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Electron spin resonance study of the LaIn$_{3-x}$Sn$_x$ superconducting system

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Abstract. The LaIn$_{3-x}$Sn$_x$ alloy system is composed of superconducting Pauli paramagnets. For LaIn$_3$ the superconducting critical temperature T_c is approximately 0.7 K and it shows an oscillatory dependence as a function of Sn substitution, presenting its highest value $T_c \approx 6.4$ K for the LaSn$_3$ end member. The superconducting state of these materials was characterized as being of the conventional type. We report our results for Gd^{3+} electron spin resonance (ESR) measurements in the LaIn$_{3-x}$Sn$_x$ compounds as a function of x. We show that the effective exchange interaction parameter J_{fs} between the Gd^{3+} $4f$ local moment and the s-like conduction electrons is almost unchanged by Sn substitution and observe microscopically that LaSn$_3$ is a conventional superconductor.

1. Introduction

The compounds of the LaIn$_{3-x}$Sn$_x$ alloy system are superconducting Pauli paramagnets. For LaIn$_3$ the superconducting critical temperature T_c is approximately 0.7 K and it shows an oscillatory dependence as a function of Sn substitution, presenting its highest value $T_c \approx 6.4$ K for the LaSn$_3$ end member [1, 2, 3]. This system was extensively studied between 1965 and 1975 partially due to the coexistence of superconductivity with a large temperature dependent magnetic susceptibility [3]. This enhanced susceptibility was believed to result from a large exchange enhancement of the La d band contribution. Also, the superconducting proprieties were attributed exclusively to the changes of the electronic states at the (In,Sn) site and the oscillatory behaviour of T_c was credited to the nonmonotonic variation of the bare density of states as a function of Sn substitution [3, 4]. These materials were characterized as being conventional superconductors [5, 6]. One evidence of this conventional superconductivity was seen by the suppression of T_c as a function of magnetic impurities doping for LaSn$_3$ [7]. The

Table 1. Previous reported experimental parameters for LaIn$_{3-x}$Sn$_x$. γ is the Sommerfeld coefficient, λ is the electron-phonon coupling parameter and $\Delta T_c/\Delta c$ is the suppression of T_c by Gd^{3+} magnetic impurities.

	γ (mJ mol^{-1} K^{-2})	λ^c	$\frac{\Delta T_c}{\Delta c}$ (K/%)
LaIn$_3$	6.3^a	0.55(5)	
LaIn$_{2.2}$Sn$_{0.8}$		0.65(5)	
LaIn$_{1.5}$Sn$_{1.5}$		0.60(5)	
LaSn$_3$	11.7^b	0.80(5)	-1.25(3)^d

^{a} Ref. [9]; ^{b} Ref. [6]; ^{c} Ref. [3]; ^{d} Ref. [7].

initial linear decrease of the critical temperature, in this case, followed the Abrikosov-Gorkov theory [8] for a single gapped superconductor. Previously reported experimental parameters for this system are listed in Table 1.

Our main goal is to study the LaIn$_{3-x}$Sn$_x$ alloys as a nonmagnetic analog for the CeIn$_{3-x}$Sn$_x$ heavy fermion system. Both series are isostructural and their crystal structures are cubic, space group Pm-$3m$ (n. 221). For the Ce compounds the antiferromagnetic transition at $T_N = 10$ K ($x = 0$) was reported to decrease upon Sn substitution until it vanishes at a critical concentration of $x_c \approx 0.7$ [10, 11]. In the vicinity of this point, logarithmic divergence of the electronic specific heat was seen, in accordance with the behaviour of heavy fermions near quantum critical instabilities [12, 13]. With further increase of Sn substitution ($x \geq 2.2$) the Ce materials show valence fluctuation effects [10, 11]. Here we report our results for Gd^{3+} electron spin resonance (ESR) measurements in the LaIn$_{3-x}$Sn$_x$ compounds used as a reference for our ESR analysis of the CeIn$_{3-x}$Sn$_x$ series [14]. We extract the effective exchange interaction parameters between the Gd^{3+} localized magnetic impurity and the conduction electrons in the normal state [15] and compare it to the value obtained by previous study of the slope of the initial reduction of T_c by the Gd^{3+} impurities [7, 8].

2. Experiment details and results

Flux-grown single crystals of Gd doped LaIn$_{3-x}$Sn$_x$ are synthesized [16], where elemental La:Gd:In:Sn are weighted in the ratio 1-y:y:10-(10x/3):10x/3, with a nominal value for y of 0.005 and $x = 0$, 1.5 and 3. Polycrystalline samples are also grown by arc melting in Argon atmosphere. In this case the reactants ratio used is 1-y:y:3-x:x, with the same nominal value for y and $x = 0$, 0.7, 1.5 and 3. X-ray powder diffraction measurements confirm the cubic type structure for all compounds synthesized. The temperature dependence of the magnetic susceptibility $\chi(T)$ is measured for $2 \leq T \leq 300$ K, after zero field cooling. All ESR experiments are performed on a fine powder ($d \leq 38$ μm) in a Bruker ELEXSYS X-band spectrometer (9.4 GHz) with a TE$_{102}$ cavity coupled to a helium-gas-flux T-controller system for $4.2 \leq T \leq 300$ K. Fine powder of crushed single
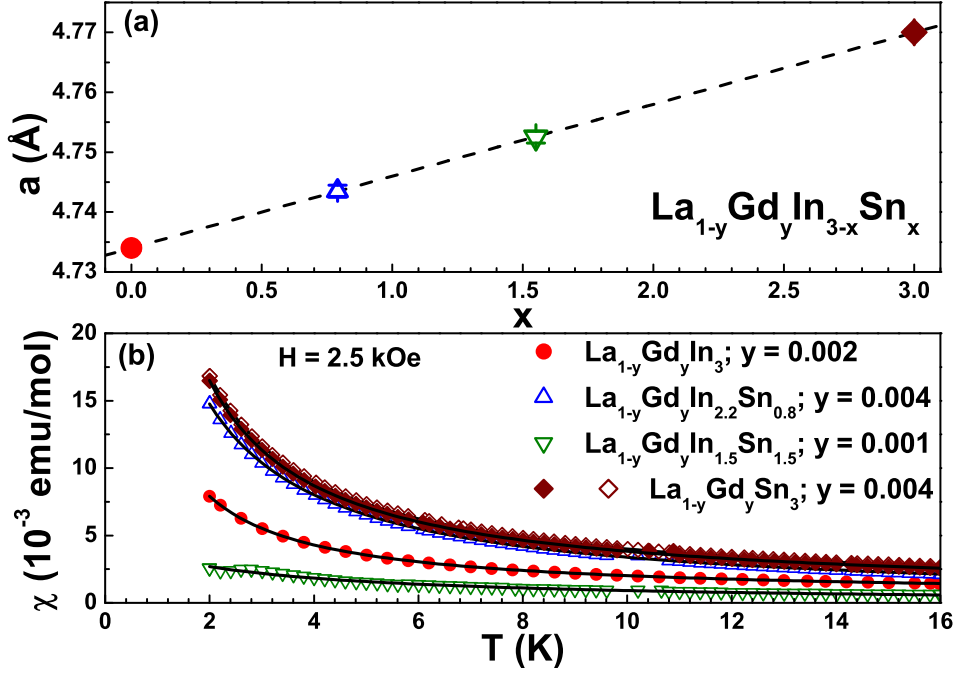
Figure 1. Gd^{3+} in $La_{1-y}Gd_yIn_{3-x}Sn_x$: (a) cubic lattice parameter a dependence as a function of x. The dashed line represents the Vegard law [11]. (b) Low temperature dependence of $\chi(T)$ at $H = 2.5$ kOe. The solid lines are the Curie-Weiss fitting. The closed symbols identify the single crystalline samples and the open ones the polycrystals.

crystals are used in the ESR experiments in order to increase the ESR signal-to-noise ratio. Through out this text, for convention, single crystalline samples are represented as closed symbols while polycrystals are seen as open symbols.

To obtain the actual Sn concentration we use the Vegard's law, which states that the $LaIn_3$ cubic lattice parameter a varies linearly with the doping of Sn [11]. Figure 1(a) illustrates the dependence of the cubic lattice parameter as a function of x, evidencing the synthesized samples. Figure 1(b) shows the temperature dependent magnetic susceptibility $\chi(T)$ data for $La_{1-y}Gd_yIn_{3-x}Sn_x$. The curves are corrected for the core diamagnetism. From the Curie-Weiss law fitting of the low temperature data and knowing the effective magnetic moment of Gd^{3+} ($\mu_{eff} = 7.94 \ \mu_B$) we estimate the Gd doping concentration and its values are given in Table 2.

Figure 2 shows the Gd^{3+} ESR X-band powder spectra in $La_{1-y}Gd_yIn_{3-x}Sn_x$ at $T = 10$ K. Each ESR spectrum consists of a single Dysonian resonance, characteristic of localized magnetic moments in a metallic host with a skin depth smaller than the size of the measured particles. From the fitting of the resonances to the appropriate admixture of absorption and dispersion Lorentzian derivatives, the g values and linewidths ΔH are obtained [17]. The solid lines are the best fit to the observed resonances and the obtained g values are presented in Table 2. Within the accuracy of the measurements, the g values were temperature and Gd concentration independent (not shown). For
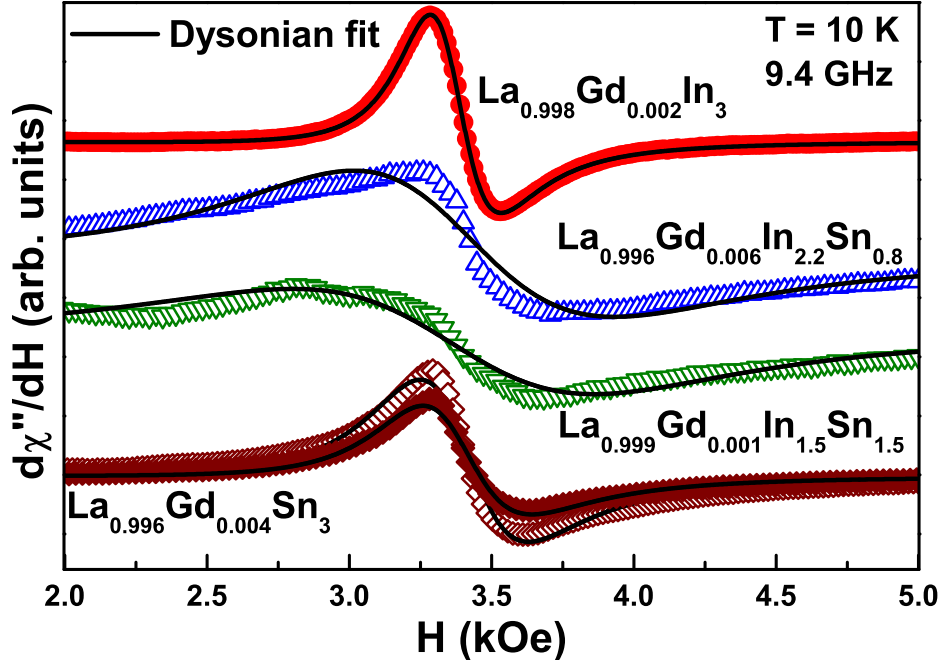
Figure 2. X-band (9.4 GHz) Gd^{3+} ESR powder spectra, at $T \approx 10$ K, in $La_{1-y}Gd_yIn_{3-x}Sn_x$. The solid lines are the Dysonian line shape analysis. The closed symbols identify the single crystalline samples and the open ones the polycrystals.

$La_{0.996}Gd_{0.004}In_{2.2}Sn_{0.8}$ a background line is present in the spectrum at $H \sim 3.4$ kOe and for $La_{0.999}Gd_{0.001}In_{1.5}Sn_{1.5}$ the ESR spectrum also show contribution of the background ($1.5 \leq H \leq 2.5$ kOe), since the signal in this sample is small due to low Gd^{3+} concentration ($\approx 0.1\%$). For $x = 3$ we observe that there is no appreciable difference in the resonance of grounded single and polycrystalline samples. This is not always the case in most systems and it cannot be established *a priori* because polycrystals synthesized by arc-melting tend to present more inhomogeneity. Since in this work samples with different Sn content were grown by different techniques we show that there are no discernable differences in the ESR spectra for a sample grown by both processes.

The temperature dependence of the Gd^{3+} ESR linewidth in $LaIn_{3-x}Sn_x$ is seen in Figure 3. For all samples the width increases linearly with temperature. The linear dependence of the linewidth was fitted to the expression $\Delta H - \Delta H_0 = bT$. The departure of the linear dependence decrease of ΔH at low temperature, seen for $x = 1.5$ may be related to short range Gd-Gd interaction or an artifact of the fitting analysis because of the background contribution in this temperature range. The values for ΔH_0 (residual linewidth) and b (thermal broadening) are presented in Table 2. The residual linewidth is defined as the ESR linewidth at $T = 0$ and it follows the residual electrical resistivity ρ_0 behaviour, since both are dependent of the disorder. Its relatively large values for $0 < x < 3$ are mainly due to the disorder effects introduced by the In-Sn substitution (see Fig. 4 of Ref. [2]). Within the accuracy of the measurements, the g and b values
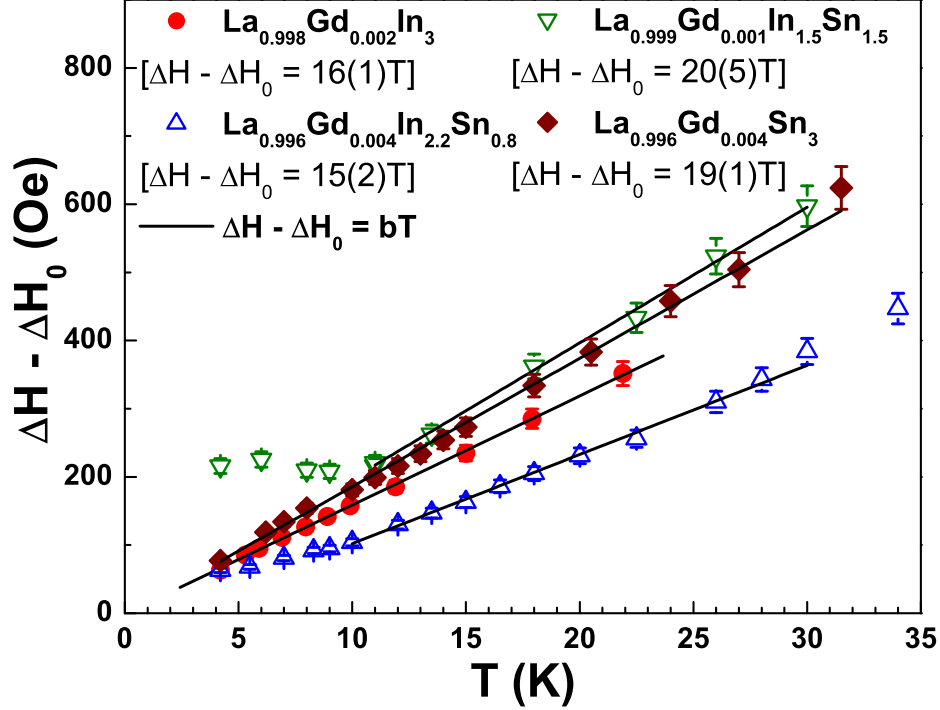
Figure 3. Temperature dependence of the Gd^{3+} ESR linewidth in $La_{1-y}Gd_yIn_{3-x}Sn_x$. The solid lines are the best fit to $\Delta H - \Delta H_0 = bT$. The closed symbols identify the single crystalline samples and the open ones the polycrystals.

Table 2. Experimental parameters for Gd^{3+} diluted in $La_{1-y}Gd_yIn_{3-x}Sn_x$.

Gd^{3+} in	g	Δg	ΔH_0 (Oe)	b (Oe/K)	y
$LaIn_3$	2.020(5)	+0.027(5)	50(5)	16(1)	0.002
$LaIn_{2.2}Sn_{0.8}$	2.010(10)	+0.020(10)	610(5)	15(2)	0.004
$LaIn_{1.5}Sn_{1.5}$	2.020(10)	+0.030(10)	470(10)	20(5)	0.001
$LaSn_3$	2.010(10)	+0.020(10)	140(5)	19(1)	0.004

are Gd concentration independent for $y < 2.0\%$ (not shown). Therefore, bottleneck and dynamic effects can be disregarded [18].

3. Analysis and discussion

In the simplest treatment of the exchange interaction, $J_{fs}(q)\mathbf{S}\cdot\mathbf{s}$, between a localized $4f$ electron spin ($\mathbf{S}$) on a solute atom (Gd^{3+}) and the free conduction electron spin ($\mathbf{s}$) of the host metal, the ESR g shift Δg (Knight shift) [19] and the thermal broadening of the linewidth (Korringa rate) [20], when bottleneck and dynamic effects are not present [18], can be written as:

$$\Delta g = J_{fs}\eta_F, \tag{1}$$

and

$$b = \frac{d(\Delta H)}{dT} = \frac{\pi k_B}{g \mu_B} J_{fs}^2 \eta_F^2, \tag{2}$$

where J_{fs} is the effective exchange interaction parameter between the Gd^{3+} $4f$ local moment and the s-like conduction electron in the absence of conduction electron momentum transfer [21], $\eta(F)$ is the "bare" density of states for one spin direction at the Fermi surface, k_B the Boltzman constant, μ_B the Bohr magneton and g the Gd^{3+} g value in insulators.

For diluted rare-earths magnetic moments in intermetallic compounds with appreciable residual resistivity, i.e., large conduction electron spin-flip scattering, equations 1 and 2 are generally used in the analysis of the ESR data. In these cases, the equations above may be rewritten as

$$b = \frac{\pi k_B}{g \mu_B} (\Delta g)^2. \tag{3}$$

3.1. Analysis of the Gd^{3+} ESR in LaIn$_3$

The g value of Gd^{3+} ESR in a number of cubic insulating materials can be well averaged and approximated to 1.993(1) and has been established as the correct one for the ESR community for the last two decades [22]. From the difference between the measured value (see table 2) and $g = 1.993(1)$, we calculate the g shift $\Delta g \simeq 27(5) \times 10^{-3}$ for the Gd^{3+} resonance in La$_{0.998}$Gd$_{0.002}$In$_3$. Knowing that $\pi k_B / g \mu_B = 2.34 \times 10^4$ Oe/K, Eq. 3 predicts a thermal broadening of $b \approx 17(5)$ Oe/K. This value is very close to the measured one, $b = 16(1)$ Oe/K. Therefore, we can conclude that the approximations made in Eqs. 1 and 2 are adequate for this compound and conduction electron-electron correlations [23, 24], q dependence of the exchange interaction [21] and multiple band effects [25] do not need to be taken into account in the analysis of our ESR data. Indeed, nuclear magnetic resonance experiments showed that for LaT$_3$ (T = Sn, In, Pb, Tl, etc.) [1, 3, 26, 27] conduction electron-electron correlations have negligible effect in these compounds. In the free conduction electron gas model, the Sommerfeld coefficient for a superconductor is given by $\gamma = (2/3)\pi^2 k_B^2 \eta_F (1 - \lambda)$, where λ is the electron-phonon coupling parameter. For LaIn$_3$ $\gamma = 6.3$ mJ/(mol K^2) [9] and $\lambda = 0.55(5)$ [3]. Hence, we estimate a total density of states at the Fermi level of $\eta_F = 0.8(1)$ states/(eV mol spin). With the experimental and derived parameters above we can use Eq. 2 to obtain the exchange interaction parameter between the Gd^{3+} $4f$ and a single s-like conduction band, $J_{fs} = 33(5)$ meV, in LaIn$_3$.

3.2. Analysis of the Gd^{3+} ESR in LaIn$_{2.2}$Sn$_{0.8}$

In La$_{0.996}$Gd$_{0.004}$In$_{2.2}$Sn$_{0.8}$, $\Delta g \simeq 20(10) \times 10^{-3}$. Eq. 3 estimates $b \approx 10(10)$ Oe/K, which is within experimental error is close to $b = 15(2)$ Oe/K, found experimentally. Thus, the model of a single s-like band and no q dependence can be used in the analysis of resonance in this material, as in the case of the Gd^{3+} ESR in LaIn$_3$ seen above. Knowing

Table 3. Derived parameters for Gd^{3+} diluted in $LaIn_{3-x}Sn_x$.

		ESR	SC
Gd^{3+} in	η_F (states eV^{-1} mol^{-1} spin^{-1})	J_{fs} (meV)	J_{fs} (meV)
$LaIn_3$	0.8(1)	33(5)	
$LaIn_{2.2}Sn_{0.8}$	0.8(1)^a	32(6)	
$LaIn_{1.5}Sn_{1.5}$	0.9(1)^a	32(8)	
$LaSn_3$	1.4(1)	20(2)	≈ 20

^{a} Ref. [3]

that the density of states for $LaIn_{2.2}Sn_{0.8}$ is $\eta_F = 0.8(1)$ states/(eV mol spin) [3], from Eq. 2 we find $J_{fs} = 32(6)$ meV (see Table 3).

3.3. Analysis of the Gd^{3+} ESR in $LaIn_{1.5}Sn_{1.5}$

The density of states of the $LaIn_{1.5}Sn_{1.5}$ sample is $\eta_F = 0.9(1)$ states/(eV mol spin) [3]. The $\Delta g \simeq 30(10) \times 10^{-3}$ value observed relates to a Korringa rate $b = 20(15)$ Oe/K by Eq. 3, which is very close to the thermal broadening seen experimentally, $b = 20(5)$ Oe/K. Consequentially, an analysis considering a single s-like band is valid as in both cases described above. From Eq. 2 we obtain $J_{fs} = 32(8)$ meV.

3.4. Analysis of the Gd^{3+} ESR in $LaSn_3$

From the Sommerfeld coefficient expression and knowing that the $LaSn_3$ compound has $\gamma = 11.7$ mJ/(mol K^2) [6] and $\lambda = 0.80(5)$ [3], we estimate $\eta_F = 1.4(1)$ states/(eV mol spin). The Korringa rate and Δg found experimentally for $La_{0.996}Gd_{0.004}Sn_3$ are 19(1) Oe/K and $20(10) \times 10^{-3}$, respectively. From Eq. 3 we get $b \approx 10(10)$ Oe/K, which indicates that, within experimental error, we can neglect multiple band and q dependence effects. Therefore, we calculate, using Eq. 2, $J_{fs} = 20(2)$ meV (see Table 3). It is interesting to compare the exchange interaction parameter J_{fs} obtained in the ESR experiment with the one obtained by the suppression of the superconducting transition temperature T_c by Gd^{3+} magnetic impurities $\Delta T_c/\Delta c$. From the Abrikosov-Gorkov theory [8] we have:

$$\left| \frac{\Delta T_c}{\Delta c} \right| = \frac{\pi^2}{8k_B} J_{fs}^2 \eta_F (g_J - 1)^2 J(J+1), \tag{4}$$

where g_J is the Landé factor. The value of $\Delta T_c/\Delta c = -1.25(3)$ K/% reported in Ref. [7] when used in Eq. 4 predicts $J_{fs} \approx 20$ meV, in accordance with the one obtained by ESR. This result provides microscopical evidence of the conventional character of the superconducting state in $LaSn_3$ and also corroborates that the mechanism of relaxation of the resonance of the Gd^{3+} ion in this compound is via a single s-like conduction band [15].
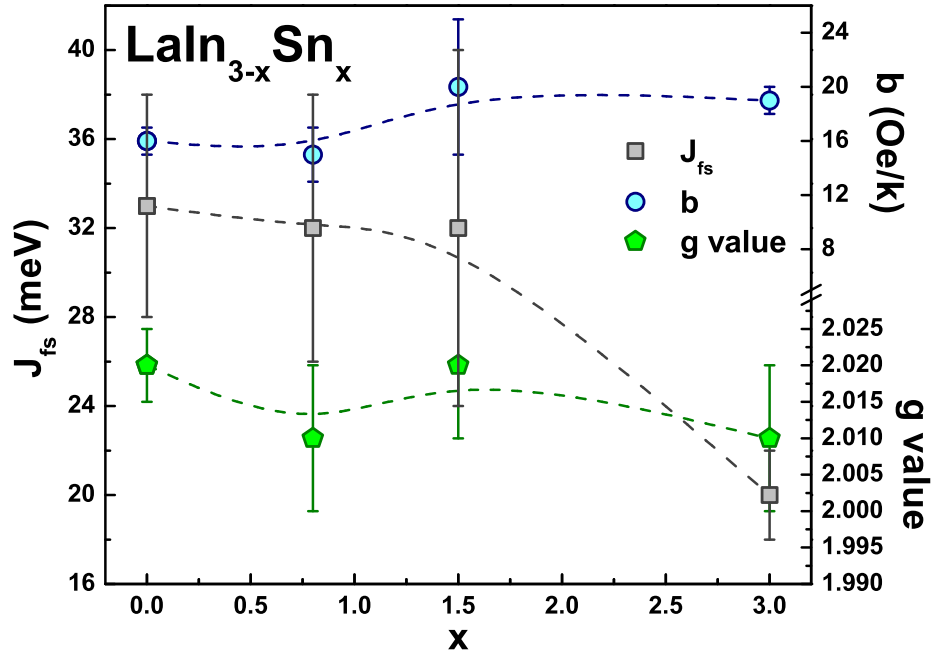
Figure 4. Evolution of the effective exchange interaction parameter J_{fs}, Korringa rate b and g value of the Gd^{3+} ESR in $LaIn_{3-x}Sn_x$ as a function of x. The dashed lines are guides to the eyes.

Figure 4 summarizes some experimental and derived parameters, obtained for the Gd^{3+} ESR in the $LaIn_{3-x}Sn_x$ system. We observe that the g shift and the Korringa rate do not change significantly with the Sn substitution. From the analysis of the experimental data we showed that the Gd^{3+} resonance relaxation in these compounds occurs via a single s-like conduction band that is independent of momentum transfer. We also obtain the values of the effective exchange interaction parameter J_{fs}, which tends to decrease with the substitution of In by Sn. Since the $LaIn_{3-x}Sn_x$ compounds increase the cubic lattice parameter (Fig. 1) as a function of x this may be responsible for decreasing J_{fs}.

4. Summary

In summary, we report Gd^{3+} ESR results in the $LaIn_{3-x}Sn_x$ superconducting system, which permitted the extraction of the effective exchange interaction parameter J_{fs} between the Gd^{3+} $4f$ local moment and the s-like conduction electrons in these compounds. We showed that J_{fs} slightly decreases as a function of Sn substitution. This is in sharp contrast to the results found for the Gd^{3+} resonance in the $CeIn_{3-x}Sn_x$ heavy fermion analog system, much due to the peculiarities of the magnetic compounds [14]. We have also observed microscopically that the superconductivity is of the conventional type in $LaSn_3$, i.e., the exchange coupling between the Gd^{3+} local moment and the conduction electrons governs the impurity relaxation and pair-braking processes.

Acknowledgments

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