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## Magnetic Properties of $\text{Eu}^{3+}$ ions for different surroundings: An investigation of the spin-orbit coupling in the structures

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**Abstract** Magnetic properties of mononuclear  $\text{Eu}^{3+}$  in some different environments are investigated by theoretical approach. It is found that the spin-orbit coupling plays a crucial role for the magnetism point of view. Using the observed magnetic data, it is predicted that the spin-orbit coupling constant should be varied with the surrounding of the magnetic center. It is also found that if the coupling constant was small enough the first excited state of the ionic term would be thermally populated.

**Keywords** spin-orbit coupling,  $\text{Eu}^{3+}$  complex, magnetic properties

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### Introduction

The investigation of the magnetic properties of 4f-orbital systems has become important for last fifty years since they behave as a single molecule magnets with a few magnetic centers in one molecular unit. It has been proven that these complexes show great promise in spintronic and quantum devices. It is already known that single molecule magnets are complexes that show magnetic hysteresis or slow magnetic relaxation originate from purely molecular origin [1]. The electronic ground state of 4f systems are characterized by filling of 4f orbitals with the configuration of  $[\text{Xe}]4f^n6s^2$  where n is the electron numbers in the f-shell. It should be pointed out here that there are some exception for La, Ce, Gd and Lu which have the configuration of  $[\text{Xe}]4f^n5d^16s^2$  that the most stable lanthanide ions are three positive ones obtained by loss of 5d and 6s electrons.

It is now already quite clear that in rare earth elements the magnetic electrons (4f shell) are screened by the higher lying 5s and 5p electron shells. Because of this screening, a direct exchange interaction between the 4f electrons with neighboring atoms is nearly impossible. So it is assumed that indirect exchange via the free conduction electrons takes place in these metals. For this screened and shrunk behavior, the orbitals are not involved for bond formation with its nearest neighbors. So generally lanthanide molecular compounds are taken as a free ion in the magnetism point of view. As mentioned above that the spin-orbit coupling of these compounds is much larger than for 3d ions. This spin-orbit coupling removes the degeneracy of the  $^{2S+1}\Gamma$  ground term. From the electronic configuration studies, it is quite certain that the energy separation between the state of lowest energy and the first excited states varies from a few hundreds to several thousands of wave numbers [2].

It is obvious that the lanthanides are transition metals. The magnetic moments of the transition metals ions are assumed to be due to electron spin only such that the orbital angular momenta are quenched by external fields [3,4]. However from the experimentally observed high values of the magnetic moments for  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  [5-8], it is clear that the orbital contributions must be taken into account at least for these ions. As pointed out earlier,



since the 4f electronic shells are well screened from outside fields by the electrons of the n=5 and n=6 shells, this is a reasonable expectation. On the other hand, there is a minimum value for the magnetic moment of trivalent ions for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  [9]. In other words agreement between observed and calculated values is good, except for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ . From the quantum mechanical calculations, it is quite clear that the magnitude of the separation between the adjacent states of a term is a measure of the strength of the spin-orbit coupling [10]. From the well analyzed studies, it is quite certain that in all cases, except  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ , it is sufficient to render the first excited state of the  $\text{Ln}^{3+}$  thermally inaccessible, and so the magnetic properties are determined only by their ground state. But especially for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ , one must include the first excited state together with the ground state configuration where these two levels are close to each other such that at room temperature the thermal population of the excited state is not out of possibility. Since the energy differences of these two levels are mainly due to the spin orbit coupling, one must carefully analyses this interaction for the magnetic studies.

In this study, we have been concentrated on the mononuclear  $\text{Eu}^{3+}$  complex in some different surroundings. Recently some mononuclear  $\text{Eu}^{3+}$  complexes in different environment has been synthesis and characterized. From the magnetic measurements it is found that the magnetic moment varies depending on the surroundings [11]. From the observed data and the theoretical analysis we have predicted the spin orbit coupling. Once the spin orbit coupling is predicted we have also analyzed the temperature dependence of the susceptibility together with the magnetic moment.

### Magnetic Susceptibility Analysis

Here it should be noted that the magnetic susceptibility for Lanthanides calculated by Hund's rule where the only ground state is taken into account. This calculation for the magnetic susceptibility is generally in good agreement with the experiments but there is a big discrepancy for  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  complexes. This discrepancy is supposed to be related to the small energy differences between the ground and first excited multiplet which is close to the kT [12]. In order to get smaller errors for these two complexes the Van Vleck susceptibility formula is used. This formula takes into account not only the ground state but also the excited states which are given as:

$$\chi = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \cdot \frac{\sum_{J=L-S}^{L+S} (2J+1) \lambda_J \exp\left\{-\frac{\lambda_{LS} J(J+1)}{2 k_B T}\right\}}{\sum_{J=L-S}^{L+S} (2J+1) \exp\left\{-\frac{\lambda_{LS} J(J+1)}{2 k_B T}\right\}} \quad (1)$$

where;

$$\lambda_J = g_J^2 J(J+1) + 2(g_J - 1)(g_J - 2) \frac{k_B T}{\lambda_{LS}} \quad (2)$$

$$\lambda_{LS} = \mp \frac{\zeta}{2S} \quad (3)$$

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \quad (4)$$

It should be noted that the  $g_J$  value for  $\text{Eu}^{3+}$  equal to  $L+2$  since  $J=0$  [13]. Although there are limited studies in the literature about the magnetic properties of the Eu-complexes, some of observed magnetic properties have been studied recently [14]. From this magnetic behavior we have analyzed the magnetic susceptibility and the magnetic moment of  $\text{Eu}^{3+}$ .

For this purpose, we choice [P6,6,6,14][Eu(NTA)4] (P6,6,6,14= trihexyl(tetradecyl)phosphonium), NTA = naphthoyltrifluoroacetone) and [Eu(O<sub>2</sub>NO)<sub>3</sub>(H<sub>2</sub>L)]·2H<sub>2</sub>O (H<sub>2</sub>L=(2-(2-hydroxy-5-(p-tolyldiazenyl)benzylidene)hydrazinecarbothioamide) where the magnetic date is presented [15, 16] and a detailed numerical values is given in Table 1. The temperature dependence of the susceptibility was calculated by using eq.1 and pictured in figure 1.a and b. It is seen that the  $\chi$  value achieves a saturated value with decreasing temperature. The change of  $\mu_{\text{eff}}$  by temperature was also calculated by using the  $\lambda_{LS}$  value. It is found that the spin orbit coupling varied when the environment of the magnetic center is changed as can be seen in table 1. For different spin orbit coupling the analyzed magnetic behavior is pictured in Figure 2 for different complexes. To compare the calculated and experimentally obtained graphs, we used the  $\mu_{\text{eff}}-T$  graphs of [P6,6,6,14][Eu(NTA)4] complexes which is taken from [14] and it is seen that the calculated and experimentally obtained  $\mu_{\text{eff}}-T$  graphs are well matched with each other.

**Table 1:** The experimental  $\mu_{\text{eff}}$  values of the complexes and calculated spin-orbit coupling parameters ( $\lambda_{LS}$ )



Sample	$\mu_{\text{eff}} (\mu_{\text{B}})$	Ref.	$\lambda_{LS} (\text{cm}^{-1})$
[P6,6,6,14][Eu(NTA)4] P6,6,6,14= trihexyl(tetradecyl)phosphonium NTA = naphthoyltrifluoroacetone	2.77	15	3654.4
[Eu(O <sub>2</sub> NO) <sub>3</sub> (H <sub>2</sub> L)]·2H <sub>2</sub> O H2L=(2-(2-hydroxy-5-(p-tolyldiazenyl)benzylidenehydrazinecarbothioamide	3.46	16	1659.5

From the theoretical prediction, it is almost evident that when the ligand field effect increased, the spin orbit coupling reduced which means that the energy separation of low lying states would be reduced with this reduction of the spin orbit coupling. It is evident that when the spin orbit coupling is large, only the ground state term would be thermally occupied but when it is small, the first excited states may be thermally populated too. This fact should not be omitted for the magnetic measurements.

As a result of this section, using the values for the spin orbit coupling one can draw the susceptibility as a function of temperature. It is obvious that the maximum and minimum values for the coupling constant taken from table 1, the variation of the susceptibility is shown in Figure 1a and Figure 1b respectively. It is hoped here that if a detailed temperature dependence is observed some theoretical prediction can easily be compared.

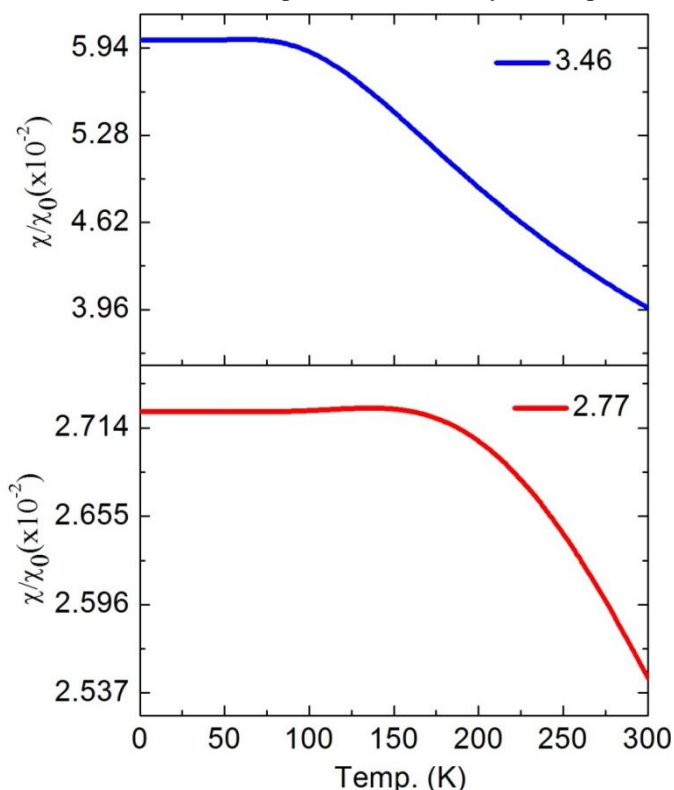


Figure 1:  $\chi/\chi_0$  parameter depending on temperature for different  $\mu_{\text{eff}}$  values

### Discussion and Conclusion

The magnetic moment for different spin orbit coupling were given in figure 2. It is apparent that magnetic moment must be reduced to increase spin-orbit coupling. This is mainly due to the fact that when the spin-orbit coupling increased the energy difference between the ground state and the first excited state increased. If this increase is high enough the possibility of thermal population of the excited state become negligible. On the other hand when the spin



orbit coupling is reduced the first excited state of the term may be thermally populated. This fact should not be omitted when the magnetic date is analyzed.

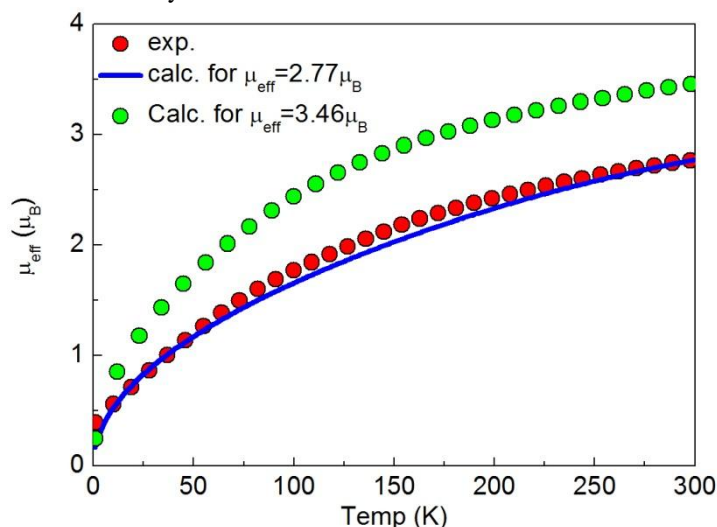


Figure 2:  $\mu_{\text{eff}}-T$  graphs for different  $\mu_{\text{eff}}$  values at room temperature and the experimental data taken from ref [15]

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