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# SPIN DYNAMICS IN THE INTERCALATES $\text{Eu}_x\text{ZrSe}_{1.95}$

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Electron Spin Resonance (ESR) measurements have been made on powders of the recently prepared intercalates  $\text{Eu}_x\text{ZrSe}_{1.95}$  in which europium was previously shown to be mostly in its +2 oxidation state. The linewidth evolution against Eu concentration and temperature were obtained using a conventional X-band reflection spectrometer. The spin-lattice relaxation rate, as measured using a modulation spectrometer, is found to contribute importantly to line broadening. The behavior of the studied materials is compared to that of other magnetically diluted  $\text{Eu}^{2+}$  systems.

## 1. INTRODUCTION

The intercalation compounds  $\text{Eu}_x\text{ZrSe}_{1.95}$  ( $x < 0.4$ ) have recently been prepared at  $-50^\circ\text{C}$  by reaction of the zirconium diselenide and europium metal using the liquid ammonia technique [1]. For  $x > 0.4$ , Eu amide is formed, which indicates that the upper limit for intercalation is  $x = 0.4$ . The ammonia (co)intercalated with Eu) was removed by heating the compounds at  $300^\circ\text{C}$  under vacuum. The X-ray diffraction study shows that the  $\text{Eu}_x\text{ZrSe}_{1.95}$  ( $x < 0.4$ ) phase adopts the 1T structural type [2] of pristine  $\text{ZrSe}_{1.95}$ . As previously noticed for the isostructural  $\text{Li}_x\text{ZrSe}_{1.95}$  compounds for  $x < 0.4$  [3], the cell volume is observed not to increase as  $x$  increases, contrary to expectation based on size effects arguments. The absence of cell parameter variation seems to be correlated to the semiconductor nature of those intercalates. To date, no fully satisfactory explanation has been given for this apparent volume compensation phenomenon at the microscopic scale. The lack of any theoretical model emphasizes the necessity of getting more experimental informations concerning the real existence of such phases.

From magnetic susceptibility measurements together with  $^{151}\text{Eu}$  Mössbauer spectroscopy, discrete  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  valence states were evidenced. This means that  $\text{Eu}^{2+}$ , which is the Eu oxidation state in the precursory metal-ammonia solutions, is further oxidized as it is inserted in the diselenide. Importantly, the whole Eu content does not alter significantly the  $\text{Eu}^{2+}$  (or  $\text{Eu}^{3+}$ ) composition (for  $x = 0.1$  and  $0.4$ , ca. 70% of Eu is divalent), demonstrating, in particular, that the oxidizing power of the host is not affected by the electron transfer amount (e.g. 0.25 and 0.92 electron per Zr mole for  $x = 0.1$  and  $0.4$  respectively).

The (recent) detailed study of  $\text{Eu-TX}_2$  intercalates (T=Transition Metal, X=S,Se) is of interest because these compounds allow a simple comparison of the oxidizing power of the miscellaneous host lamellar-dichalcogenides. As a matter of fact, we found that the  $\text{Eu}^{3+}$  composition increases as the electron affinity of the host increases. In this regard, a reasonable estimate of the host electron affinity can be made using the d-electron level energy

values of the transition metals since the d-levels are the acceptor levels [4]. So, the  $\text{Eu}^{3+}$  fraction is 30, 50, 80% for  $\text{ZrSe}_2$ ,  $\text{TaS}_2$  [5] and  $\text{TiS}_2$  [6] respectively, which fits with expectation knowing that the d-state energy values are -8.46, -9.57 and -11.04 eV for Zr, Ta and Ti respectively [7].

However, because the  $\text{Eu}_x\text{ZrSe}_{1.95}$  compounds exhibit no expansion of the van der Waals gap upon intercalation, it might be thought that the intercalation is not effective and that a second Eu-phase is formed, the diselenide being unchanged. This work is devoted to an Electron Spin Resonance (ESR) study which shows that  $\text{Eu}_x\text{ZrSe}_{1.95}$  behaves as a magnetically diluted system, which is in favor of the real formation of intercalates, with no evidence for any second Eu-phase.

## 2. EXPERIMENTAL

The preparation of the materials is described in detail in ref. [1]. The EPR measurements were performed in the temperature range 20-300K, on powders, using a reflection spectrometer working at X-band and equipped with an ESR 9 Oxford cryostat. The samples ( $x = 0.1, 0.2$  and  $0.4$ ) were handled in a dry box and sealed in silica tubes to prevent contamination since intercalation compounds may be sensitive to oxygen and water [8]. Integrated intensities (I.T) were determined digitally. To estimate the contribution of spin-lattice relaxation to the linewidth, the relaxation time  $T_1$  was measured using a modulation spectrometer designed for  $T_1$  which may be as short as  $10^{-10}$ s. This method is valid in both cases of homogeneous and inhomogeneous broadening provided that saturation effects are negligible [9], which has been checked for the studied compounds.

## 3. RESULTS AND DISCUSSION

The EPR spectra of the studied intercalates consist of an intense single symmetrical line centered at  $g = 1.99 \pm 0.01$  having a Lorentzian shape and observable in the whole studied temperature range. We hence attribute this signal to

$\text{Eu}^{2+}$  which is in fact the only paramagnetic species liable to be at the origin of a paramagnetic resonance in the present case. It has the electron configuration  $4f^7$  with a well isolated  $^8S_{7/2}$  ground state. In the studied materials, neither the fine nor the hyperfine structure are resolved.  $\text{Zr}^{3+}$  ( $d^1$ ,  $\text{Zr}^{4+}$  is reduced to  $\text{Zr}^{3+}$  upon intercalation) and  $\text{Eu}^{3+}$  ( $4f^6$ ), which are the other possible ions with unpaired electrons, are known to exhibit no EPR signal. For octahedrally coordinated  $d^1$  ions (we discuss below the question of localization of the transferred electrons on Zr), the spin and orbital momenta cancel each other at lower temperatures [10], i.e. below room temperature for  $\text{Zr}^{3+}$  which has a spin-orbit coupling constant  $\lambda=500\text{cm}^{-1}$ . This has been confirmed by the study of pristine zirconium diselenide susceptibility which, due to its inevitable non-stoichiometry, also contains some  $\text{Zr}^{3+}$  [10]. For  $\text{Eu}^{3+}$ , the ground state has  $J=0$  and the paramagnetism is temperature independent.

Importantly, we interpret the fact that (i) the samples do not behave as metals as regards the tuning of the cavity, and (ii) we do observe a symmetrical line for  $\text{Eu}^{2+}$ , as the signature of the semi-conducting nature of the studied system. Otherwise, the signal would adopt a dysonian shape or would not be detectable due to the skin effect, as in the case of metallic  $\text{Eu}_x\text{TiS}_2$  [6]. Accordingly, for  $\text{Eu}_x\text{ZrSe}_{1.95}$ , the transferred electrons upon intercalation are well localized on Zr sites in the whole Eu concentration range as also observed for  $\text{Fe}_x\text{ZrSe}_2$  ( $x<0.25$ ) [11]. Such a non-metallic behavior has been accounted for by considering an Anderson-type localization [11].

We now first discuss the concentration dependence of the linewidth and, second, we shall discuss the thermal evolution of the linewidth.

**Concentration dependence of the linewidth.** - At room temperature (Fig.1), i.e., in the high temperature regime since no magnetic ordering could be detected above 4K [1], the peak-to-peak linewidth ( $\Delta H_{pp}$ ) is found to be a linear function of the square root of the total Eu concentration ( $x$ ). Notice that the exact  $\text{Eu}^{2+}$  concentration is actually  $0.7x$  [1]. Such a behavior has often-times been observed for semi-conducting dilute systems, e.g.  $\text{Eu}_x\text{Sr}_{1-x}\text{S}$  [12] and

$\text{Cu}_2x\text{Cr}_2x\text{Sn}_{2-2x}\text{S}_4$  [13]. As far as the spin-spin relaxation contribution to the line broadening is concerned (i.e. the exchange narrowed dipolar width), this behavior results from the fact that if a fraction  $x$  of the lattice sites is filled magnetically and  $x > 0.1$ , then the second moment ( $M_2$ ) is proportional to  $x$  [14]. The width being proportional to

$$\sqrt{M_2}$$

is thus a linear function against:

$$\sqrt{x}$$

However, as discussed below, the spin-spin relaxation is not the only source of line broadening for the studied compounds.

The major consequence of the concentration dependence of  $\Delta H_{pp}$  is that the assumption of an  $\text{Eu}^{2+}$ -containing second phase is ruled out because, in such a case, the linewidth should be independent on  $x$ . Besides, the likely  $\text{Eu}^{2+}$  second phase in the studied system is  $\text{EuSe}$ . At X-band, the corresponding EPR line is 840 G wide [15], which is not observed (for  $x=0.2$ , the fact that  $\Delta H_{pp}=840$  G is fortuitous).  $\text{Eu}(\text{NH}_2)_2$  could also be considered because it may arise from the decomposition of the precursory  $\text{Eu-NH}_3$  solutions. Its EPR signal is approximately 1000 G wide [16]. But, in the preparation route we use, the samples are made ammonia free by heating them at  $300^\circ\text{C}$  under vacuum. If Eu amide is formed, it is expected to decompose to yield nitride [17] in which Eu is trivalent. Thus, the  $\text{Eu-NH}_3$  decomposition cannot be evidenced studying the EPR of the final products. We hence performed an EPR measurement for  $\text{Eu}_{0.4}(\text{NH}_3)_y\text{ZrSe}_{1.95}$  from which ammonia is extracted to yield the studied  $\text{Eu}_{0.4}\text{ZrSe}_{1.95}$ . No 1000 G line appeared, showing that no amide was formed. Thus, we conclude that no side reaction occurs.

**Temperature dependence of the linewidth.** - All samples exhibit a similar behavior as a function of temperature ( $T$ ) (Fig.2). As  $T$  decreases, the linewidth first decreases slightly and then increases as  $T$  approaches zero. No g-shift was observed.

The lower temperature behavior accounts for the occurrence of critical spin fluctuations related to a possible onset of magnetic long-range ordering. The possible critical temperatures ( $T_c$ ), as estimated using fits of a  $(T-T_c)^{-\alpha}$  law

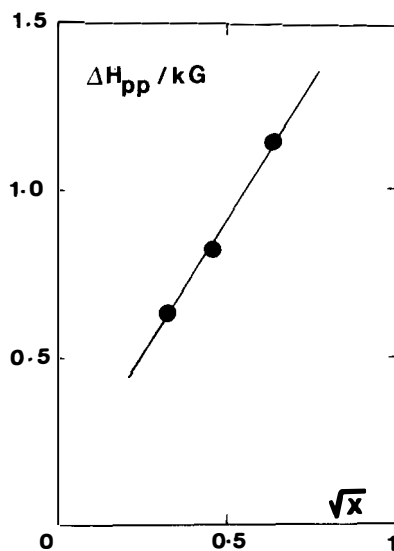


Fig. 1- Concentration dependence of the room temperature linewidth for  $\text{Eu}_x\text{ZrSe}_{1.95}$ . The effective  $\text{Eu}^{2+}$  concentration is  $0.7x$ .

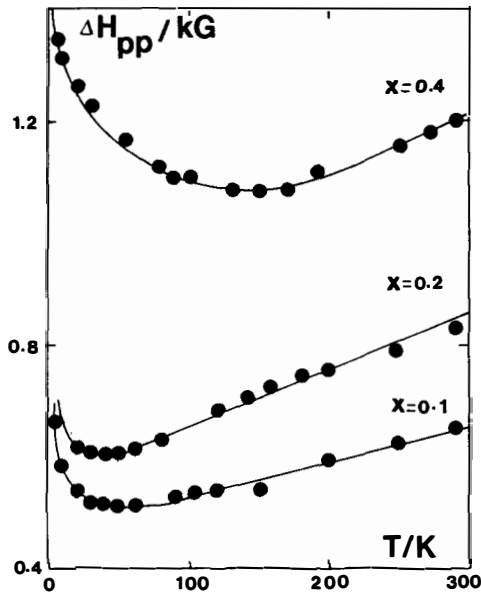


Fig.2- Temperature dependence for the peak-to peak linewidth for  $\text{Eu}_x\text{ZrSe}_{1.95}$ .

to the data, are found much lower than 4K and thus inaccessible to our instrument. This study hence corroborates the previous Mössbauer spectroscopy results that we obtained for the  $x=0.4$  sample which was shown to be paramagnetic down to 4.2K [1]. In this regard, considering that EuSe (in which Eu is not diluted) has a Néel temperature equal to 4.6K [18] and assuming  $T_c$  is proportional to the concentration (molecular field theory) and insensitive to the crystal geometry, we estimate the critical temperatures in the studied materials (if real) to be lower than 2K. The relative spin concentration (I.T) is found to decrease as T decreases (Fig.3), which indicates the predominance of antiferromagnetic interactions as for EuSe. It is interesting to note that, in contrast, the Eu sulfides are predominantly ferromagnetic: EuS is ferromagnetic with  $T_c=16.6\text{K}$  [18] and  $\text{Eu}_x\text{Sr}_{1-x}\text{S}$  exhibits paramagnetic to ferromagnetic phase transition for higher Eu contents [19].

We discuss now the higher temperature behavior. For insulators or semiconductors, since  $\text{Eu}^{2+}$  (S-state)

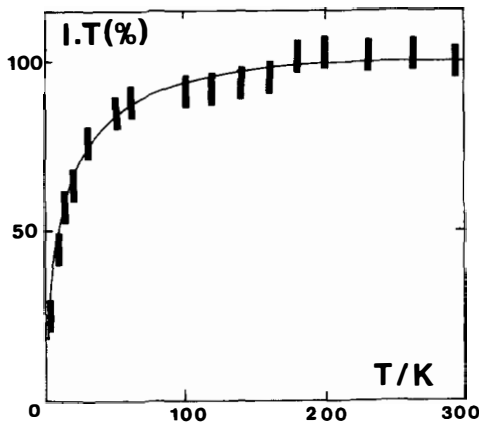


Fig.3- Relative spin concentration as a function of temperature for  $\text{Eu}_{0.4}\text{ZrSe}_{1.95}$ .

has no first-order spin-orbit coupling, the spin-lattice relaxation contribution to the linewidth should be negligible, leading in particular to a linewidth independent on temperature, as usually argued for  $\text{Eu}^{2+}$  materials (e.g. in the case of  $\text{Eu}_x\text{Sr}_{1-x}\text{S}$  [12, 20]).

To illustrate this quantitatively, Deville et al. [21] have estimated from the data obtained for  $\text{Eu}:\text{CaF}_2$  in the range  $T < 30\text{K}$  [22], that a typical 300K  $\text{Eu}^{2+}$  spin-lattice relaxation time ( $T_1$ ) should be ca.  $1.3 \times 10^{-7}\text{s}$ . Using

$$\Delta H_{pp}^{SL} = 2(\sqrt{3} \cdot \gamma \cdot T_1)^{-1}$$

the corresponding line broadening is equal to 0.3 G.

But, contrary to expectation, the  $T_1$  measurements indicate much shorter  $T_1$  for the studied compounds. For  $x=0.2$  at 300K, we found  $T_1=1.4 \times 10^{-10}\text{s}$ . The spin-lattice relaxation makes thus a significant contribution ( $\Delta H_{pp}^{SL}=227\text{G}$ ) to the observed linewidth ( $\Delta H_{pp}=840\text{G}$ ). Since the relaxation rate increases as T increases (Fig.4), as expected, the linewidth increases as T increases, as effectively observed (Fig.2). Besides,  $T_1^{-1}$  is found to increase as x increases. Due to the technique employed, our results for  $x=0.10$  and  $0.40$  are not accurate enough to be reported here. However, the facts that (i) the observed linewidth is proportional to

$$\sqrt{x}$$

(fig.1) and (ii) the calculated dipolar broadening for dilute systems obeys the same relationship, suggest that  $T_1^{-1}$  is also proportional to

$$\sqrt{x}$$

As the studied materials behave as semiconductors (see above the ESR line characteristics), no Korringa-like mechanism can be invoked to explain the observed short  $T_1$ . In our opinion, the coupling between  $\text{Eu}^{2+}$  and  $\text{Zr}^{3+}$  centers (which are expected to be strongly coupled to the lattice via spin-orbit coupling,  $^3T_{2g}$  ground state) alone can be at the origin of the intense observed  $\text{Eu}^{2+}$  spin-lattice relaxation.

*Exchange parameter.* - Finally, the exchange parameter  $|J_1|$  between  $\text{Eu}^{2+}$  first near neighbors may be estimated considering that the linewidth is the sum of  $\Delta H_{pp}^{SL}$  (temperature dependent) and  $\Delta H_{pp}^{\text{exch}}$  (temperature independent), the latter contribution being the exchange narrowed dipolar linewidth. For  $x=0.2$ , using Anderson and Weiss model [23] and the procedure used in refs. [12,13] for isotropic systems in which each moment has six nearest neighbors (the  $\text{Eu}^{2+}$  sublattice in  $\text{Eu}_x\text{ZrSe}_{1.95}$  is

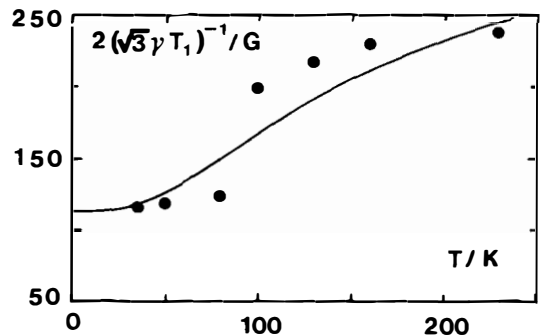


Fig.4- Spin-lattice relaxation rate as a function of temperature for  $\text{Eu}_{0.2}\text{ZrSe}_{1.95}$ . The continuous line is a guide for the eye.

triangular with  $a \approx 3.76 \text{ \AA}$  [1]) and assuming that dipolar interactions are the only contribution to  $M_2$ , we calculate  $M_2$  equal to  $1.5 \times 10^6 \text{ G}^2$ , which yields  $|J_1|$  equal to 0.1 K.

#### 4. CONCLUSION

The present ESR study demonstrates the existence of  $\text{Eu}_x\text{ZrSe}_{1.95}$  as semiconducting 1T-structural type

intercalates. The remarkable features of this series are (i) the absence of interlayer expansion of the host upon intercalation (although the europium cations have a much larger radius than that of the octahedral vacancy of pristine diselenide: 1.10 and 0.72 Å, respectively) and (ii) their non-metallic character.

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