

# NMR AND MAGNETIC SUSCEPTIBILITY OF THE INTERMETALLIC PSEUDO-BINARY COMPOUNDS: $Ce_{1-x}R_xAl_3$ WITH $R = Y$ AND $La$

BY V. NICULESCU, IULIU POP

University of Cluj\*

AND M. ROSENBERG

Solid State Physics Department., University of Bucharest\*\*

(Received May 18, 1972)

The NMR and magnetic susceptibility of the intermetallic pseudo-binary compounds  $Ce_{1-x}Y_xAl_3$  ( $x = 0.1; 0.05; 0.1$ ) and  $Ce_{0.9}La_{0.1}Al_3$  were investigated. As a result of the magnetic dilution of the rare-earth sublattice, the indirect exchange interaction between the Ce ions *via* the conduction electrons polarization is weakened and the negative paramagnetic Curie temperature decreases with the increase in the Y concentration. The higher values of the temperature independent term in the magnetic susceptibility of  $Ce_{1-x}Y_xAl_3$  compounds as compared with  $CeAl_3$  is due to the increase in the orbital susceptibility of the *d*-electrons as a result of the  $4d^25s^1$  outer electron configuration of the metallic Y.

The presence of a second peak with a lower Knight shift in the  $Al^{27}$  NMR spectrum is the evidence that besides the Al sites surrounded in the first coordination sphere as in  $CeAl_3$  there are also Al nuclei positioned in the vicinity of an Y or La ion.

## 1. Introduction

In a previous paper [1] the results of the investigation of the NMR and magnetic susceptibility of pseudo-binary intermetallic compounds  $Ce_{1-x}R_xAl_3$  with  $R = Gd, Tb$  and  $Er$  in small amounts ( $x_{max} = 0.07$ ) were presented. It was shown that all the rare-earth ions in the intermetallic compounds preserve their individuality contributing with the free-ion magnetic moment to the Curie-Weiss term of the magnetic susceptibility and by exchange polarization of the conduction electrons to the Knight shifts of the NMR line of  $^{27}Al$ .

At low concentrations of R, it was possible to separate in the NMR spectra the line

---

\* Address: Physics Faculty, University of Cluj, Cluj, Kogălniceanu 1, Romania.

\*\* Address: Physics Faculty, University of Bucharest, Bucharest, Academiei 14, Romania.

of Al nuclei positioned in the neighbourhood of an R ion and that of Al nuclei surrounded by Ce ions only. We were also interested in the behaviour of the  $Ce_{1-x}R_xAl_3$  pseudo-binary compounds where R was a non-magnetic ion like Y or the rare-earth La.

The hexagonal type  $Ni_3Sn$  lattice of  $CeAl_3$  is not altered by substituting Ce with Y or La in concentrations lower than 10%. Samples with  $x = 0.01$ ; 0.05 and 0.10 for Y and  $x = 0.10$  for La were prepared and checked for homogeneity as described in [1] for the  $Ce_{1-x}Gd_xAl_3$  compounds.

The experimental technique for the recording of  $^{27}Al$  NMR spectra and measurement of the temperature dependence of the magnetic susceptibility was the same as the previous one described in [1].

## 2. Results and discussion

### A. Magnetic susceptibility

Similarly as for the  $CeAl_x$  intermetallic compounds [2-4] and  $Ce_{1-x}R_xAl_3$  with  $R = Gd, Tb$  and  $Er$ , the temperature dependence of the magnetic susceptibility as shown

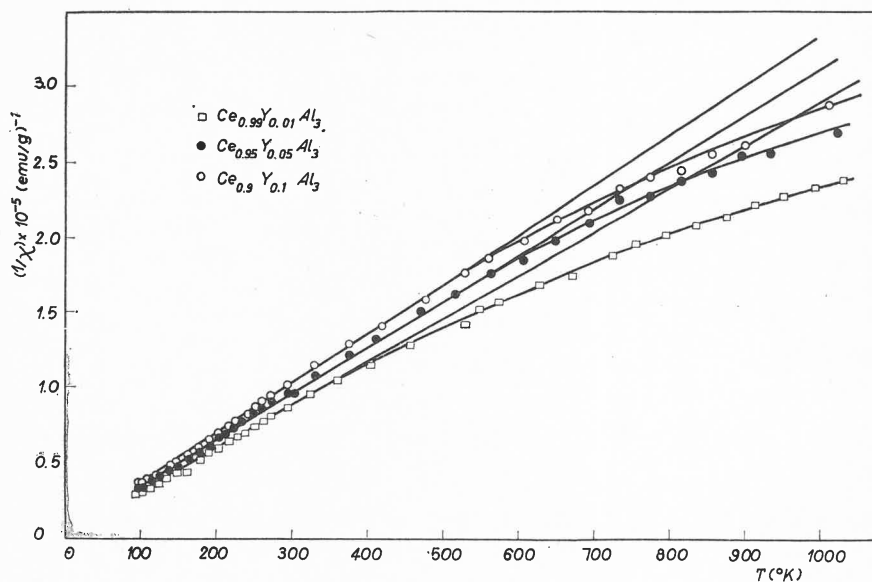


Fig. 1. The temperature dependence of the reciprocal susceptibility of the  $Ce_{1-x}Y_xAl_3$  compounds

in Fig. 1 for  $Ce_{1-x}Y_xAl_3$  and in Fig. 2 for  $Ce_{0.9}La_{0.1}Al_3$  is expressed by

$$\chi = \chi_0 + C(T - \theta_p)^{-1}, \quad (1)$$

where  $\chi_0$  is a temperature independent term.

The magnetic moment per molecule  $\mu_{ef}$ , the paramagnetic Curie point  $\theta_p$ , the temperature independent susceptibility  $\chi_0$  and the Curie-Weiss term (denoted  $\chi_f$ ) at 300°K are given in Table I for all the four investigated compounds.

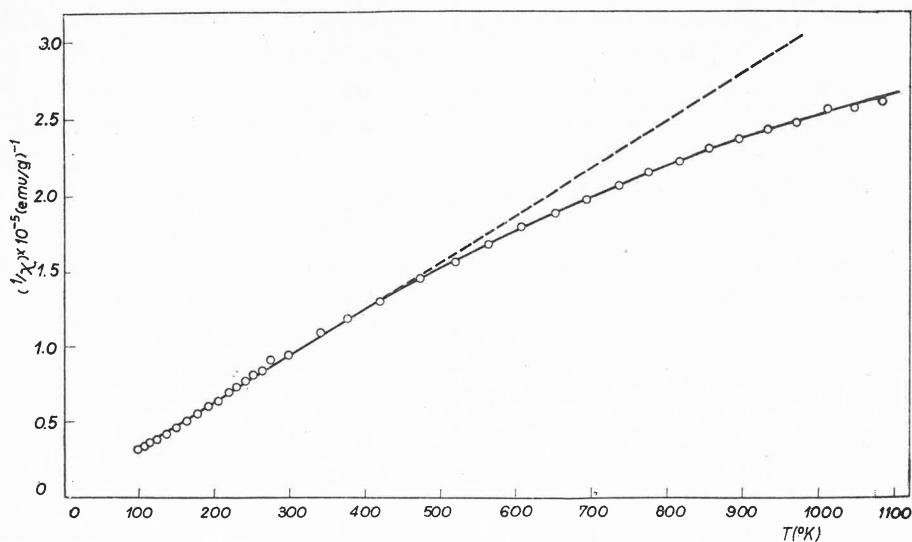


Fig. 2. The temperature dependence of the reciprocal susceptibility for  $\text{Ce}_{0.9}\text{La}_{0.1}\text{Al}_3$

TABLE I

The values of some magnetic features of the compounds  $\text{Ce}_{1-x}\text{R}_x\text{Al}_3$  ( $\text{R} = \text{Y}, \text{La}$ ) as compared with  $\text{CeAl}_3$ . The susceptibilities are given in  $10^{-6}$  emu/g

Compounds	$M$	$\chi_0$	$\chi(300^\circ\text{K})$	$\theta_p(^{\circ}\text{K})$	$\mu_{\text{ef}}(\text{exp})$	$\mu_{\text{ef}}(\text{calc})$	$\chi_f(300^\circ\text{K})$
$\text{CeAl}_3$	221.05	1.3	11	-25	2.525	2.56	10.6
$\text{Ce}_{0.99}\text{Y}_{0.01}\text{Al}_3$	220.629	1.4	11.2	-8	2.475	2.53	9.8
$\text{Ce}_{0.95}\text{Y}_{0.05}\text{Al}_3$	218.385	1.55	10	-7	2.37	2.43	8.45
$\text{Ce}_{0.9}\text{Y}_{0.1}\text{Al}_3$	215.83	1.62	9.5	-6	2.29	2.304	7.88
$\text{Ce}_{0.9}\text{La}_{0.1}\text{Al}_3$	220.95	1.22	10.6	$-4 \pm 2$	2.37	2.304	9.38

The magnetic moment per molecule was then calculated, taking the free-ion value  $\text{Ce}^{3+}$  and assuming that the substitution by Y or Ce corresponds to a simple magnetic dilution of the rare-earth sublattice. The obtained values are also given in Table I and a good agreement with the experimental values can be noticed.

The Curie-Weiss behaviour of the Ce cores as free-ion magnetic moments is the evidence for the high degree of localization of the Ce  $4f$ -electrons in these compounds as well as in the  $\text{CeAl}_x$  compositional series [4] and  $\text{Ce}_{1-x}\text{R}_x\text{Al}_3$  with  $\text{R} = \text{Gd}, \text{Tb}, \text{Er}$  [1].

The temperature-independent term  $\chi_0$  is the sum of five different contributions

$$\chi_0 = \chi_P + \chi_{\text{orb}}^{p,d} + \chi_{\text{VV}}^{4f} + \chi_L + \chi_{\text{dia}} \quad (2)$$

where  $\chi_P$  is the Pauli paramagnetism term,  $\chi_{\text{orb}}^{p,d}$  the orbital contribution of the collective outer  $p$  and  $d$ -electrons,  $\chi_{\text{VV}}^{4f}$  the contribution of the Van Vleck paramagnetism of the local-

ized 4f electrons,  $\chi_L$  the Landau diamagnetic term and  $\chi_{\text{dia}}$  the contribution of diamagnetic ionic cores of the aluminium and rare-earth atoms. Comparing the different contributions in (2) with those of pure  $\text{CeAl}_3$ , we have to expect a decrease in  $\chi_{\text{VV}}^{4f}$  for both the Y and La substituted Ce in  $\text{CeAl}_3$ , due to the lack of 4f electrons at the Y and La sites and a small decrease in  $\chi_{\text{dia}}$  (in absolute value) for the  $\text{Ce}_{1-x}\text{Y}_x\text{Al}_3$  due to the lower diamagnetic susceptibility of Y ( $-12.10^{-6}$  emu/mol) as compared with Ce ( $-20.10^{-6}$  emu/mol). Therefore a small decrease in  $\chi_0$  for  $\text{Ce}_{0.9}\text{La}_{0.1}\text{Al}_3$  is to be expected in agreement with the experimental data. For the Y substituted  $\text{CeAl}_3$  the decrease in  $\chi_{\text{VV}}^{4f}$  is probably higher than the decrease in absolute value of  $\chi_{\text{dia}}$ , expecting thus a decrease in  $\chi_0$  with increasing Y concentration. Actually a rather important increase is observed. This may be explained in terms of a higher contribution to  $\chi_{\text{orb}}^{p,d}$  of the Y atoms. Indeed, the outer electronic configuration of Y in the metallic lattice seems to be  $4d^25s^1$  [5] as compared with  $5d^16s^2$  for Ce, with  $\chi_{\text{orb}}^{4d} = 75.10^{-6}$  emu/mol for the former [5] and  $38.8.10^{-6}$  emu/mol for the latter [3]. Therefore  $\chi_{\text{orb}}^{p,d}$  is expected to increase with the Y concentration, thus giving rise to the observed increase in  $\chi_0$ .

The dilution of the magnetic sublattice results in a decrease of the absolute value of the paramagnetic Curie point  $\theta_p$ , its sign remaining negative. Assuming as in  $\text{CeAl}_3$  an indirect exchange coupling between the rare-earth ions *via* the conduction electrons polarization, the paramagnetic Curie point is [6-9]

$$\theta_p = -3\pi Z^2 \Gamma^2 (4kE_F)^{-1} (g_J - 1)^2 J(J+1) \sum_{(RE)_j} F(2k_F R_{(RE)_i(R E)_j}), \quad (3)$$

where

$$F(\varrho) = \frac{\varrho \cos \varrho - \sin \varrho}{\varrho^4}. \quad (4)$$

The negative sign of  $\theta_p$  is the evidence for the positive sign of  $\Sigma F(\varrho)$ . The decrease of  $|\theta_p|$  is probably a result of a reduction in the value of  $\Sigma$  owing to the substitution of some number of magnetic R ions by nonmagnetic ions.

## B. NMR line shape and Knight shift

For all the four investigated compounds the NMR spectra were recorded in the temperature range 150–450°K. The room temperature spectra are shown in Fig. 3. The features of the NMR line shape for the compounds  $\text{Ce}_{1-x}\text{Y}_x\text{Al}_3$  are given in the Table II. The most striking feature is the appearance of a left-sided second peak with a lower Knight shift than the main line. The intensity of the second peak increases with the Y concentration broadening the whole line for  $\text{Ce}_{0.9}\text{Y}_{0.1}\text{Al}_3$  and  $\text{Ce}_{0.9}\text{La}_{0.1}\text{Al}_3$ .

The Knight shift of the main peak is about the same as that of  $\text{CeAl}_3$  and is strongly temperature-dependent. In Fig. 4 are given the temperature dependence of the K. S. in the case of  $\text{Ce}_{0.95}\text{Y}_{0.05}\text{Al}_3$  for the main line and also for the whole line. The variation of the K. S. for the other compounds is similar. The half line width of the main peak and of the whole line are also temperature dependent (Fig. 5). As for  $\text{CeAl}_3$ , the K. S.

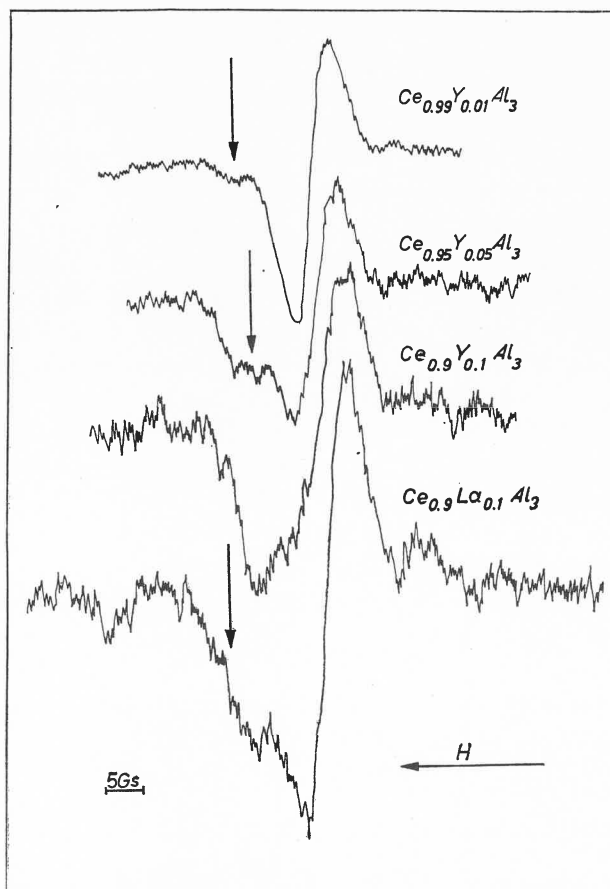


Fig. 3. The NMR line shape for the compounds  $Ce_{1-x}R_xAl_3$  at the room temperature

TABLE II

The features of the NMR line and K. S. for the  $Ce_{1-x}Y_xAl_3$

Compound	$\delta H(300^\circ K)$ (Gs)	$\delta H(150^\circ K)$ (Gs)	$K(300^\circ K)$ (%)	$K(150^\circ K)$ (%)
$Ce_{0.99}Y_{0.01}Al_3$	$5.7 \pm 0.2$	$6.9 \pm 0.2$	$0.216 \pm 0.004$	$0.32 \pm 0.004$
$Ce_{0.95}Y_{0.05}Al_3$	$5.8 \pm 0.2$	$7.4 \pm 0.2$	$0.196 \pm 0.005$	$0.286 \pm 0.005$
$Ce_{0.9}Y_{0.1}Al_3$	$11.2 \pm 0.5$	$15.1 \pm 0.5$	$0.132 \pm 0.007$	$0.228 \pm 0.007$
$Ce_{0.9}Y_{0.1}Al_3$	$9.4 \pm 0.5$	$13.8 \pm 0.5$	$0.168 \pm 0.005$	$0.26 \pm 0.005$

for all compounds is proportional to the Curie term  $\chi_f$  of the magnetic susceptibility (Fig. 6).

The strong positive K. S. in  $CeAl_3$  [4] is due to the enhanced spin polarization of the conduction electrons through the exchange interaction with the localized  $4f$  electron

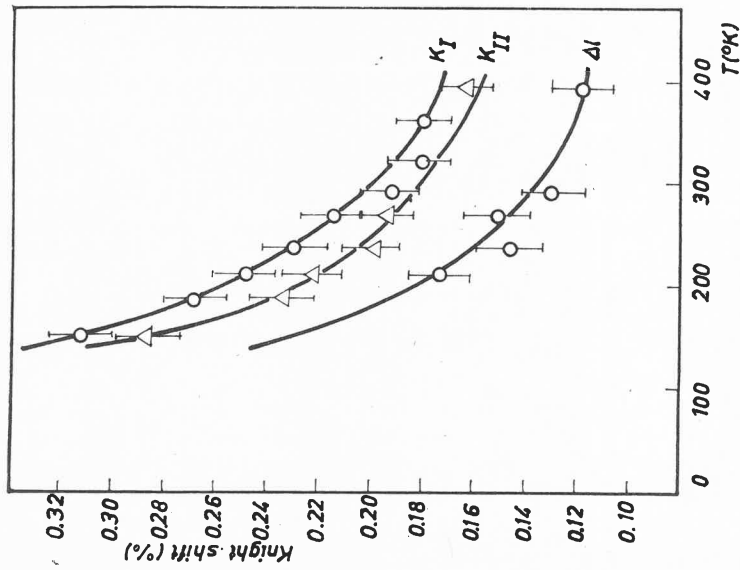


Fig. 4

Fig. 4. The temperature dependence of the K. S. for  $Ce_{0.95}Y_{0.05}Al_3$ .  $K_I$  is K. S. for the main line;  $K_{II}$  for the whole line and  $\Delta I$ , for the satellite one  
 Fig. 5. The temperature dependence of the half width of the line for  $Ce_{0.95}Y_{0.05}Al_3$ . a) The main line b) The whole line

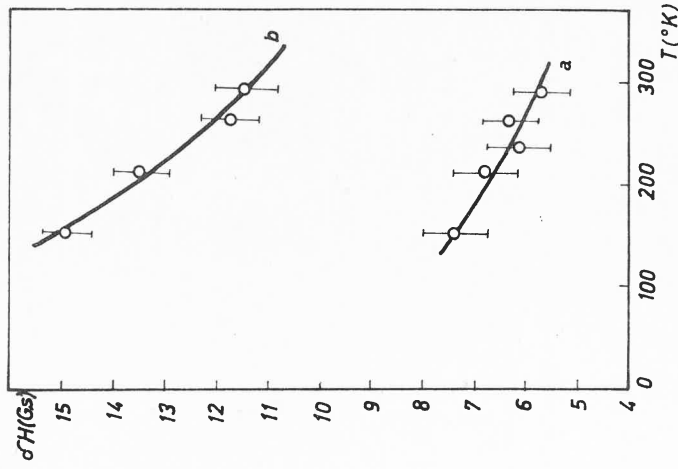


Fig. 5

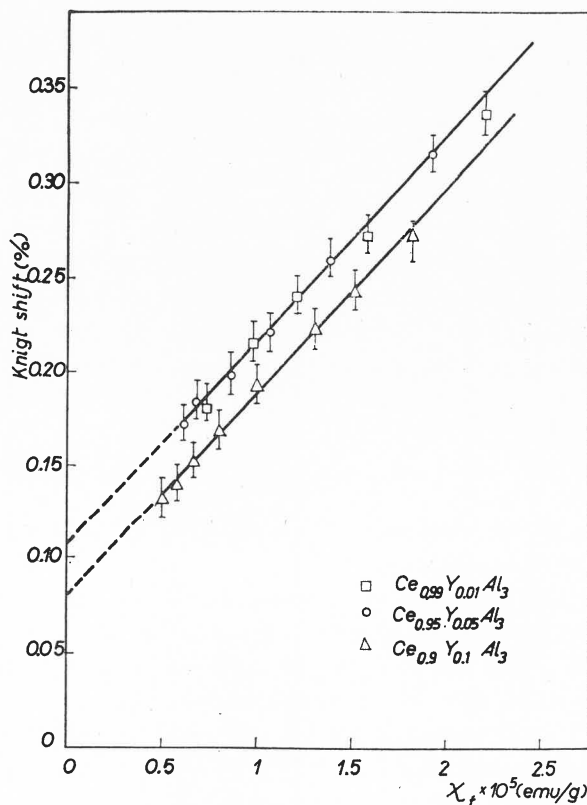


Fig. 6. The K. S. plotted vs  $\chi_f$ , a) K. S. of the main line for  $\text{Ce}_{0.99}\text{Y}_{0.01}\text{Al}_3$  and  $\text{Ce}_{0.95}\text{Y}_{0.05}\text{Al}_3$ . b) K. S. of the whole line for  $\text{Ce}_{0.9}\text{Y}_{0.1}\text{Al}_3$

spins  $S$  of the Ce ions. The total K. S. is related to  $\chi_f/n_f$ , the susceptibility per rare-earth ion, [9]

$$K = K_0[1 + J_{sf}(g_J - 1)\chi_f / (2n_f g_J \mu_B^2)], \quad (5)$$

where  $g_J$  is the  $4f$  electron  $g$ -value and  $K_0$  is the K.S. due to Pauli paramagnetism.

The presence of only Ce as magnetic rare-earth atom in our compounds, allows to take into account only an elementary exchange interaction  $-\Gamma \vec{S}_i \vec{S}_j$ , with an exchange integral  $\Gamma$  and the phenomenological exchange constant  $J_{sf}$  becomes

$$J_{sf} = -6\pi Z \Gamma \sum_{\text{Ce}} F(2k_F R_{\text{Al}\cdot\text{Ce}}), \quad (6)$$

where  $Z$  is the number of conduction electrons per atom and  $F$  having the same shape as in (4),  $R_{\text{Al}\cdot\text{Ce}}$  being the distance between a cerium ion and the Al site at which is the K. S. measured.

The occurrence of two peaks, the left-hand side one increasing in intensity with the Y concentration is the evidence for the existence of minimum two unequivalent Al sites for low amounts of Y.

Indeed, for  $x = 0.01$ , about 4% of the Al ions have between their neighbours in the first coordination sphere a Ce ion replaced by an Y one. Let us denote such a nucleus by  $Al_{II}$ . For the Al nuclei surrounded in the first coordination sphere as in  $CeAl_3$  (denoted  $Al_I$ ) the K. S. does not change sensibly if the interaction with the nearest neighbour is the prevailing one. Under the last assumption we must expect a decreased value of  $\sum_{Al \cdot Ce}$  for  $Al_{II}$  and thus a smaller K. S. than for  $Al_I$ .

For increased concentrations of Y or La the surrounding of Al sites by non magnetic R ions must exhibit a statistical spread and a broadening of the lines is to be expected.

The observed temperature dependence of the half width for the main line is similar to that of  $^{27}Al$  in  $CeAl_3$ . In the case of broadened lines the faster increase in line width at lower temperatures is probably due to the different temperature dependences of the Knight shift at the  $Al_I$  and  $Al_{II}$  sites.

### 3. Conclusions

The main effects of the substitution of Ce in  $CeAl_3$  by small amounts (up to 10%) of Y and La are the following:

1) The indirect exchange interaction between the Ce ions *via* the conduction electron polarization is weakened and the negative paramagnetic Curie point decreases from  $-25^\circ K$  for  $CeAl_3$  to  $-6^\circ K$  for  $Ce_{0.9}Y_{0.1}Al_3$  and  $-4^\circ K$  for  $Ce_{0.9}La_{0.1}Al_3$ .

2) The increase in the value of the temperature independent term of the magnetic susceptibility from  $1.3 \cdot 10^{-6}$  emu/g for  $CeAl_3$  to  $1.62 \cdot 10^{-6}$  emu/g for  $Ce_{0.9}Y_{0.1}Al_3$  is explained by the higher contribution of Y atoms to the orbital susceptibility of the *d* electrons as compared with Ce, taking for the former an outer electron configuration  $4d^2 5s^1$ .

3) The presence of a left side satellite in the NMR spectra of the investigated compounds is explained in terms of unequivalent surrounded Al sites in respect to the presence of non magnetic ions on some of the Ce sites. It seems therefore possible to distinguish between Al nuclei which have the same first coordination sphere as in  $CeAl_3$  and Al nuclei which have as one of the neighbours an Y ion which locally weakens the polarization of the conduction electrons and therefore leads a decrease of the K. S.

### REFERENCES

- [1] V. Niculescu, Iuliu Pop, M. Rosenberg (to be published in *J. Phys. Chem. Solids*, 1973).
- [2] V. Niculescu, Iuliu Pop, M. Rosenberg, *Phys. Letters*, **34A**, 265 (1971).
- [3] V. Niculescu, Iuliu Pop, M. Rosenberg, *Studia Univ. Babeş-Bolyai, Ser. Fiz.*, **2**, 59 (1971).
- [4] V. Niculescu, Iuliu Pop, M. Rosenberg, *Phys. Status Solidi* (b), **53**, 701 (1972).
- [5] W. E. Gardner, J. Penfold, M. A. Taylor, *Proc. Phys. Soc.*, **85**, 893 (1965).
- [6] M. A. Ruderman, C. Kittel, *Phys. Rev.*, **96**, 99 (1959).
- [7] T. Kasuya, *Progr. Theor. Phys. (Kyoto)*, **16**, 45 (1956).
- [8] K. Yosida, *Phys. Rev.*, **106**, 893 (1957).
- [9] P. G. De Gennes, *J. Phys. Radium*, **23**, 510 (1962).