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NUCLEAR ORIENTATION EXPERIMENTS ON CERIUM INTERMETALLIC COMPOUNDS

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Résumé. — Des expériences d'Orientation Nucléaire effectuées sur les composés In_3Ce , Pb_3Ce , Sn_3Ce montrent que le premier composé est bien ordonné, que Sn_3Ce est un réseau Kondo et que d'autres expériences doivent être faites pour confirmer l'état Kondo de Pb_3Ce . Une interprétation simple est donnée au comportement de ces terres rares anormales.

Abstract. — Nuclear orientation experiments on In_3Ce , Pb_3Ce , Sn_3Ce show that the first compound is well ordered, that Sn_3Ce is a Kondo lattice and that further experiments must be performed in order to confirm the Kondo state of Pb_3Ce . A simple interpretation is proposed to explain the behaviour of these abnormal compounds.

1. Introduction. — Recent nuclear orientation experiments (N.O.) [1] have shown that the compound Al_2Ce is well ordered down to 5 mK and that Al_3Ce appears as a Kondo lattice [2] [3]. From magnetic measurements, this last conclusion is dubious as the crystalline anisotropy of the $|\pm 3/2\rangle$ cerium ground state of the crystal field [4] is expected to lead to a strong moment induced by the applied field H ; in addition a possible long range order as in Al_2Ce would not be detected by an antiferromagnetic behaviour as this contribution cancels generally in a hexagonal polycrystalline sample. If there is no doubt that the magnetic fluctuations of Ce moments is higher in Al_3Ce than in Al_2Ce , it is not well established that Al_3Ce represents the ideal case of a Kondo lattice described in references [3-5].

Thus we have performed N.O. experiments in other Ce intermetallic compounds in order to determine at very low temperatures their magnetic ground state as a function of their electronic parameters. All the chosen compounds have a high linear coefficient γ of their specific heats, $C = \gamma T$.

2. Experimental conditions. — The radiation nuclei of $^{137\text{m}}\text{Ce}$ are obtained by bombarding a lanthanum foil in a 35 MeV proton beam. The samples are prepared by melting a small amount of radioactive LaCe alloys with the constituents of the intermetallic compound; the lanthanum concentration is lower than 0.5 percent.

The samples are cooled using a dilution refrigerator and the temperature measured by a N.O. thermometer of Co^{60}Co reaches 8 mK with an applied field up to 70 kOe. The gamma rays emitted along H were detected by a planar $\text{Ge}(\text{Li})$ detector.

3. Representation of the results. — The experimental results are described in terms of the axial anisotropy $E(0)$ which is the difference of warm and cold counts normalized by the warm counts. For a magnetic coupling, if the local quantization axis of every nucleus coincides with H , $E(0)$ must be positive for the $^{137\text{m}}\text{Ce}$ nuclei. In the paramagnetic regime [6], the variation of the associated effective field, H_{eff} , with H gives directly the strength of the Kondo coupling assuming : i) the proportionality between H_{eff} and M the magnetization, ii) a susceptibility law expressed by :

$$\chi = \frac{\mu_{\text{eff}}^2}{3 k_B T_K}.$$

The hypothesis of a unique axis of quantization is ruled out when interactions occur. For example, in low field for an antiferromagnetic coupling between the spins, the local moments choose to be antiparallel to each other and perpendicular to the applied field; for such a configuration, the sign of the anisotropy is reversed since the equatorial and axial anisotropies have opposite signs.

4. Results. — In low fields, the long range order of Al_2Ce has recently been detected by the occurrence

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of a reversed sign of the gamma anisotropy after a full magnetization process [1]. The figure 1 represents the anisotropy $E(0)$, detected under the same conditions for the different compounds at 10 mK. In_3Ce like Al_2Ce is well ordered with a predominant antiferromagnetic component. It must be underlined that for In_3Ce contrary to Al_2Ce , the antiferromagnetic component is detected directly in the first magnetization curve.

FIG. 1. — For different intermetallic compounds, axial gamma ray anisotropy of $^{137\text{m}}\text{Ce}$ nuclei at 10 mK as a function of the applied field.

The Sn_3Ce sample shows a magnetic response characteristic of an induced moment created by the applied field. From the initial slope of $\partial H_{\text{eff}}/\partial H$, a Kondo temperature can be derived :

$$T_K = 40 \pm 20 \text{ K}.$$

The Pb_3Ce compound seems to follow a N.O. response very similar to that of the dilute alloy of Al_2LaCe where the cerium is a Kondo impurity with a T_K equal to 400 mK [7]. No detectable antiferromagnetic component is observed. A possible Kondo temperature will be :

$$T_K = 3 \pm 1 \text{ K}.$$

5. Discussion. — The In_3Ce compound has a higher antiferromagnetic component than Al_2Ce which is, furthermore, not reversed for the strongest applied field $H = 70 \text{ kOe}$. These two properties are in excellent agreement with the values of the temperature maximum T_M of the specific heat reported in

table I and also with the highest ordering temperature T_N attributed to In_3Ce . The observation of the antiferromagnetic behaviour of In_3Ce during the first magnetization process indicates the weakness of its magnetic anisotropy compared to that of Al_2Ce .

TABLE I

Specific heat results of the γ coefficient of the linear temperature dependence and of the observation of a sharp maximum at a temperature T_M .

	γ in mJ/mole K^2	T_M in K	Ref.
Al_2Ce	180	3.8	[14]
In_3Ce	140	10.8	[20]
Pb_3Ce	225	< 1 K	[19]
Sn_3Ce	53	—	[19]

A general discussion and a specific comparison of these abnormal rare earth compounds are difficult as many aspects must be considered in order to discuss their particular behaviour. The three main parameters are : i) the local resonant exchange coupling k - f between the localized moment S and the spin of the conduction electrons s

$$H = -2 \Gamma S \cdot s;$$

ii) the electronic response of the Fermi sea to this local perturbation which produces an indirect coupling among the localized spin by the wellknown Ruderman-Kittel oscillation related to the Fermi surface ; iii) the crystal field which has a strong effect on the Kondo coupling [8] and which may lead to a crystalline anisotropy by the mixing between the different levels with the applied field [9].

Benoit *et al.* [10] have recently derived a crude model where the Kondo effect is introduced simply by a magnetization law of the single cerium ion (see ref. [6])

$$M \sim \text{Arctg } g\mu_B H/k_B T_K$$

and where exchange couplings between the localized moments are restricted to a ferromagnetic interaction and an antiferromagnetic interaction between the first and second neighbours of a linear chain of Ce ions (the two corresponding exchange constants J_1, J_2 are simply related to Γ^2). For classical moments and constant exchange couplings, the ground state at 0 K is respectively a helical ordered structure, a modulated ordered structure and finally a paramagnetic *Kondo Lattice* state when the Kondo temperature increases continuously. It must be emphasized that even in the helical magnetic order the local moment of each ion can be strongly reduced from its saturation value.

The neutron and N.O. results on Al_2Ce which indicate a modulated long range order can be easily understood and the competition between the Kondo and exchange couplings clearly demonstrated.

The crude model of Benoit *et al.* [10] can be applied to any singlet state given either by the Kondo state or the crystal field splitting. The specific characteristic of the Kondo state is the strong resonance of the conduction electrons below T_K . In dilute alloys, the occurrence of a strong local density of states at the Fermi level below T_K [12] produces a linear temperature contribution to the specific heat, $C = \gamma T$, which is inversely proportional to the Kondo temperature.

If the magnetic interaction among ions can be reduced to a molecular field associated with the ordering temperature T_N , the different values of γ can be regarded as the combination of two opposite processes. Firstly, the simple ion property leads to the γ enhancement by the Kondo coupling below $T \ll T_K$; secondly the magnetic interactions reduce this enhancement by the decoupling of the Kondo state with the applied field $H = H_M$ (see Schotte and Schotte [13] for the depression of the Kondo anomaly by the applied field).

By analogy with the Blandin-Friedel description of the appearance of local magnetism [21], it can be expected that a maximum of γ would be located near the occurrence of long range order. If a γ maximum corresponds to the range of T_K of the magnetic modulated structure, the estimation of the Kondo-coupling by the γ values may lead to spurious results. For example by increasing the pressure (or the ratio T_K/T_N) the bare Kondo temperature increases but γ may increase or decrease depending upon its relative position compared to the γ maximum (Fig. 2).

FIG. 2. — Full line, for constant exchange coupling, J_1, J_2 , possible variation of γ as a function of T_K/J_1 for the abnormal cerium compounds. For $T_K < T_{K1}$, a helical structure occurs, $T_{K1} < T_K < T_{K2}$ a modulated structure and $T_K > T_{K2}$ a paramagnetic Kondo lattice. The single Kondo behaviour is drawn as a dashed line.

Theoretically, the parameter of the single ion (T_K) can be derived from the high temperature results. In table II, we report the values of $\Gamma\rho$, T_K and Δ the splitting between the Γ_7 doublet ground state and the Γ_8 quadruplet of the crystal field which are obtained by Lethuillier [14] from its susceptibility

TABLE II
Single ion parameters estimated by Lethuillier from their high temperature susceptibility results [14]

	$\Gamma\rho$	T_K in K	Δ in K
Al_2Ce	— 0.11	0.19	150
In_3Ce	— 0.14	1.7	150
Pb_3Ce	— 0.07	0.007	100
Sn_3Ce	— 0.33	140	45

results (ρ is the density of states of the conduction electrons at the Fermi level). The weakness of T_K for Al_2Ce and Pb_3Ce are dubious.

For Al_2Ce , the low value of T_K seems to be ruled out by both N.O. and neutron measurements which are understood only if $T_K \sim T_N$. It must be emphasized that Lethuillier's determination is derived from the study of dilute alloys of $\text{Al}_{1-x}\text{La}_x\text{Ce}$ and $\text{Al}_2\text{La}_{1-x}\text{Ce}_x$. Steglich [15] has recently given an evaluation of $T_K \sim 6$ K in better agreement with our conclusions. Likewise for Pb_3Ce , the weakness of T_K and T_N given in tables I-II cannot explain the low saturation of the magnetization observed in our N.O. experiments.

This controversy seems to illustrate the difficulty in deriving quantitatively the bare parameter of the single ion from a high temperature susceptibility measurement. In fact for these abnormal rare earths another interpretation of this apparent discrepancy is that the single ion parameter of Benoit *et al.* [10] is linked more to the collective Kondo condensation described by Jullien *et al.* [3] than to the bare parameter of every ion. This appears clearly as their low temperature properties cannot be understood in a simple scheme of individual 4f virtual levels [14].

The Sn_3Ce compound is characterized by a Kondo coupling which is rather weak for an interpretation of its behaviour in terms of an intermediate valency. At low temperature our estimation of $T_K = 40$ K is lower than the value $T_K \sim 140$ K obtained from the high temperature susceptibility results [15]; this difference is in excellent agreement with a well resolved crystal field splitting of $\Delta \sim 50$ K. The Sn_3Ce compound can certainly be described as a Kondo lattice with an ionic description of the Ce moment. This remark is supported by the small variation of the lattice parameter with the temperature [17] and the absence of any variation of the isomeric shift of Sn in Sn_3Ce below the characteristic temperature $\theta \sim 140$ K [18].

6. Conclusion. — Our N.O. experiment shows that In_3Ce is well ordered like Al_2Ce . The weakness of the crystalline anisotropy of In_3Ce suggests that this compound can be either in the helical range of T_K or near the long range magnetic instability (point T_{K2}). Up to date, the simple example of a Kondo lattice

seems to be Sn_3Ce which is near a valency instability. Our experiments suggest that the Pb_3Ce compound is another excellent case, other experiments must be performed in order to test this conclusion.

All the abnormal compounds measured here by N.O. seem to be qualitatively well understood in terms of a competition between the Kondo lattice condensation and the long range order due to magnetic interactions

between neighbours. The exact description of the Al_3Ce compound is still unclear ; the crossing point T_K may have important topological proprieties.

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