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Transition from Kondo to intermediate valence regime in $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}$: an ESR study

A N Medina, F G Gandra†, W R Azanha and L P Cardoso

Universidade Estadual de Campinas, Instituto de Física, 13083-970, Campinas, SP, Brazil

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Abstract. We report on electron spin resonance (ESR) results for the series of compounds $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}$ doped with Gd. We show that from the Gd g -value and linewidth one can determine the concentration x_c where the system goes from Kondo single impurity to Kondo lattice (and intermediate valence) regimes. The observed behaviour in both the g -value and the slope of the linewidth– T curves is explained using the indirect interaction between Gd and Ce moments. The calculation leads to the determination of the Ce–Gd exchange parameter $J_{\text{Ce-Gd}} = 4.8$ meV and the Ce–conduction electron exchange parameter $|J_{f-s}| = 19$ meV, for $x = 1$.

1. Introduction

Intermetallic compounds based on Ce have attracted great attention due to their interesting physical properties [1] related to the Ce 4f electron. It is known that the dilution of such compounds with La promotes a tuning of the s – f interaction in analogy with the application of external pressure on the undiluted sample. As a consequence it is possible to induce different regimes on Kondo systems as function of the Ce concentration [2, 3]. It has been shown particularly for the series $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}$, using several techniques (resistivity, susceptibility, specific heat etc) [4–6], that the system is characterized as a Kondo single impurity for the low concentration side ($x < 0.7$), changing to a Kondo lattice behaviour above this value. Furthermore, when x is very close to 1, the Ce ion presents intermediate valence ($\cong 3.5$) [7]. Among the quoted techniques, the electrical resistivity has been widely used to characterize the different regimes, which have a $-\ln T$ or T^2 dependence in each case. However it is not possible to determine a clear turning point between both regimes using resistivity.

The ESR technique can be a useful tool to probe the density of states and exchange parameter of rare-earth magnetic impurities diluted into a metallic host [8]. Therefore the ESR technique is very sensitive to variations on the exchange parameter [9–13] and may be an alternative tool to observe the turning point. Since the ESR of Ce^{3+} cannot be detected in this kind of compound (the large exchange parameter broadens the line beyond detection), Gd is used as a magnetic probe instead. We expect to observe a g -shift and changes in the behaviour of the linewidth–temperature curves, which are proportional to the exchange interaction between the Gd and Ce moments, when the Ce concentration is changed.

It is our purpose in this paper to show that ESR can be used as a sensitive technique to observe the transition from Kondo single impurity to Kondo lattice regimes in the $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}$ system.

† E-mail: gandra@ifi.unicamp.br.

2. Experiment

Polycrystalline samples with $0 \leq x \leq 1$ in steps of 0.1 with 0.5% of Gd impurity were prepared using an arc-furnace and high purity elements. The samples were treated at 600 °C for 14 days in argon. In general the samples are brittle, specially for the high concentration side. X-ray diffraction patterns ($\theta : 2\theta$ scans) of the samples were carried out at 300 K in a Philips PW1710 diffractometer using Cu $K\alpha$ radiation and a graphite secondary monochromator. The electrical resistivity was measured using standard four-probe dc method in the temperature range between 1.5 and 300 K. The ESR experiments were carried out at 9.3 GHz with 2 mW power in a home-made spectrometer between 5.5 and 25 K.

2.1. X-rays

X-ray diffraction patterns were obtained for all samples of the $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}:\text{Gd}$ system. The compounds presented orthorhombic symmetry and lattice parameters $a = (3.79 \pm 0.01) \text{ \AA}$, $b = (10.51 \pm 0.03) \text{ \AA}$ and $c = (4.36 \pm 0.01) \text{ \AA}$ for $x = 1$ which are in good agreement with the literature reported values [14]. In figure 1 we show the relative variation of the lattice parameters and the unit cell volume as a function of the Ce concentration. The results show that the lattice parameters a and b vary almost by the same amount while c has a relative variation about three times smaller. This can be related to the observation of magnetic anisotropy in single crystals of CeNi [4, 15], with the easy magnetic axis coincident with the c axis. The reduction of the unit cell volume as x increases is similar to the application of external pressure and induces the change of Kondo impurity to Kondo lattice regimes. The observed volume variation can be described by two lines intersecting around $x = 0.7$, which is very close to the reported transition value. Above this concentration the volume reduces faster due to the reduction of the Ce ionic radius as a consequence of the Ce valence increase [4, 16].

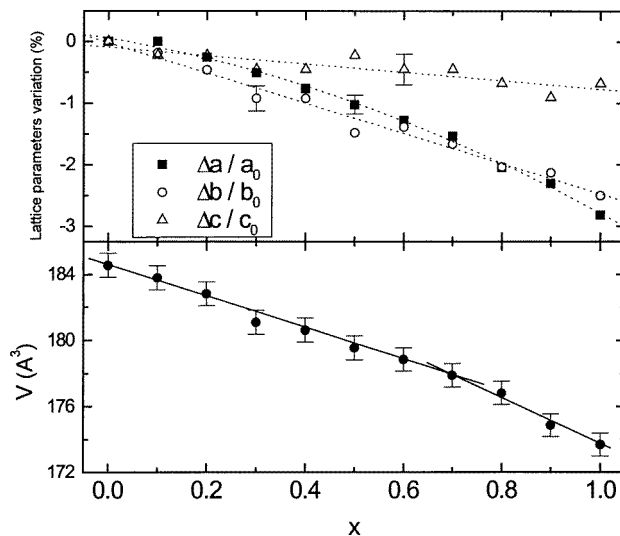


Figure 1. Relative variation of the lattice parameters a , b and c (upper figure) and unit cell volume variation (bottom figure) with Ce concentration.

2.2. Resistivity

Our samples were doped with 0.5% Gd which was used as a probe for the ESR experiments. It was then necessary to run resistivity experiments from 1.5 to 300 K to characterize the samples with the Gd magnetic impurity. The results show that the addition of the Gd does not change the resistivity behaviour which is in good agreement with the literature data [4]. In figure 2 we plot the normalized resistivity for several concentrations where a clear $-\ln T$ dependence is observed for $x \leq 0.5$ (upper figure) and a T^2 dependence is found for $x \geq 0.9$ (bottom figure). However, for the intermediate concentrations $x = 0.6, 0.7$ and 0.8 , it is hard to consider one predominant regime. The fit for both dependencies on T is quite poor for these concentrations. Consequently, the critical concentration (x_c) can be determined to be within the range from $x = 0.5$ to $x = 0.8$.

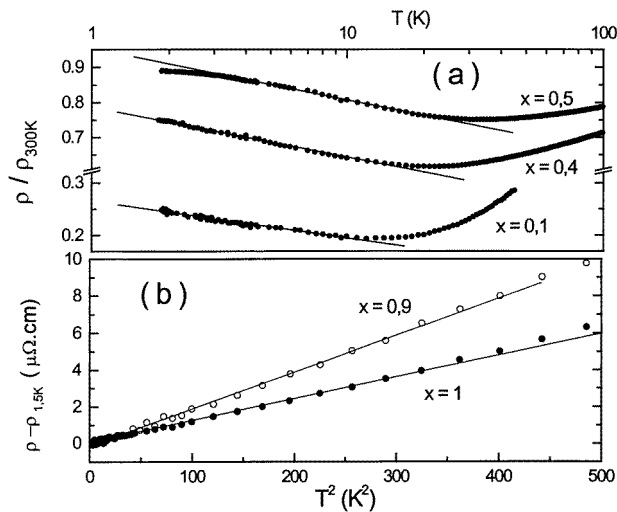


Figure 2. Behaviour of the resistivity for several Ce concentrations. In the upper figure we show the $-\ln T$ behaviour for $x < 0.6$ characteristic of single impurity Kondo systems. In the lower figure, the T^2 dependence for high concentration evidences the change of regime.

2.3. ESR

The ESR spectrum of Gd^{3+} in $(La_{1-x}Ce_x)Ni$ is shown for several concentrations at 5.5 K in figure 3. For the intermediate concentrations a second line is observed. This broad line is due to Ni aggregates or other phases of the compound which are formed during the sample preparation. This line is also observed for the non-doped samples. The Gd spectra were fitted to a Dysonian [17] line and the best fit was obtained for g -values close to 2 and linewidths $\Delta H \cong 500$ G. For each sample, the g -values are essentially constant in the studied temperature range while the linewidth followed a linear dependence, $\Delta H = a + b_{eff}T$. However, the g -value increases from $g = 2.00$ for LaNi up to $g \approx 2.03$ for $x = 0.7$. For higher concentrations, g decreases down to $g \approx 2.00$, and its behaviour can be described by two straight lines intersecting at x_c , as shown in figure 4. Although the relative variation of the g -value reaches 1.5%, the ESR lines are not narrow, giving rise to error bars for the g -value around 0.5%. For this reason, x_c can assume values between 0.5 and 0.7.

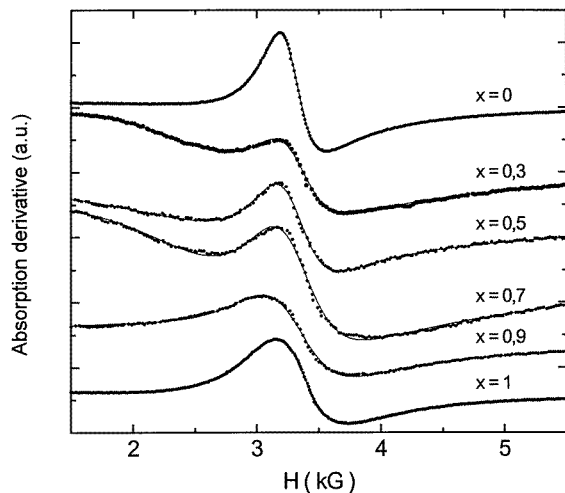


Figure 3. ESR of Gd^{3+} at $T = 5.5$ K for several Ce concentrations. Dots are experiment and the line is the fit to a Dysonian line. A second broad line was considered in the fit as explained in the text.

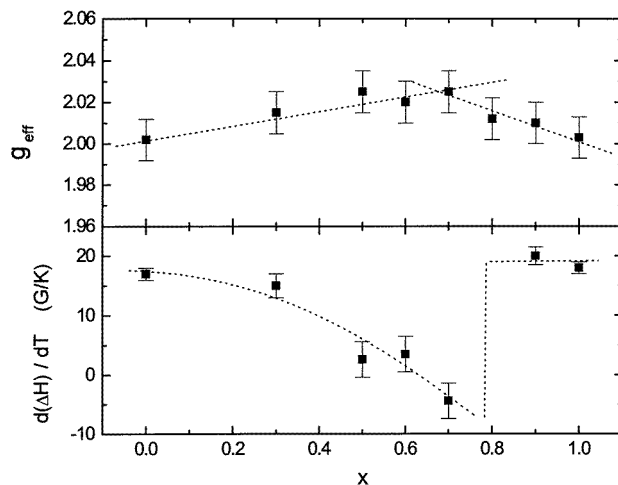


Figure 4. Effective g -factor of Gd^{3+} and linewidth thermal broadening coefficient as function of the Ce concentration showing the regime transition close to $x = 0.6$. The dotted lines are just a guide to the eyes.

The effective slope b_{eff} of the linewidth with the temperature reduces from about $(17 \pm 1) \text{ G K}^{-1}$ at $x = 0$ to negative values at $x = 0.7$. Going further to higher concentrations, the slope returns to $b_{eff} \approx 20 \text{ G K}^{-1}$, which is close to the initial value. This peculiar behaviour of the effective slope will define x_c clearly as discussed below.

3. Discussion

It is well known that for a bottlenecked system the linewidth behaviour with the temperature is strongly dependent on the concentration of the local moment ion (Gd). This regime can

be destroyed with the addition of other magnetic ions and, consequently, the slope of the linewidth should increase [18]. In our case, measurements of the thermal broadening and g -shift for $x = 0$ and $x = 1$ show that these parameters are independent of the Gd concentration ($<1\%$), confirming that $(La_{1-x}Ce_x)Ni:Gd$ is not bottlenecked.

Although we have described the linewidth varying linearly within the studied temperature range, this is not necessarily true for all temperatures and concentrations. In fact we observed a negative slope for $x = 0.7$, what is a clear indication of indirect magnetic interaction between the Gd moment and other magnetic ion, Ce in our case. For $x = 0$ the usual Korringa behaviour is observed. When a small quantity of Ce replaces La in the lattice an indirect interaction between Ce and Gd (RKKY interaction) takes place giving rise to an extra channel for the relaxation process and also a different internal field. Jaccarino [19] showed that the g -shift is given by

$$\Delta g = \frac{\chi_{Ce}}{g_{Gd}\mu_B^2} x \sum_i J_{ij} \quad (1)$$

where χ_{Ce} is the Ce molar susceptibility, J_{ij} is the RKKY oscillatory function, μ_B is the Bohr magneton and x is the Ce concentration. Altshuler *et al* showed that the extra contribution to the linewidth is [11, 13]

$$\Delta H_1(x, T) = \frac{-\pi z (J_{Gd} n(\varepsilon_F)) J_{Ce} H_{res} \chi_{Ce}}{2N_d \mu_B^2} x \quad (2)$$

where J is the s-f exchange parameter, $n(\varepsilon_F)$ is the density of states, z is the number of conduction electrons per formula unit and H_{res} is the resonance field. Both contributions are proportional to the Ce susceptibility. For small x , χ_{Ce} is essentially independent of the concentration [4] and therefore, Δg is proportional to x . In the high concentration region, the Ce effective moment is reduced when x increases and promotes the consequent reduction of Δg , as observed in figure 4. To explain the linewidth behaviour, we must consider the temperature dependence of ΔH_1 . For each x , the linewidth can be assumed to be $\Delta H = a + bT + c\chi_{Ce}$. For low concentrations the susceptibility is given by a Curie law [4] such that a competition between a linear term and a $1/T$ term takes place. However, within the limited temperature range used, ΔH showed a linear behaviour with an effective slope b_{eff} . For $x = 0$ the slope is $b \approx 17 \text{ G K}^{-1}$. As x increases, the $1/T$ term becomes predominant such that b_{eff} reaches negative values. On the other hand, when x is close to 1, χ_{Ce} presents just a weak dependence on the temperature in the range of interest and, consequently, ΔH has the same slope as the reference compound.

For $x = 0$, the slope is given by the Korringa relation [9–13]

$$b = \frac{4\pi K_B g}{\mu_B} \left(\frac{g_j - 1}{g_j} \right)^2 (J_{Gd} n(\varepsilon_F)) \quad (3)$$

where g_j is the Landé g -factor, leading to the determination of $[J_{Gd} n(\varepsilon_F)] = 0.027$. This result should provide a g -value around 2.02, that is close to the observed value $g = 2.00(\pm 0.015)$. Considering that $\gamma = (2/3)\pi^2 k^2 n(\varepsilon_F) = 5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [5], we calculate $n(\varepsilon_F) = 1.06 \text{ states eV}^{-1}$ and $J_{Gd} = 25 \text{ meV}$. These values are of the same magnitude as found for other materials [11, 20]. Assuming that $[J_{Gd} n(\varepsilon_F)]_{x=1} = 0.027$ and taking $\chi = 2 \times 10^{-3} \text{ emu mol}^{-1}$ [4, 5] and $b = 18 \text{ G K}^{-1}$ for $x = 1$, we obtain from equation (2) $J_{Ce-Gd} = 4.8 \text{ meV}$ and $|J_{Ce}| = 19 \text{ meV}$.

In conclusion, we have shown that the ESR results can establish a critical concentration which determines the transition from Kondo single impurity to Kondo lattice regimes. This was clearly observed as a discontinuity in the effective slope of the temperature dependence of the linewidth and on the g -value with the concentration (or unit cell volume).

The behaviour of the ESR parameters was explained considering the magnetic interaction between the Gd moment and the Ce ion. In addition, we determined the Ce exchange parameter for CeNi.

Acknowledgments

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References

- [1] 1995 *SCES'94 Proc. Int. Conf. Strongly Correlated Electron Systems, Physica B* **206/207**
1996 *SCES'96 Proc. Int. Conf. Strongly Correlated Electron Systems, Physica B* **223/224**
- [2] Brandt N B and Moshchalkov V V 1984 *Adv. Phys.* **33** 373
- [3] Medina A N, Hayashi M A, Cardoso L P, Gama S and Gandra F G 1998 *Phys. Rev. B* **57** 5000
- [4] Isikawa Y, Mori K, Fujii A and Sato K 1986 *J. Phys. Soc. Japan* **55** 3165
- [5] Isikawa Y, Mori K, Mizushima T, Fujii A, Takeda H and Sato K 1987 *J. Magn. Magn. Mater.* **70** 385
- [6] Sato K, Umohara I, Isikawa Y, Mori K and Takeda H 1993 *J. Appl. Phys.* **73** 6623
- [7] Gignoux D, Givord F and Lemaire R 1983 *J. Less Common Met.* **94** 165
- [8] Barnes S E 1981 *Adv. Phys.* **30** 801
- [9] Gandra F G, Pontes M J, Schultz S and Oseroff S B 1987 *Solid State Commun.* **64** 859
- [10] Gandra F G, Schultz S, Oseroff S B, Fisk Z and Smith J L 1985 *Phys. Rev. Lett.* **55** 2719
- [11] Krivenko S A, Zenin A G and Khaliullin G G 1991 *Sov. Phys.-JETP* **73** 576
- [12] Elschner B and Scholtt M 1988 *J. Magn. Magn. Mater.* **76/77** 444
- [13] Al'tshuler T S, Kataev V E and Khaliullin G G 1983 *Sov. Phys.-Solid State* **25** 1239
- [14] Gignoux D and Gomez-Sal J C 1984 *Phys. Rev. B* **30** 3967
- [15] Fillion G, Gignoux D, Givord F and Lemaire R 1984 *J. Magn. Magn. Mater.* **44** 173
- [16] Garcia Soldevilla J, Gómez Sal J C, Rodríguez Fernández J, Espeso J I, Monconduit L, Allemand J and Paccard D 1997 *Physica B* **230–232** 117
- [17] Dyson F J 1955 *Phys. Rev.* **98** 349
- [18] Kwapulinska E and Kaczmarek K 1990 *J. Magn. Magn. Mater.* **88** 51
- [19] Jaccarino V 1961 *J. Appl. Phys. Suppl.* **32** 102
- [20] Rettori C, Oseroff S, Rao D, Pagliuso P, Barberis G, Sarrao J, Fisk Z and Hundley M 1997 *Phys. Rev. B* **55** 1016