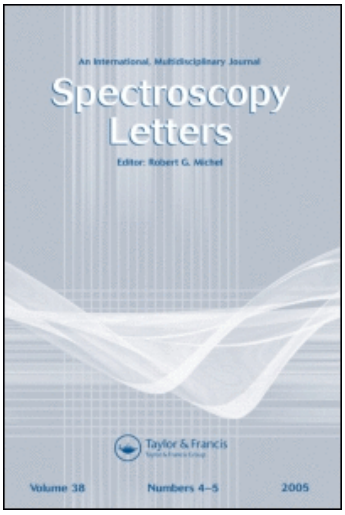

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Temperature Dependence of the Widths and Shifts in the Energy Levels of Eu^3 in the Luminescence Spectra of Europium Tris-thenoyl-trifluoroacetonate with 1,10-Phenantroline

V. E. Karasyov[a]; A. G. Mirochnick[a]
[a] Institute of Chemistry Far East Science Centre, Academy of Sciences of the USSR, Vladivostok-22, USSR

To cite this Article Karasyov, V. E. and Mirochnick, A. G.(1981) 'The Temperature Dependence of the Widths and Shifts in the Energy Levels of Eu^3 in the Luminescence Spectra of Europium Tris-thenoyl-trifluoroacetonate with 1,10-Phenantroline', Spectroscopy Letters, 14: 10, 647 — 658
To link to this Article: DOI: 10.1080/00387018108062624
URL: http://dx.doi.org/10.1080/00387018108062624

SPECTROSCOPY LETTERS, 14(10), 647-658 (1981)

THE TEMPERATURE DEPENDENCE OF THE WIDTHS AND SHIFTS IN THE ENERGY LEVELS OF Eu^{3+} IN THE LUMINESCENCE SPECTRA OF EUROPIUM TRIS- THENOYL-TRIFLUOROACETONATE WITH 1,10-PHENANTROLINE

KEY WORDS: Luminescence Spectra, Europium, β-diketones

V.E.Karasyov and A.G.Mirochnick

Institute of Chemistry
Far East Ssience Centre,
Academy of Sciences of
the USSR. Vladivostok-22,
690022. USSR.

ABSTRACT

The temperature dependence of the widths and shifts in the energy levels of Eu^{3+} in the luminescence spectra of crystals of europium tris-thenoyl-trifluoroacetonate are measured. The experimental data are interpreted from the point of view of the theory of the spectra of impurity centres in crystals.

The thermal behavior of the widths and positions of sharp optical transitions of (4f) impurity ions in rare-earth crystals was actively investigated by a number of authors [1-3] and succescfully interpreted in terms of interactions between lattice vibrations (phonons) and ions. In general, the molecular and impurity crystals, where the changes of a nuclear equilibrium positions and vibrational frequencies during optical transition are small were investigated.

In this paper we investigated in detail the temperature dependence of the widths and positions of Stark manifolds in the luminescence spectra of $Eu(TTA)_3phen$ (TTA- thenoyltrifluoroacetone, phen- 1,10-phenanthroline). In europium β-diketones the chemical bond between Eu^{3+} ion (luminnscence center) and ligands have far more complex nature than studied in [1-3]. The coordination polyhedron of most β-diketones is a sligthly distorted tetragonal antiprizm with eight-apex structure . Thus, Eu^{3+} is surrounded by sixth oxygen and two nitrogen atoms. The interactions between Eu^{3+} and ligands in $Eu(TTA)_3phen$ have ionic character with weak covalent component. The electronic transitions of inner isolated (4f) electronic shell of Eu^{3+} ion are responsible for luminescence, in connection with this, the interaction between optical transitions and phonons is small and according [1,2] the descrip-

tion from the point of view of the theory of the spectra of impurity centres in crystals is possible.

We restrict our presentation of the luminescence spektrum of $Eu(TTA)_3phen$ to three groups(Stark manifolds) of optical transitions $^5D_0-^7F_j(j=0,1,2)$. The values Of the maximums of the lines(cm^{-1}) are: 17241($^5Do-^7F_0$); 16940,16915,16725($^5D_0-^7F_1$) and 16356, 16321,16229,16141,15979($^5D_0-^7F_2$).The intensity of the lines of $^5D-^7F_{0,1}$ transitions is very small in comparison with the intensity of the strong lines of the $^5D_0 - ^7F_2$ transition which emitts the basic radiant energy.

The temperature dependence of the line-widths of the $^5D - ^7F_j(j=0,1,2)$transitions in the 77 - 300 K temperature range is shown in Fig.1and 2. One can see that all widths increase as temperature increases;the widths of a given manifold exhibit characteristic and similar temperature dependences. The temperature dependence in the 100 - 300 K temperature range is superlinear, and in the 77- 100K range is weaker. This weak temperature dependence in the 0 - 100 K temperature range probably explained by "residual" temperature independent Gaussian contribution .

Line-width may be resolved into homogeneous (Lorentzian) and inhomogeneous(Gaussian)contributions using the numerical tables compiled by Posener [4].

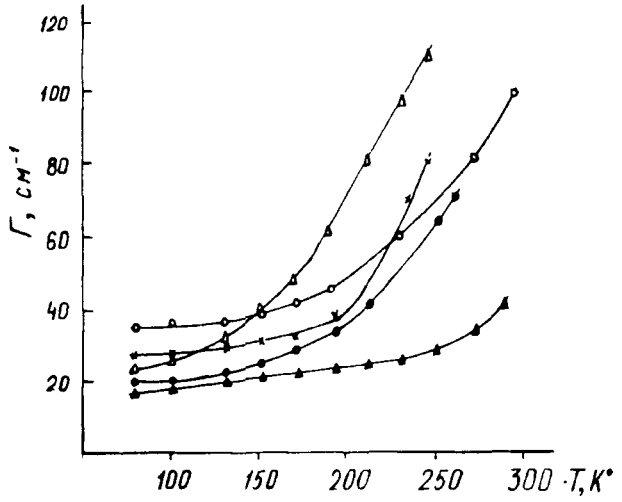

FIG.1- Temperature dependence of the linewidths of five strong lines of the $^5D_0$ $^7F_2$ transition. ▲ - 16356cm^{-1}, ● - 16321cm^{-1}, Δ - 16229cm^{-1}, X - 16141cm^{-1}, O - 15979cm^{-1}. Error bars on experimental points are ±10%

For example, the analysis of the line shape $\tilde{\nu}$ = 16229 cm^{-1}, $^5D_0$-$^7F_2$ transition at 77 K is shown in Fig.3. The line shape is described by a Voigt function, where for given value of the abscissa K and ordinate H are given values of coefficient "a" : $\frac{\Delta\nu_L}{\Delta\nu_G} = 1.2\ a$ (1)

from Fig.3:	K= 1.5	H= 0.254	a= 0.60
	K= 2.0	H= 0.140	a= 0.75

THE coefficients "a" for different K are closely, it means that, indeed, the line shape is described by a Voigt function. Thus: $a_{mean} = 0.67$

$\frac{\Delta\nu_L}{\Delta\nu_G}$=0,81 (2)

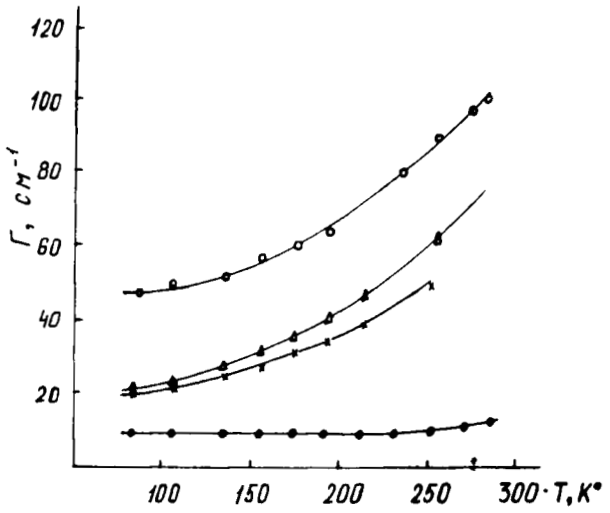

Fig.2 - Temperature dependence of the linewidths of the lines of the $^5D_0 - {}^7F_{0,1}$ transitions ●-17241cm^{-1}($^5D_0 - {}^7F_0$); x-16940cm^{-1}, Δ-16915cm^{-1}, o-16725cm^{-1} ($^5D_0 - {}^7F_1$).

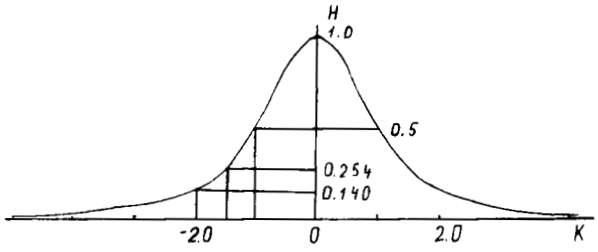

Fig.3 - Low-temperature line shape of 16229cm^{-1} ($^5D_0 - {}^7F_2$).

On the other hand, according [3] for ratio of the Gaussian and Lorentzian countours:

$$\frac{\Delta\nu_L}{\Gamma} + \frac{(\Delta\nu_G)^2}{(\Gamma)^2} = 1 \qquad (3)$$

where Γ - total half-width of the countour. In our case $\Gamma = 22cm^{-1}$ and from system of eq.(1) and (3) we found: $\Delta\nu_L = 12cm^{-1}$, $\Delta\nu_G = 15cm^{-1}$; the residual linewidth (Gaussian contribution) we can find by extrapolation of the temperature dependence of total linewidth to T= 0. For $\tilde{\nu} = 16229cm^{-1}$ we found $\Delta\nu_G = 15cm^{-1}$, that in good agreement with value, which we found by above-described analysis of a Voigt countour. The analysis of the line shapes is shown that at 77 K the countours of the lines $\tilde{\nu}$ =17241 cm^{-1}($^5D_0 - {}^7F_0$); $\tilde{\nu}$ =16229cm^{-1}, $\tilde{\nu}$ = 16321cm^{-1}, $\tilde{\nu}$ = 16141cm^{-1}($^5D_0 - {}^7F_2$) are described by a Voigt function and the lines $\tilde{\nu}$ = 16940cm^{-1}, $\tilde{\nu}$ = 16915cm^{-1} have Lorentzian shape($^5D_0 - {}^7F_1$)

One can see (Fig.1 and 2) that broadening experimentally observed of the Stark manifolds $^5D_0 - {}^7F_j$(g =1,2) is well described by the theory of the spectra of impurity centres in crystals. The following expression(Debye approximation)is describing the temperature dependence of the homogeneous linewidth:

$$\Gamma_L(T) = \alpha\left(\frac{T}{\theta}\right)^7 \int_0^{\theta/T} \frac{x^6 e^x dx}{(e^x-1)^2} = \alpha\left(\frac{T}{\theta}\right)^7 \xi_6\left(\frac{\theta}{T}\right) \qquad (4)$$

where Θ - is an effective Debye temperature, α -constant integral $\xi_6(\frac{\Theta}{T})$ has been tabulated by Ziman [5]. Thus, for the lines $\tilde{\nu}$ =16229cm^{-1},16321cm^{-1}($^5D_0$ - $^7F_2$) we found Θ = 150 ± 50 K; α_1 =205cm^{-1}, α_2 =106cm^{-1}, respectively; for $\tilde{\nu}$ = 16940cm^{-1} ($^5D_0$ - $^7F_1$) Θ = 150 ±50K One can see (Fig.2) that linewidth of the singlet transition $^5D_0$ - $^7F_0$ is increased by only 3cm^{-1} over 77 - 300 K temperature range. For any given optical transition the total linewidth may be expressed as the sum of the high- and low-lying transition states. So all transitions studied have common $^5D_0$ exited level(in practice, temperature independent), we may conclude that thermal broadening of the states $^7F_{1,2}$ determine, in general, the broadening mechanisms in the linewidths of the transitions $^5D_0$ - $^7F_{1,2}$, respectively.

From comparison the temperature dependence of the experimental homogeneous linewidths of the $^5D_0$ - $^7F_{1,2}$ (Fig.4) transitions with temperature dependence described by expression(4) we may conclude that broadening of the energy levels $^7F_{1,2}$ is determined by a predominant Raman relaxation processes.

The thermal shift can be qualitatively explained in the following way: It is known that during emission of a γ - quantum in the Mossbauer effect or the zero- phonon line in the case of an optical transi-

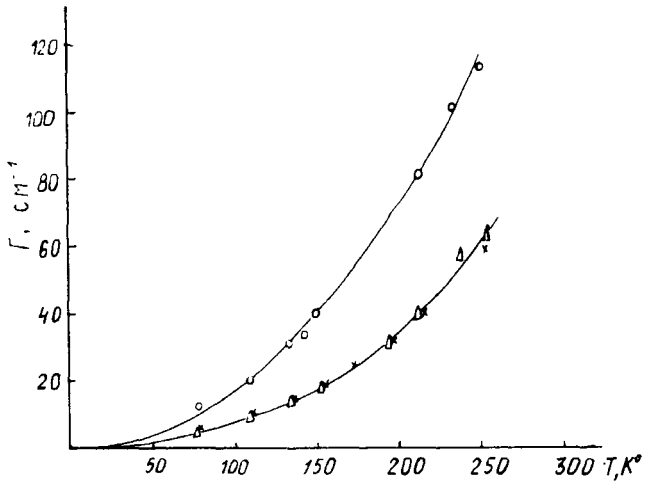

Fig.4 - Temperature dependence of the homogeneous linewidths. O - 16229cm^{-1}, Δ - 16321cm^{-1} ($^5D_0 - {}^7F_2$); X - 16940cm^{-1} ($^5D_0 - {}^7F_1$)

tion the emitted frequency is modulated with the thermal vibrations of the lattice. As a rezult the position of the zero - phonon line is described by the expression:

$$\nu = \nu_0 - \frac{1}{2}\frac{\nu_0}{c^2}\langle v^2 \rangle \qquad (5)$$

The mean square velosity $\langle v^2 \rangle$ of atomic vibrations in a lattice increases as the temperature increases which causes a decrease of the frequency of the zero-phonon line.

The temperature shifts of investigated lines are shown in Fig.5 and 6. One can see that temperature shifts for different Stark manifolds are qualitatively different. Thus, upon warming the line 17241cm^{-1}

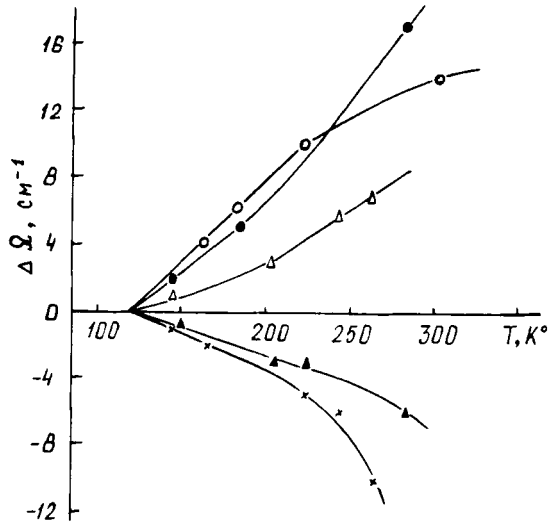

Fig.5 - Peak positions of five strong lines of the $^5D_0 - {}^7F_2$ transition plotted against temperature. Δ - 16356cm^{-1}, ● - 16321cm^{-1}, o - 16229cm^{-1}, ▲ - 16141cm^{-1}, × - 15979cm^{-1}

($^5D_0 - {}^7F_0$) shift to the blue; two lines 16940cm^{-1} and 16915cm^{-1}($^5D_0 - {}^7F_1$)shift to the blue, but 16752 cm^{-1} shift to the red. Further, three lines of the $^5D_0 - {}^7F_2$ transition 16356cm^{-1}, 16321cm^{-1}, 16229cm^{-1} shift to the blue, but two lines 16141cm^{-1}, 15979cm^{-1} shift to the red. We think that observed shifts to the blue upon warming (these shifts are not described by expression(5) are connected to the nephelauxetic effect and to the direct effects of thermal expan sion outweighing the effects of vibrations. Upon war-

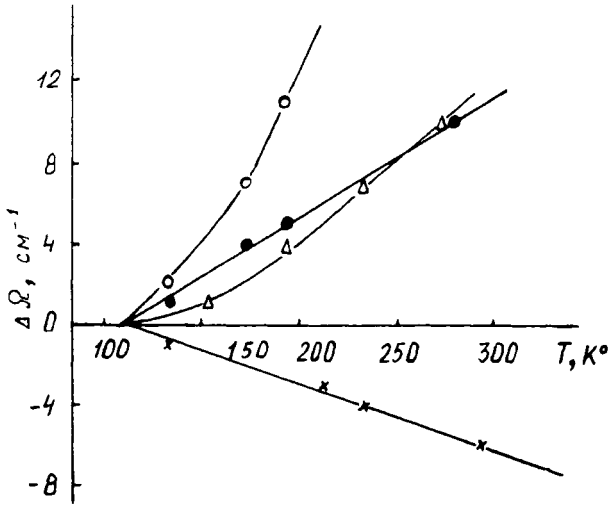

Fig.6 - Peak positions of the lines of $^5D_0$- $^7F_{0,1}$ transitions plotted against temperature. Δ - 17241cm^{-1}(position $^5D_0$ state versus temperature;the ground state $^7F_0$ is zero reference point); ● - 16940cm^{-1}, o - 16915cm^{-1}, × - 16752cm^{-1} ($^5D_0$ -$^7F_1$)

ming the average distances between Eu^{3+} and ligands are increased.As a result, the screening of the 4f-electrons by the overlapping charge clouds of the surrounding ligands is decreased and effective nuclear charge is increased. The Eu^{3+} ion exitation energy is increased and this leads to observed shifts to the blue. Thus, the emission freuquencies in Eu(TTA)$_3$phen depends not only by thermal vibrations, but the direct effects of thermal expansion. Expansion and its effect

might be expected to be large in a relatively soft crystals such as β- diketones.

The qualitatively different temperature shifts of the $^5D_0 - {}^7F_{0,1,2}$ transitions is described, probably, that Stark sublevels have a different symmetry types. The point symmetry of chelate $Eu(TTA)_3phen$ is C_{2v} [6]. The long axe of chelate has orientation along axe x; z - symmetry axe; xz - symmetry plane For group C_{2v}, the components of electric(P) and magnetic(M) dipole moments of transitions have a next symmetry types [6]:

$$P_z - A_1 ; \quad P_x, M_y - B_1$$
$$M_z - A_2 ; \quad P_y, M_x - B_2$$

Stark sublevels of the $^5D_0 - {}^7F_j$ transitions have next symmetry types [6]:

$^5D_0 - {}^7F_1$ 16940cm^{-1} - B_1, 16915- B_2, 16752cm^{-1} A_2

$^5D_0 - {}^7F_2$ 16356cm^{-1} - B_1, 16351cm^{-1} - B_2, 16229cm^{-1} A_1

The components of electric and magnetic dipole moments of $^5D_0 - {}^7F_j$ transitions have a different orientation to the long axe of chelate. The temperature expansion or contraction of the average distancies between Eu^{3+} and ligands cause selective action on the electric and magnetic dipole moments of transitions $^5D_0 - {}^7F_j$ with different orientation to the long

axe of the chelate, that, probably, lead to qualitatively different temperature shifts of lines.

REFERENCES

1. W.M.Yen, W.C.Scott,A.L.Schawlow. Phys. Rev.,136, 1A, 271, 1964.

2. S.A. Johnson, H.G.Freis, A.L.Schawlow, W.M.Yen. J.Opt.Soc.Am.,57,734, 1967.

3. V.I.Bonchkovski,S.A.Sazonova, B.S.Skorobogatov. Optika i Spektroscopiy., 32, 4,724 ,1972.

4. D.W.Posener. Austr. J. Phys.,12,184,1959.

5. J.M.Ziman. Proc.Roy.Soc.London, A226, 436,1954.

6 .V.F.Zolin,L.G.Koreneva, M.A.Samokhina. Zhurnal prikladnoi spektroscopii., 33 , 5 ,887, 1980.

Received: July 16, 1981
Accepted: August 8, 1981