure 3 shows both cases: $\delta(S^2) > \delta(S^{k+4})$ calculated via Eq. (21) and $\delta(S^2) < \delta(S^{k+4})$. In Ref. [21], now as a function of an external magnetic field, it is observed...
and simulated repulsion between neighbouring levels with the same irreps. In very low site symmetries all Stark sublevels are described by similar irreducible representations (irreps) [3].

For the case when $S^4$ and $S^6$ are comparable to $S^2$, as $S^4$ and $S^6$ have opposite sign in comparison to $S^2$, the barycentre may not change appreciably and the maximum splitting will remain linear with $S^2$.

5. Conclusions

The levels of the Eu$^{3+}$ ion have been revisited by considering the J-mixing effect using first order perturbation theory without approximations. A reduction in the $^7F_1$ level splitting is predicted and the barycentre energy position can become lower. This latter is in the opposite sense when compared to the shift due to the spin–orbit coupling. The relation between the $^7F_1$ level splitting and the $S^2$ strength parameter shows that the J-mixing contributes to reduce the splitting. In sites with high symmetry the J-mixing can be negligible depending on the energy separation between neighbouring Stark levels. The prediction of lowering the barycentre energy position with increasing $\Delta E$ is being made for the first time. Very satisfactory predictions is found between theory and experiment to all analysed systems.

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