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Simple way to test the validity of $^{2S+1}L_J$ barycenters of rare earth ions (e.g. $4f^2$, $4f^3$ and $4f^6$ configurations)

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Abstract

The energy displacement of non-degenerated electronic $^{2S+1}L_J$ levels, ($J=0$ or $1/2$), along the nephelauxetic scale of a rare earth ion can be easily connected with the evolution of the barycenter position of different $^{2S+1}L_J$ levels of $4f^n$ ground configurations. Linear slopes are obtained and presented for different crystal field (cf) levels for Nd^{3+}, Pr^{3+} and Eu^{3+}, corresponding to the $4f^2$, $4f^3$ and $4f^6$ configurations, respectively. A $^{2S+1}L_J$ level barycenter positioned out of slope suggests incorrect assignment of the level. Moreover, some missing Stark components of a given $^{2S+1}L_J$ level can be correctly extrapolated on the basis of the corresponding barycenter deduced from the slope. It is particularly evident in the case of low J values. The example of the $^2P_{3/2}$ level for Nd^{3+} doped $Ca_4GdO(BO_3)_3$ (GdCOB) crystal is given as an illustration.

Keywords: Praseodymium; Neodymium; Europium; Nephelauxetic scale; Energy level barycenters

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1. Introduction

A degeneracy of electronic levels of free rare earth (RE) ions embedded in crystalline compounds is partially or completely lifted according to the local symmetry around the RE ion. In any symmetry lower than a cubic a great number of lines is observed in the emission as well as in the absorption spectrum. Due to this complexity the spectroscopic analysis must be completed very carefully.

The assignment of the electronic transitions is a very hard task, especially when several crystal field (cf) levels are commingled, e.g. the $^3P_1$ with the $^1I_6$ level for Pr^{3+}, configuration $4f^2$, or the $^4D_{1/2}$ for Nd^{3+}, configuration $4f^3$, situated in the UV region between the $^2I_{11/2}$ and $^4D_{5/2}$ levels. Fortunately, there are some electronic levels for $4f^2$, $4f^3$ and $4f^6$ configurations situated in the visible spectral range quite isolated from other observed spectral lines: $^3P_0$ and $^2P_{1/2}$ for praseodymium and neodymium, respectively, and $^5D_0$ for europium. The $^3P_0$, $^2P_{1/2}$ and $^5D_0$ levels are non-degenerated by the crystal field. The maximal number of lines predicted for different J levels depends on the number of electrons in $4f^n$ configuration. For an even or an odd number of electrons in the f shell, $2J+1$ or $J+1/2$ lines are expected, respectively. If the compound is single phased and if the rare earth ion possesses a unique site in the structure, only one line must be observed for $J=0$ or $1/2$ in the absorption/emission spectrum. So, the evolution of these single lines along the nephelauxetic scale can be easily connected with the evolution of different $^{2S+1}L_J$ level barycenter (bc) positions of $4f^n$ ground configurations. We present results obtained for different crystal field levels. It is evident from following observations that a $^{2S+1}L_J$ level barycenter situated far from the slope underlines a wrong identification of the wavenumber of the level.

2. Results and discussion

2.1. $4f^2$ configuration

Praseodymium is quite suitable for our purpose. There are many experimental assessments concerning the optical feature of Pr^{3+} embedded in various crystalline matrices.

From [1,2] and our own experimental measurements [3,4] we established the nephelauxetic scale for various energy levels of Pr^{3+}. We consider the $^3P_0$ level as well as the energy level barycenters of the $^3P_1$ and $^1D_2$ levels.

The relations of the $^3P_1$ and $^1D_2$ level barycenters as a function of the $^3P_0$ level are presented in Figs. 1 and 2,

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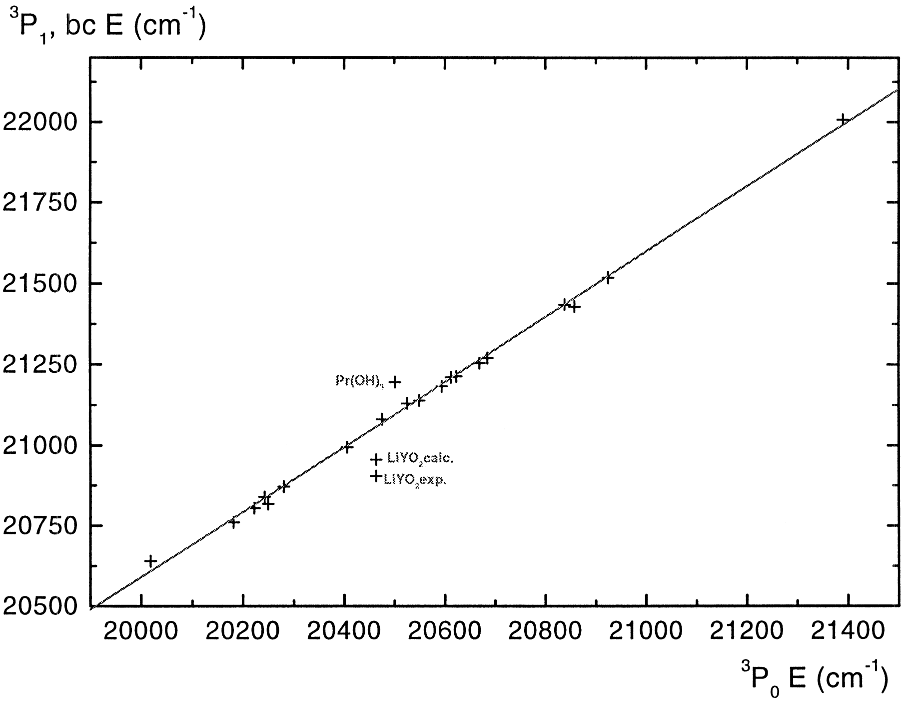

Fig. 1. The wavenumbers of the $^3P_1$ level bc as a function of those of the $^3P_0$ level along the praseodymium nephelauxetic scale.

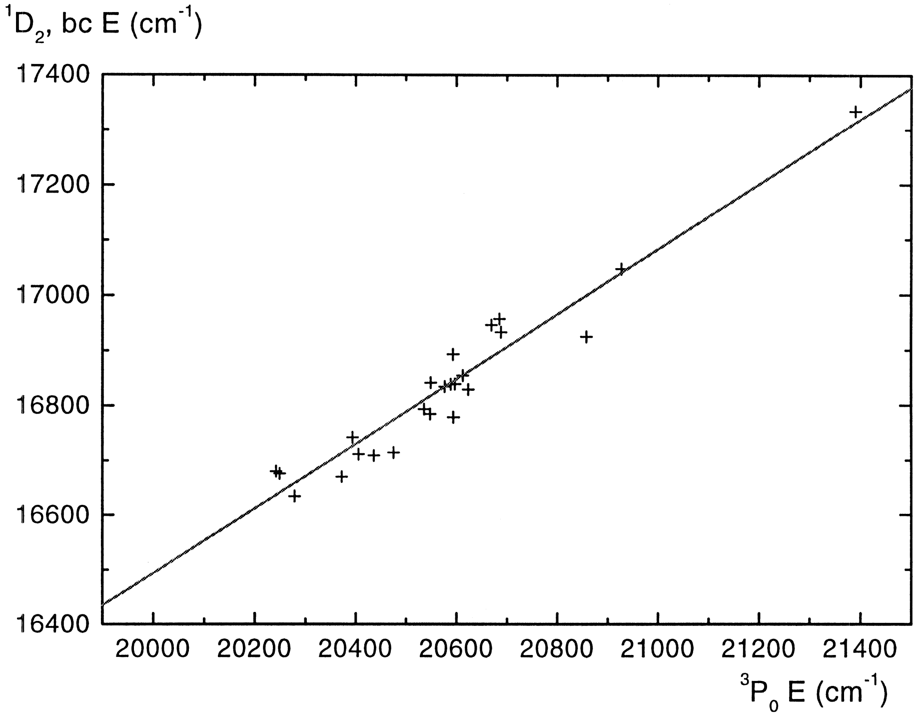

Fig. 2. The wavenumbers of the $^1D_2$ level bc as a function of those of the $^3P_0$ level for different praseodymium compounds.

respectively. It is evident from Fig. 1 that the $^3P_1$ level in $LiYO_2$: Pr^{3+} [5] is badly assigned and this is also true for $Pr(OH)_3$ [1]. The $^3P_1$ calculated level barycenter in $LiYO_2$: Pr^{3+} is also wrong. It indicates that the phenomenological set of the free ion and/or crystal field parameters must be improved in this case [5]. For the $^1D_2$ level presented in Fig. 2 there are some barycenter values away from the slope, probably due to erroneous experimental data. Nevertheless, it gives the general peculiarity.

2.2. 4f^3 configuration

To support our statement discussed previously, we assume the same approach on neodymium. A very nice example is the Nd^{3+} doped $Ca_4GdO(BO_3)_3$ (GdCOB) crystal. In Fig. 3 is shown the evolution of the $^4F_{3/2}$ level bc as a function of $^2P_{1/2}$ level. In the reference supplied in Fig. 3 are given the values of the energy levels of the ^4I term and $^4F_{3/2}$ level for $Ca_4GdO(BO_3)_3$: Nd^{3+} (GdCOB), $YAl_3(BO_3)_4$: Nd^{3+} (YAB) and $Ca_5(PO_4)_3F$: Nd^{3+} (FAP). From the corresponding $^4F_{3/2}$ barycenters situated at 11 441 (GdCOB), 11 386 (YAB) and 11 490 cm^{-1} (FAP) the wavenumbers of the $^2P_{1/2}$ level have been assumed from Fig. 3 at 23 156, 23 071 and 23 237 cm^{-1} for GdCOB, YAP and FAP, respectively. In the Nd^{3+}: GdCOB absorption spectrum performed at 4.2 K, the $^2P_{1/2}$ level is found at 23 150 cm^{-1}. The extrapolated wavenumber from the slope (23 156 cm^{-1}) is in good agreement with the experimental data (23 150 cm^{-1}). For YAB and FAP no data for the $^2P_{1/2}$ level exist. The respective wavenumbers should be 23 071 and 23 271 cm^{-1}.

To argue our observations we present another example for neodymium ion. In the low concentration sample (5%) only one line is observed for the $^2P_{3/2}$ level situated at 25 964 cm^{-1} instead of the two lines expected (see Fig. 4). From the slope representing the $^2P_{3/2}$ level barycenter as a function of the $^2P_{1/2}$ level we can deduce 26 062 cm^{-1} as the approaching barycenter (Fig. 5) [1,2,6]. Therefore, the second component is supposed to be at 26 160 cm^{-1}, see arrows in Fig. 6.

Effectively, in the 7% neodymium doped GdCOB crystal the second component is found at 26 151 cm^{-1} giving 26 057 cm^{-1} as the $^2P_{3/2}$ barycenter (Fig. 7), not far from the extrapolated value at 26 062 cm^{-1}.

This analysis can be also used to verify the calculated energy level barycenters obtained by the simulation of the energy level schemes deduced from spectroscopic measurements. Moreover, it is available for the cf parameters as well as for the free ion parameters. On the basis of this consideration any missing, non-degenerated J level in the crystalline compound, $J=0$ or $1/2$, can be deduced from these slopes. So, the $^4D_{1/2}$ level of Nd^{3+}, situated in the UV range, useful for simulation of the free ion parameters, but often situated in the transfer energy band, can be extrapolated within small error (Fig. 8). Consequently, the set of the phenomenological crystal field parameters can be improved.

The linear evolution presented as a function of non-degenerated levels for the 4f^n configuration is also ob-

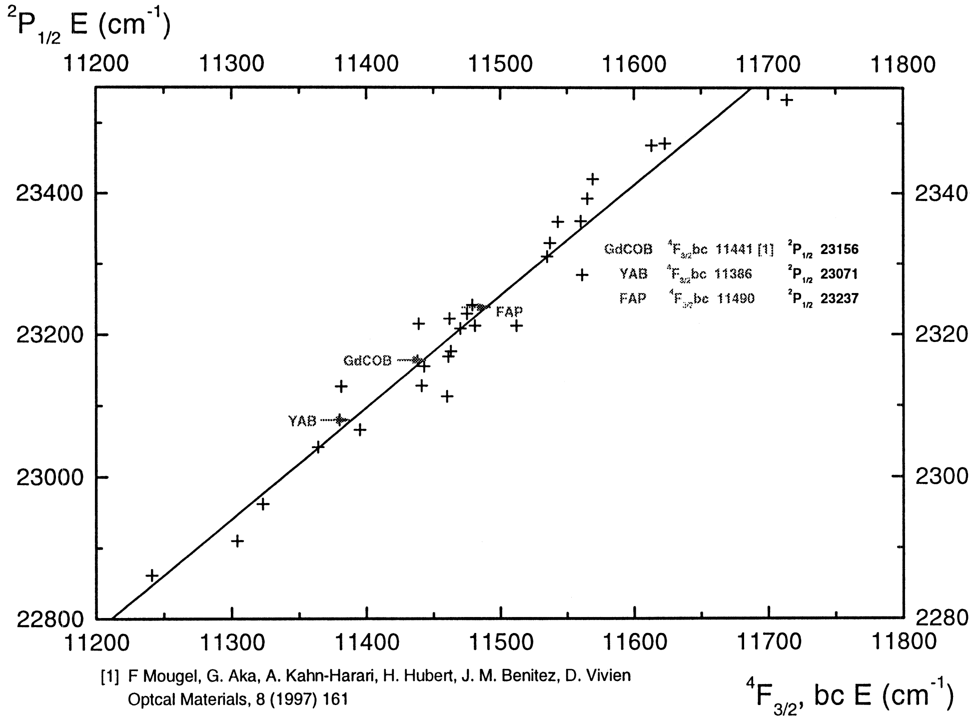

Fig. 3. The wavenumbers of the $^4F_{3/2}$ level bc as a function of those of the $^2P_{1/2}$ level along the neodymium nephelauxetic scale.

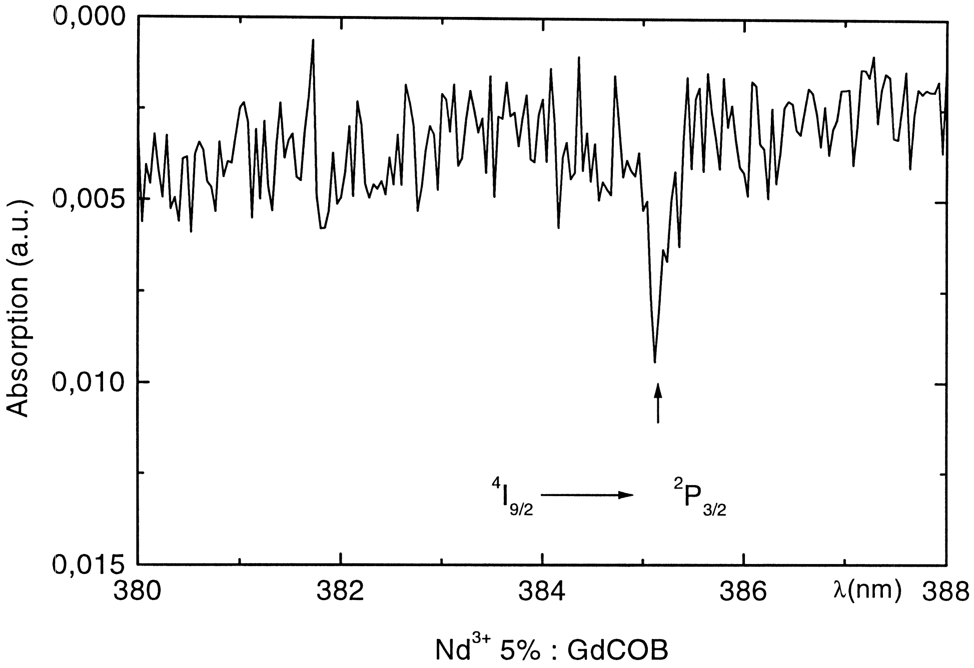

Fig. 4. Low temperature absorption spectrum of 5% Nd^{3+}: $Ca_4GdO(BO_3)_3$ (GdCOB) relative to the $^4I_{9/2}\rightarrow{}^2P_{3/2}$ transition.

served in the case of any two energy level barycenters. So, in Fig. 9 is presented the $^2P_{3/2}$ level barycenter as a function of the $^4F_{3/2}$ level barycenter. Moreover, in Nd^{3+}: GdCOB crystal, used as an example, the $^2P_{3/2}$ level barycenter deduced from this slope is always found at 26 061 cm^{-1}. This value has been already presumed from Fig. 5.

2.3. $4f^6$ configuration

This analysis can be developed for other rare earth ions, for example, for the europium ion. The emission of Eu^{3+} is intensely studied and this ion is frequently used as the local structural probe for identification of the crystallographic phases, the presence of impurity in compounds as

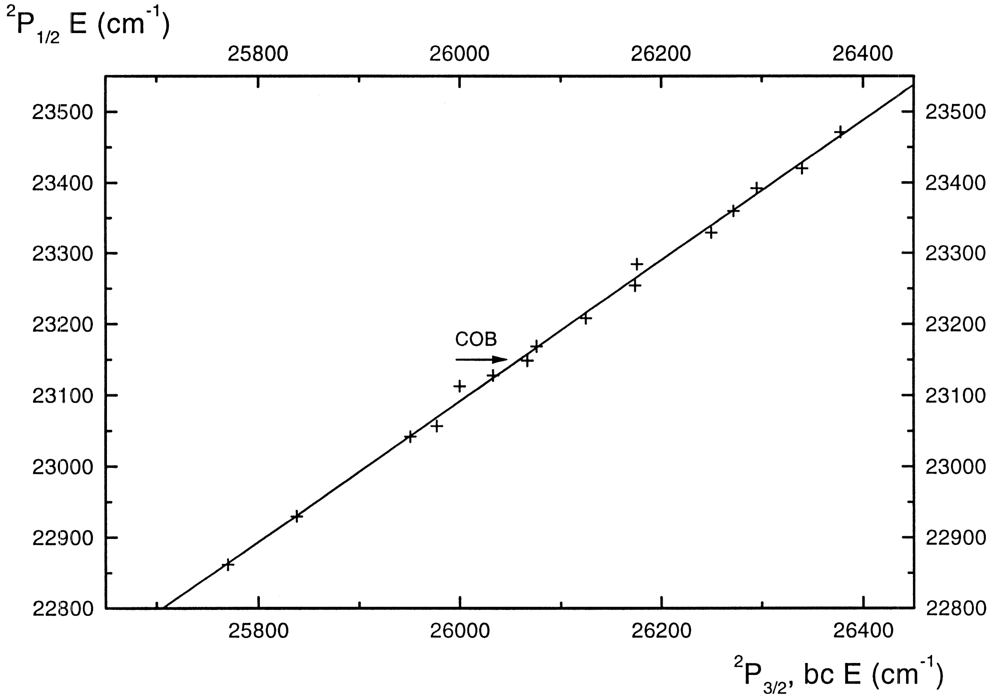

Fig. 5. Barycenters of the $^2P_{3/2}$ level as a function of the $^2P_{1/2}$ level along the neodymium nephelauxetic scale.

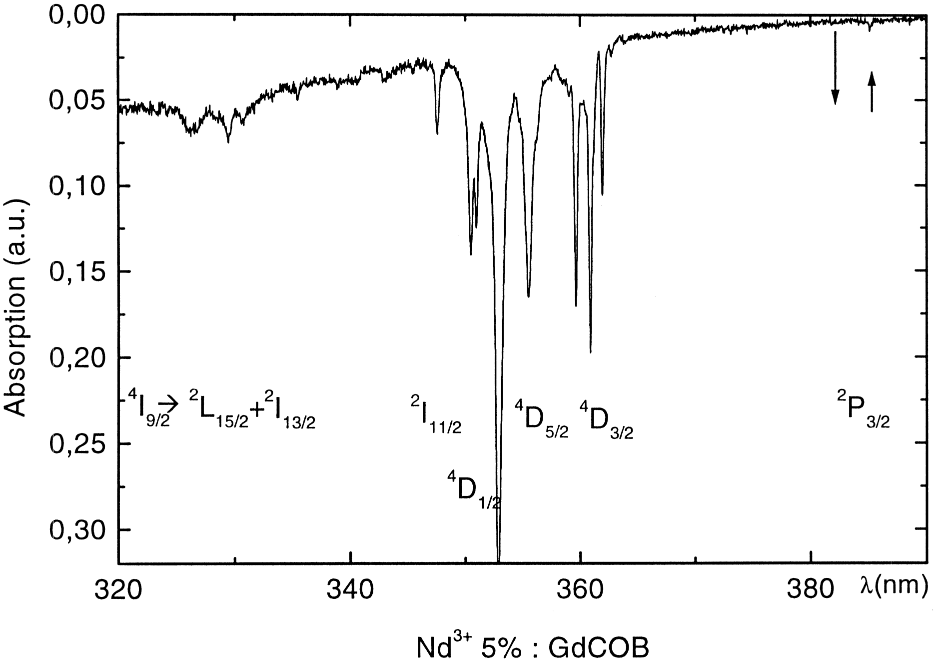

Fig. 6. Low temperature absorption spectrum of 5% Nd^{3+} doped $Ca_4GdO(BO_3)_3$ (GdCOB).

well as for the determination of the cf parameters. The europium ion, Eu^{3+} ($4f^6$ configuration), possesses the ground level manifold, ^7F_J, and the first excited level, $^5D_0$, situated at 12 000 cm^{-1} above the highest ^7F_J level.

In Fig. 10 is presented the $^5D_0$ level as a function of the $^7F_1$ barycenter [1,2]. It is obvious from slope that for the $^5D_0$ level situated at 17 150, 17 250 and 17 350 cm^{-1} for example, the relevant barycenters of the $^7F_1$ level are at 330, 380 and 425 cm^{-1}, respectively. These values are the average values, but in fact, these barycenter values suggest the attribution of the emission lines in the $^5D_0 \rightarrow {}^7F_1$ spectral range to the conforming $^7F_1$ sublevels allowed by the local symmetry around the europium ion. Some points are far from the curve, especially three points corresponding to the compounds having the $^5D_0$ level situated at very high energy. These 'bad' data correspond to

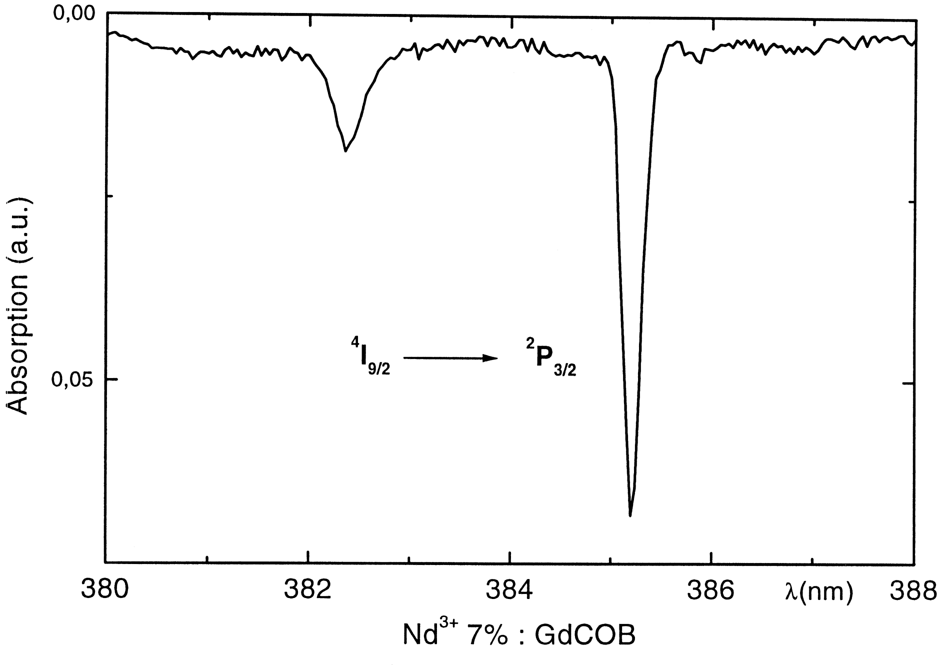

Fig. 7. Low temperature absorption spectrum of 7% Nd^{3+} doped $Ca_4GdO(BO_3)_3$ (GdCOB) relative to the $^4I_{9/2} \rightarrow {}^2P_{3/2}$ transition.

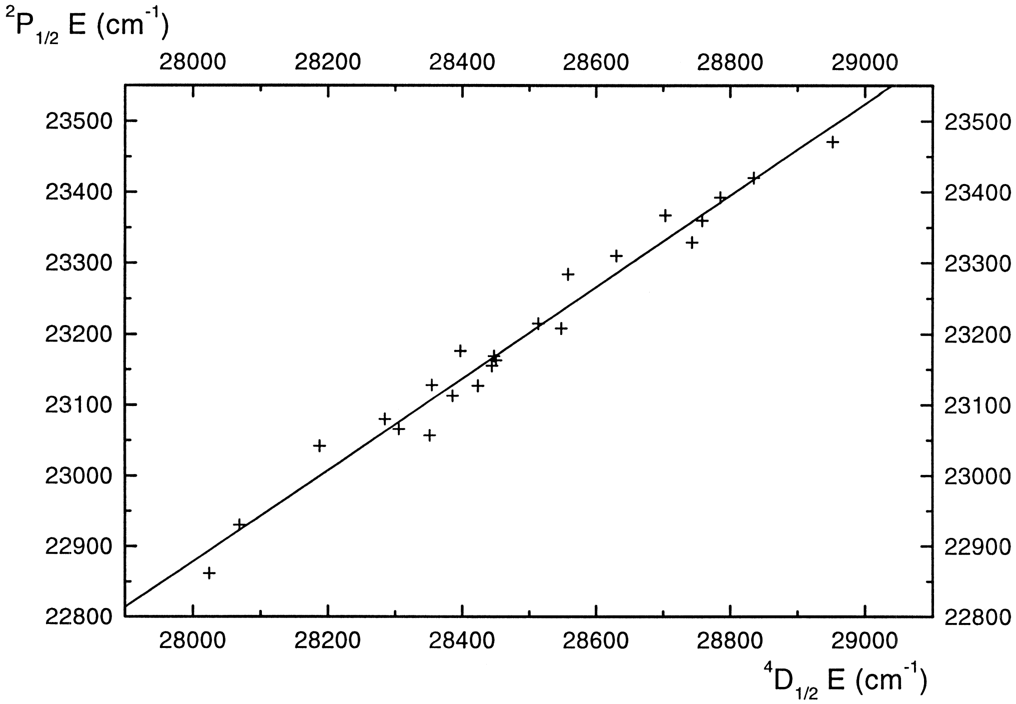

Fig. 8. The $^4D_{1/2}$ level as a function of the $^2P_{1/2}$ level along the neodymium nephelauxetic scale.

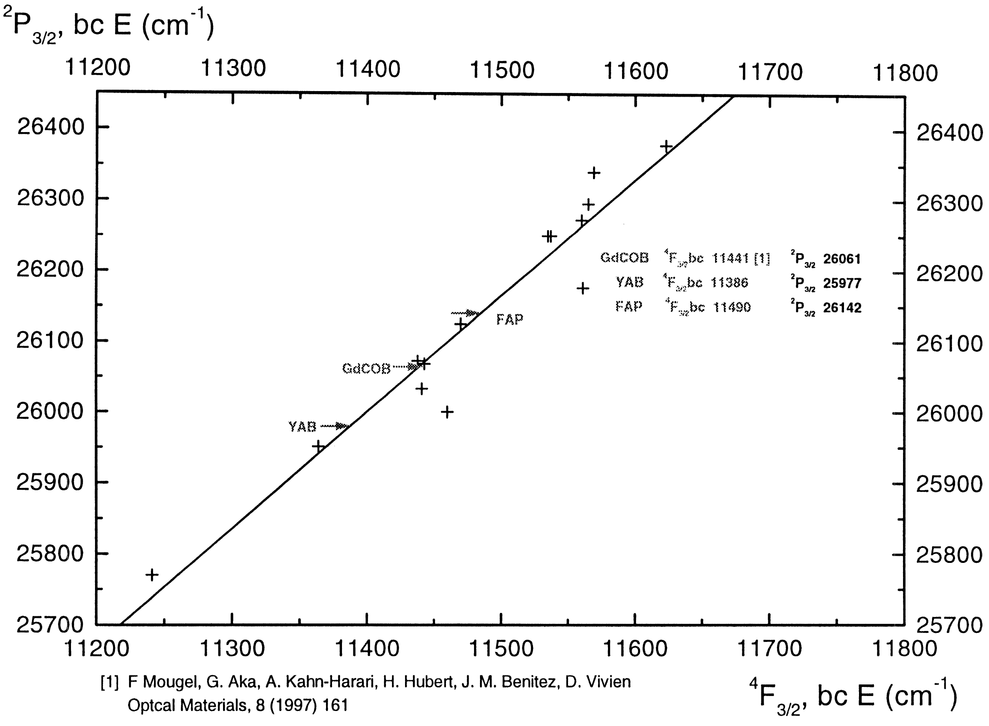

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Fig. 9. The $^4F_{3/2}$ level bc as a function of the $^2P_{3/2}$ level bc along the neodymium nephelauxetic scale.

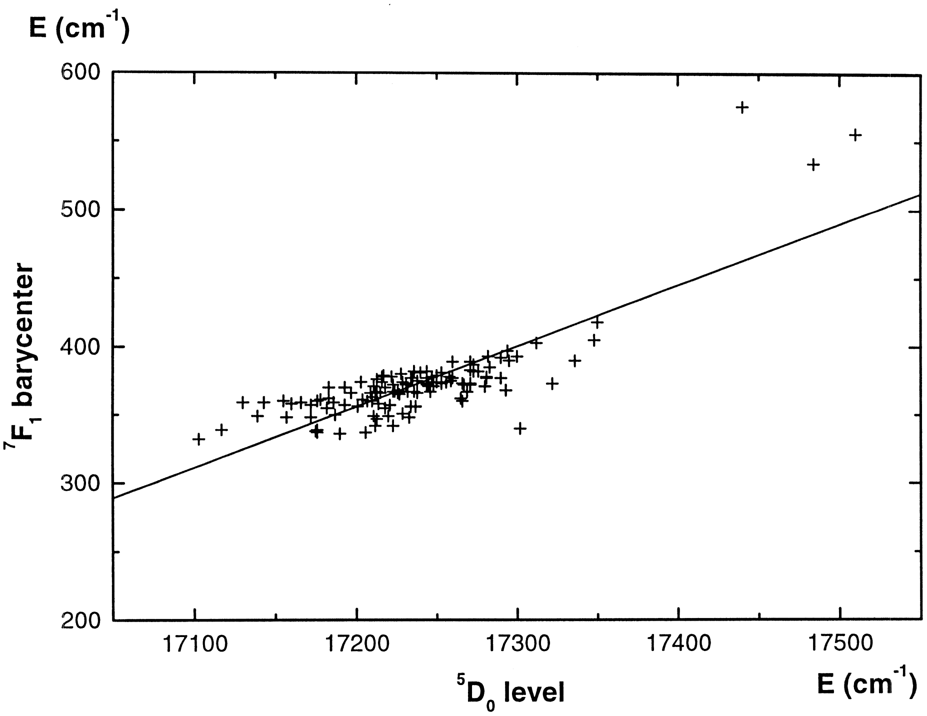

Fig. 10. The $^7F_1$ level barycenter as a function of the $^5D_0$ level for different crystalline compounds.

fluoroapatite phases [7,8]. In theses phases uncommonly great overall splitting of $^7F_1$ level is found, between 600 and 1000 cm^{-1}, exhibiting very high two rank cf parameters.

Due to these high B_q^2 values, the $^7F_1$ and $^7F_2$ levels, as well as $^7F_2$ and $^7F_3$ levels, are mixed. In this case the simulation of the experimental energy level scheme of ^7F_J manifolds in apatite is rather impossible on the reduced basis of 49 ^7F_J levels.

The $^5D_0$ value at 17 300 cm^{-1} with $^7F_1$ barycenter at 340 cm^{-1} is also far from the slope. It corresponds to the S_6 site of the Eu^{3+}: Y_2O_3-C cubic phase [9]. It seems that the assignment of the levels may be erroneous.

In Fig. 11 are gathered the overall splittings of the $^7F_1$ level in various europium or europium doped compounds. (Note: The asterisk denotes doubly degenerated levels). It goes from zero splitting in the elpasolite phase, $Cs_2NaEuCl_6$: Eu^{3+}, to very high splitting in fluoroapatite, $Ca_5(PO_4)_3F$: Eu^{3+}, of about 1000 cm^{-1} [8]. It means two rank crystal field strength parameter, N_v, 0 cm^{-1} in the former and 4500 cm^{-1} in the later case [10,11].

In addition to the result presented in Fig. 10, it is possible to link $^5D_0$ level with $^5D_1$ or $^5D_2$ level barycenters, or any other barycenter of the 4f^6 configuration (Fig. 12). The values used for this slopes are as follows [1]:

Compound	LaF_3	EuF_3	KY_3F_{10}	$LaCl_3$	$EuCl_3$, $6H_2O$	Y_2O_3-C	$Cs_2NaEuCl_6$	Y_2O_2S
$^5D_0$	17 293	17 290	17 269	17 267	17 259	17 221	17 209	17 143
$^5D_1$	19 054	19 050	19 028	19 031	19 019	18 972	18 963	18 897

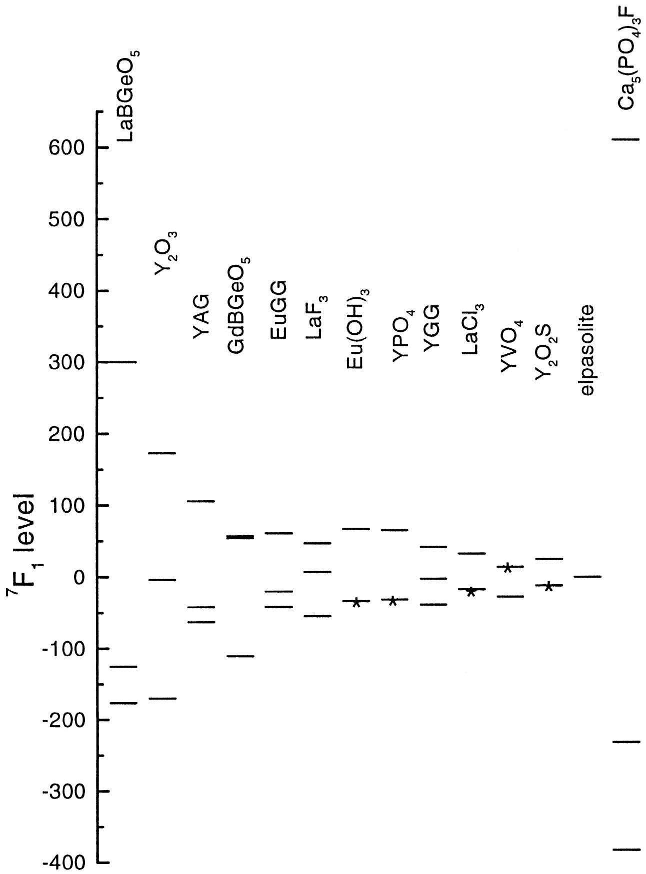

Fig. 11. The $^7F_1$ level splittings for different europium pure, or europium doped, crystalline compounds. Abbreviations: YAG: $Y_3Al_5O_{12}$, EuGG: $Eu_3Ga_5O_{12}$, YGG: $Y_3Ga_5O_{12}$, elpasolite: $Cs_2NaEuCl_6$.

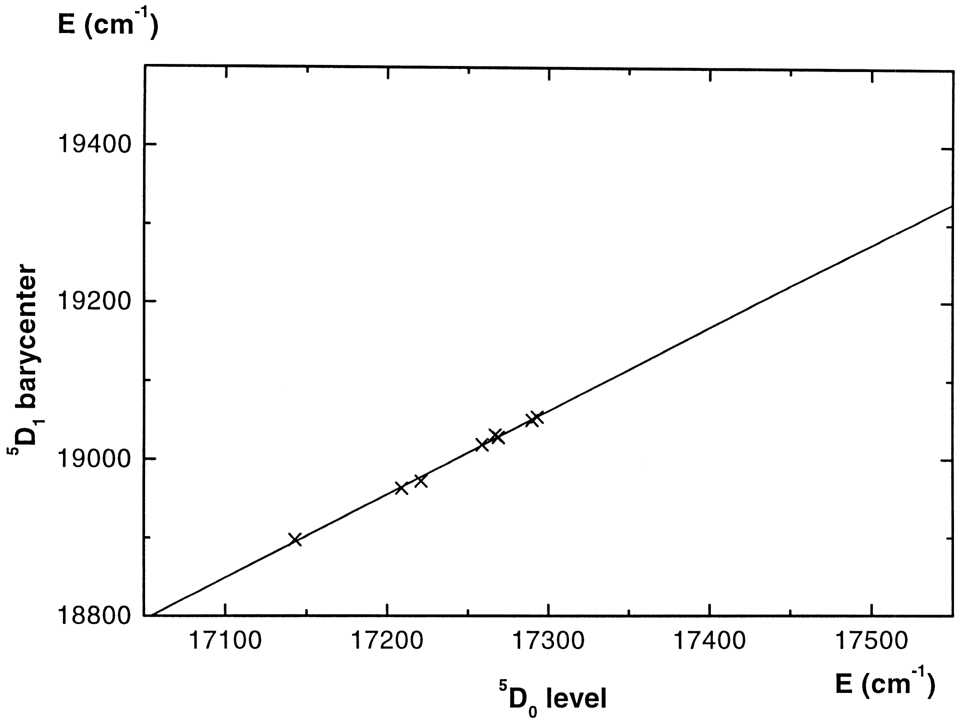

Fig. 12. The $^5D_1$ level barycenter as a function of the $^5D_0$ level for different crystalline compounds.

The $^7F_1$ level barycenter of the apatite as a function of the $^5D_0$ level is situated far from a curve (Fig. 10). If we present the $^7F_1$ level barycenter as a function of the $^7F_2$ level barycenter, see Fig. 13, this 'bad' point is then correctly located. The energy difference $^7F_2$bc$-{}^7F_1$bc with a ΔE value equal to 670–700 cm^{-1}, can be also used as a validity test in the case of europium.

3. Conclusion

The linear evolution of energy levels of f–f transitions, as well as the linear evolution of the crystal field parameters in isostructural series, is largely demonstrated [12,13]. In this paper we present a novel approach in the apprehension of energy levels which could be applied for all studied

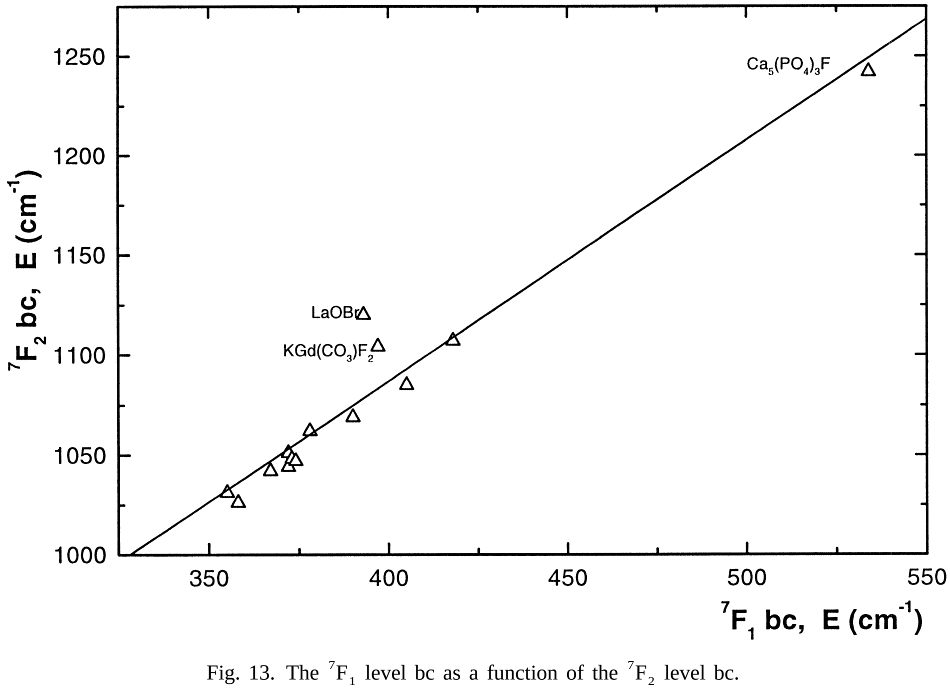

Fig. 13. The $^7F_1$ level bc as a function of the $^7F_2$ level bc.

compounds of a given rare earth. The linear evolution of the energy level barycenters in function of non-degenerated crystal field levels in praseodymium ($^3P_0$), neodymium ($^2P_{1/2}$) and europium ($^5D_0$) can be useful as a validity test in the assignment of absorption/emission data to different electronic levels. This approach can be enlarged to other rare earths in the lanthanide series, if enough spectroscopic data are available for comparison. The apprehension of the most reliable experimental energy level scheme facilitates the crystal field simulation and determination of the phenomenological crystal field parameters as well as the free ion parameters.

By this approach some lacking levels could be extrapolated from appropriate slopes with very low inaccuracy. The example of neodymium doped calcium gadolinium oxoborate (GdCOB) is outgoing. Following this advance we deduced the wavenumber of the $^2P_{1/2}$ level from $^4F_{3/2}$ barycenter at 23 156 cm^{-1} instead of the 23 150 cm^{-1} value experimentally determined.

This assumption is an experimental finding evidenced by several examples. So, it is important to point out that the $^{2S+1}L_J$ level barycenter as a function of a non-degenerated level, or any other barycenter of a well isolated level in the $4f^n$ ground configuration, shows a linear dependence within the experimental error. If this barycenter is situated out of the slope it underlines an incorrect assignment of a $^{2S+1}L_J$ level.

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