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# MAGNETISM AND SUPERCONDUCTIVITY OF ANOMALOUS RARE-EARTH METALS AND ALLOYS

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**Résumé.** — Les terres rares anormales sont caractérisées par la présence d'un niveau 4f étroit à proximité du niveau de Fermi, ce qui produit un important effet de diffusion résonnante variable avec la pression, la température et la nature de la matrice pour les alliages. Le modèle de diffusion résonnante explique le diagramme de phase anormal du cérium pur, la variation de la température de la transition supraconductrice du lanthane pur, l'effet Kondo et la transition du magnétisme au non-magnétisme dans les alliages avec des impuretés de cérium et d'ytterbium.

**Abstract.** — The anomalous rare-earths are characterized by the presence of a narrow 4f level close to the Fermi level, which produces a large resonant scattering effect varying with pressure, temperature and the nature of the host for alloys. The resonant scattering model gives an explanation of the anomalous phase diagram of pure cerium, the variation of the superconducting transition temperature in pure lanthanum, the Kondo effect and the transition from magnetism to non magnetism in alloys with cerium and ytterbium impurities.

**1. Introduction.** — The rare-earth metals can be divided in two groups :

— The « normal » rare-earths [1] have a valency (or number of conduction electrons) equal to 3 and an integer number of 4f electrons independent of pressure and temperature. They are described by the ionic model, by use of the classical s-f exchange Hamiltonian :

$$H = -I\mathbf{sS} \quad (1)$$

— The « anomalous » rare-earths have a valency different than 3 and a non integer number of 4f electrons which can vary with pressure and temperature [2]. These metals are characterized by the presence of a narrow 4f level close to the Fermi level, which produces a large resonant scattering effect. The ionic model is no more valid and we use generally the Anderson Hamiltonian for describing the anomalous rare-earths :

$$\begin{aligned} H = & \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{m,\sigma} E_0 n_{m\sigma} + \\ & + \sum_{k,m,\sigma} (V_{km} C_{k\sigma}^* C_{m\sigma} + V_{km}^* C_{m\sigma}^* C_{k\sigma}) \\ & + \frac{1}{2} \sum_{m,m'} U_{mm'} n_{m\sigma} n_{m'-\sigma} \\ & + \frac{1}{2} \sum_{m,m'} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma} \quad (2) \\ & (m \neq m') \end{aligned}$$

Cerium, ytterbium, europium and probably lanthanum are « anomalous » rare-earths metals. The same duality exists in alloys with rare-earth impurities : the ionic model can describe the alloys with normal rare-earth impurities [1], while the resonant scattering model is used for the alloys with cerium and ytterbium impurities [2]. This paper is devoted to a brief review of the properties of anomalous rare-earth metals and alloys : cerium, lanthanum, ytterbium (we do not speak of europium, because there is not enough experimental information) and alloys with cerium and ytterbium impurities.

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**II. Cerium.** — 1. EXPERIMENTAL SITUATION. — Cerium has a phase diagram with five solid phases : two face-centered cubic  $\alpha$  and  $\gamma$  phases, one double hexagonal  $\beta$  phase, one body-centered cubic  $\delta$  phase and the  $\alpha'$  phase above 50 kbar (Fig. 1) [2] [3]. The  $\alpha'$

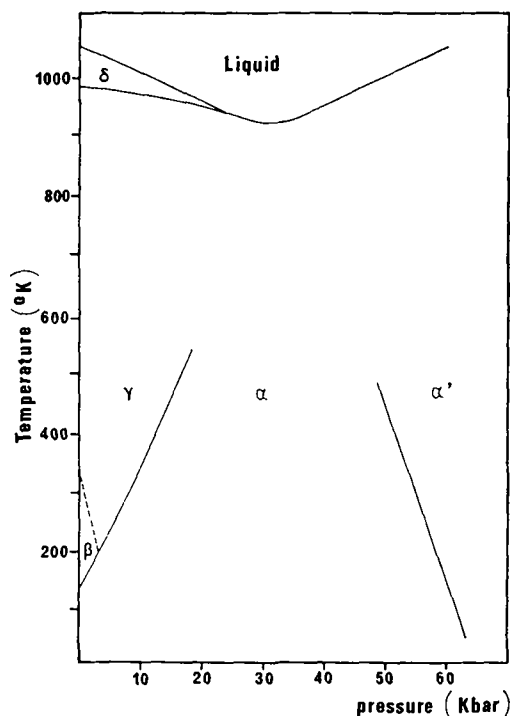


FIG. 1. — Phase diagram of cerium.

phase was firstly discovered as a face-centered cubic phase [4] as the  $\alpha$  and  $\gamma$  phases but more recently it was found hexagonal-close packed [5].

The f. c. c.  $\gamma$  phase is a paramagnetic one with a  $2.5 \mu_B$  localized magnetic moment. The f. c. c.  $\alpha$  phase is not magnetic with a Pauli-type paramagnetism. The  $\alpha'$  phase is superconducting below 1.7 °K.

At room temperature, the atomic radius decreases, at 7 kbar by a first-order transition, from 1.824 Å in  $\gamma$ -cerium to 1.72 Å in  $\alpha$ -cerium and then continuously

in  $\alpha$ -cerium till 1.67 Å at 50 kbar. Above the  $\alpha \leftrightarrow \alpha'$  first-order transition, the atomic radius remains equal to 1.65 Å up to 80 kbar, from Franceschi and Olcese data [4] (Fig. 2). The valency of cerium is 3.11 in

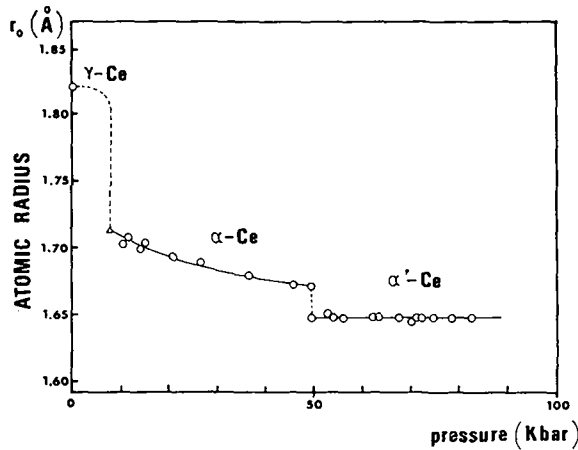


FIG. 2. — Atomic radius of cerium (in Å) at room temperature, as a function of pressure.

the  $\gamma$  phase, 3.67 in the  $\alpha$  phase at 7 kbar, 3.88 in the  $\alpha'$  phase at 50 kbar and remains equal to 4 in the  $\alpha'$  phase [6].

The discontinuities of atomic volume and resistivity and the heat of transformation which are very important at normal pressure, decrease when temperature and pressure increase along the line of the  $\alpha \leftrightarrow \gamma$  transition and disappear at the critical point C ( $T_c \sim 550$ -600 °K and  $P_c \sim 18$ -20 kbar).

2. THE  $\alpha \leftrightarrow \gamma$  TRANSITION [2]. — The  $\alpha \leftrightarrow \gamma$  transition has been explained by the virtual bound state theory in the Hartree-Fock approximation, by use of the Anderson Hamiltonian [2]. The 4f level is close to the Fermi level, which gives an important mixing between 4f and conduction electrons. The extra density of states introduced by the presence of 4f levels is a lorentzian with a half-width  $\Delta = 0.02$  eV. The smallness of  $\Delta$  leads to two new points in the study of 4f virtual bound states :

—  $\Delta$  is much smaller than the  $U_{mm}$ , Coulomb and  $J_{mm}$  exchange integrals : the orbital moment does not remain quenched. At zero temperature, the magnetic transition is a first-order one from a non magnetic state to a spin and orbital magnetic state corresponding almost to the 4f<sup>1</sup> configuration.

—  $\Delta$  is of order  $kT$  at room temperature and there is a large effect of the temperature. The jump in the magnetic moment or in the number of 4f electrons decrease with increasing temperature and above a critical temperature, the magnetic transition becomes a second order one.

By extending the virtual bound state model to the case of a pure metal, we can explain the main features of the  $\alpha \leftrightarrow \gamma$  transition and especially the changes of atomic volume, valency, resistivity and magnetic moment and the existence of a critical point C. The continuous change of magnetic moment above the critical point has not yet been checked experimentally.

3. EXCHANGE-ENHANCEMENT EFFECT IN  $\alpha$ -CERIUM — Since the 4f level is just above the Fermi level in  $\alpha$ -cerium just after the  $\alpha \leftrightarrow \gamma$  transition, we can wait for an exchange-enhancement effect [7].

At room temperature, above roughly 7 kbar, cerium is made only of the  $\alpha$  phase and the measurements can be very precise. Mc Pherson et al. [8] have recently measured the magnetic susceptibility  $\chi$  of  $\alpha$ -cerium between 10 and 18 kbar.  $\chi$  decreases approximately linearly from  $5.6 \times 10^{-4}$  e. m. u./mole at 10 kbar to  $4.6 \times 10^{-4}$  e. m. u./mole at 18 kbar. The magnetic susceptibility of  $\alpha$ -cerium is only weakly temperature dependent upon to liquid helium temperatures. Moreover, Phillips et al. [9] had previously measured the  $\gamma$  electronic specific heat constant at 11 kbar on a sample containing only  $\alpha$ -cerium and they found  $\gamma = 11.3$  mJ/mole °K<sup>2</sup>.

In non magnetic  $\alpha$ -cerium, the fourteen-fold degenerate 4f level lies at a distance  $E$  much larger than  $\Delta$  above the Fermi level. The total number of 4f electrons (or the valency  $N_c = 4 - N$ ) and the 4f density of states  $n_f(E_F)$  for one spin direction are given by :

$$N = \frac{14}{\pi} \frac{\Delta}{E} \quad (3)$$

$$n_f(E_F) = \frac{7}{\pi \Delta} \left( \frac{\Delta}{E} \right)^2 = \frac{\pi}{28 \Delta} N^2 \quad (4)$$

So, the total magnetic susceptibility of  $\alpha$ -cerium is :

$$\chi = 2 \mu_B^2 \{ n_f(E_F) \cdot S + n_s(E_F) \} \quad (5)$$

$n_s(E_F)$  is the density of states for the sd band and  $S$  is the exchange-enhancement factor for the 4f electrons :

$$S = \frac{1}{1 - \bar{U} n_f(E_F)} \quad (6)$$

$\bar{U}$  is an average value of the effective exchange integral.

Without taking into account any mass enhancement factor for the 4f electrons, the electronic specific heat constant  $\gamma$  is

$$\gamma = \frac{2 \pi^2}{3} k_B^2 \{ n_f(E_F) + n_s(E_F) \}. \quad (7)$$

The data of Franceschi and Olcese [4] give  $N_c$ ,  $N$  and  $n_f(E_F)$  by use of (4) and with taking  $\Delta = 0.02$  eV. The data of Mc Pherson et al. [8] lead to the determination of  $S$  by use of (5) and of  $\bar{U}$  by use of (6). The value of  $n_s(E_F)$  is determined by the measurements of Phillips et al. [9] : for, at 11 kbar,  $N_c = 3.7$  and  $n_f(E_F) = 0.5$  st/eVat. The formula (7) gives

$$n_s(E_F) = 1.9 \text{ st/eVat}$$

which is equal to the value used for lanthanum and which is in agreement with the estimations based on the specific heat measurements in  $\gamma$ -cerium.

Thus the following table gives, for each pressure  $p$  (in kbar), the values of  $N$ ,  $n_f(E_F)$  (in st/eVat),  $E$  (in eV),  $\chi$  (in  $10^{-4}$  e. m. u./mole),  $S n_f(E_F)$  (in st/eVat) coming from the experimental data, the deduced values for  $S$  and  $\bar{U}$  (in eV) and the predicted  $\gamma$  value (in mJ/mole °K<sup>2</sup>). We use here  $\Delta = 0.02$  eV.

$p$	$N$	$n_f(E_F)$	$E$	$\chi$	$Sn_f(E_F)$	$S$	$\bar{U}$	$\gamma$
11	0.3	0.5	0.3	5.5	6.6	13	1.85	11.3
18	0.27	0.41	0.33	4.6	5.2	12.5	2.25	10.9
50	0.12	0.08	0.75					9.3

So, the recent data of Mc Pherson et al. lead unambiguously to a very large exchange-enhancement factor in  $\alpha$ -cerium between 10 and 18 kbar. From our present analysis, the  $S$  factor decreases very slowly with pressure and consequently the average value  $\bar{U}$  for the effective exchange integral increases rapidly with pressure. This could be understood by the Schrieffer-Mattis formula [42] which gives an increase of  $\bar{U}$  with  $E$ . Further experiments on  $\chi$  and  $\gamma$  at higher pressures would be very interesting from this point of view.

There is presently no explanation for the  $\alpha \leftrightarrow \alpha'$  transition. But, if the  $S$  factor is not too small in  $\alpha$ -cerium at 50 kbar, a possibility of explanation can be looked for in the difference of energy between the exchange-enhanced electrons of  $\alpha$ -cerium and the electrons without exchange enhancement of  $\alpha'$ -cerium, as suggested by Goodenough [12].

A previous analysis [7] based on the experiments of magnetic susceptibility and specific heat at normal pressure had also concluded to a strong exchange-enhancement factor, but the experimental data are not precise because cerium is made of mixed  $\alpha$  and  $\beta$  phases at low temperatures and normal pressure. Using for example the experimental values  $\chi = 2 \times 10^{-3}$  e. m. u./mole of Edelstein and  $\gamma = 21$  mJ/mole  $^\circ\text{K}^2$  of Lounasmaa and using (5) and (7), we had obtained  $S$  equal to 13. But recently Panousis and Gschneidner [10] have found a considerably smaller  $\gamma$  value :  $\gamma = 9.79$  mJ/mole  $^\circ\text{K}^2$  on a sample containing only the  $\alpha$  phase at normal pressure. So, the values derived for  $\alpha$ -cerium with samples containing  $\alpha$  and  $\beta$  phases are open to serious criticism and we prefer the results of Mc Pherson et al. for the determination of  $S$ .

4. SUPERCONDUCTIVITY OF CERIUM [11]. — In the preceeding resonant scattering framework, the explanation of superconductivity in  $\alpha'$ -cerium is very simple. In the  $\alpha'$ -phase, the atomic radius is constant with pressure, which indicates that the 4f character has completely disappeared. The  $\alpha'$ -cerium behaves as a « normal » tetravalent and superconducting metal with a pressure independent superconducting transition temperature, for example as thorium, in which there is no 4f character to inhibit superconductivity. The 4f character is probably sufficiently important in the  $\alpha$ -phase to inhibit superconductivity or to lower its appearance below the experimentally used temperature.

III. Lanthanum [11]. — Lanthanum is the only pure rare-earth metal superconducting at normal pressure. Its critical temperature  $T_c$  has an anomalous pressure dependence, increasing from 5.2  $^\circ\text{K}$  at normal pressure to 9.3  $^\circ\text{K}$  at 40 kbar and reaching almost 12  $^\circ\text{K}$  at roughly 100 kbar. The relative variation of its atomic volume under a 40 kbar pressure is 12 %, which is larger than that of normal rare-earths. This experi-

ment suggests that the valency in lanthanum is a little smaller than 3 at normal pressure.

So, the theoretical model which we have recently developed [11] for explaining the variation of  $T_c$  with pressure assumes the presence of an inner 4f shell above the Fermi level. Only the conduction electrons participate to the superconductivity mechanism and the « normal » lanthanum, i. e. without 4f character at very high pressure, has a high superconducting temperature  $T_{c0}$  of order 12  $^\circ\text{K}$ . On the contrary, the 4f electrons tend to inhibit superconductivity and, as the 4f character decreases with increasing pressure,  $T_c$  increases with pressure and tends to  $T_{c0}$  at very high pressure. The basis of this model is in contradiction to previous models which attributed the origin of superconductivity to the presence of 4f electrons.

In our model, the density of states is given by (4), the number of 4f electrons by (3) and the valency is  $N_c = 3 - N$ .  $N$  is supposed to be smaller than 1 and  $E$  much greater than  $\Delta$ .

The critical temperature is given by :

$$\ln \frac{T_{c0}}{T_c} = \ln \frac{1.14 \omega_D}{T_{c0}} \times \frac{n_f(E_F) \left\{ 1 + n_f(E_F) U_{\text{eff}} \ln \frac{1.14 \omega_D}{T_{c0}} \right\}}{n_s(E_F) - n_f^2(E_F) U_{\text{eff}} \ln \frac{1.14 \omega_D}{T_{c0}}} \quad (8)$$

We take  $\omega_D = 142$   $^\circ\text{K}$ ,  $T_{c0} = 12$   $^\circ\text{K}$ ,

$$n_s(E_F) = 1.9 \text{ st/eVat},$$

$\Delta = 0.02$  eV. In order to check the theoretical model, we insert the experimental values of  $T_c$  in formula (8) and deduce  $E$ ,  $n_f(E_F)$  and  $N_c$ , as follows :

$p$ (kbar)	$T_c$ ( $^\circ\text{K}$ )	$n_f(E_F)$ (st/eVat)	$E$ (eV)	$N_c$
0	5.2	0.52	0.29	2.70
20	8.0	0.26	0.41	2.78
40	9.3	0.17	0.51	2.825

The recent discovery of superconductivity at high pressure with a pressure dependent  $T_c$  in Barium [13], yttrium and cesium [14] can lead to some critics against the preceeding model. So, the assumption of a small 4f character at normal pressure (or valency of order 2.7) has to be checked experimentally and the understanding of a high  $T_{c0}$  value for « normal » lanthanum calls for new theoretical investigations.

IV. Ytterbium. — Three experimental points are outstanding in ytterbium :

— The phase diagram has three solid phases : a f. c. c. phase with a valency close to 2 stable at normal pressure and room temperature, a b. c. c. phase with a valency close to 3 above 40 kbar at room temperature

[2] and a new h. c. p. phase recently discovered to exist at normal pressure and low temperatures in very pure ytterbium sample [15, 16] (Fig. 3). From Bucher

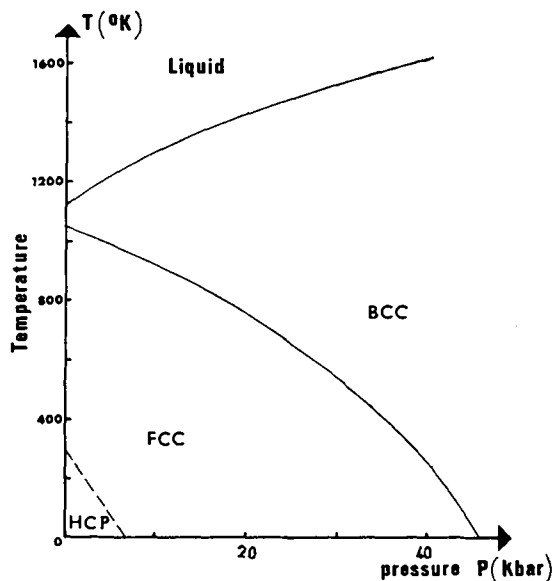


FIG. 3. — Phase diagram of Ytterbium.

et al. [15], at normal pressure, the h. c. p. phase is diamagnetic and has a  $\gamma = 3.30$  mJ/mole  $^{\circ}\text{K}^2$  value while the f. c. c. phase is paramagnetic with a magnetic moment corresponding to 0.8 % 4 f holes and has a  $\gamma = 8.36$  mJ/mole  $^{\circ}\text{K}^2$  value.

— The resistivity of ytterbium is characteristic of a metal at normal pressure, of a semi-metal till roughly 15 kbar, then of a semi-conductor with a small gap till the f. c. c.  $\rightarrow$  b. c. c. transition and at last of a metal in the b. c. c. phase [2, 17, 18]. At 45 kbar in the b. c. c. phase, no evidence of a magnetic transition has been found from resistivity curves [17].

— The presence of 4 f levels has been recently found by optical [19] and X-ray [20] photoemission experiments. The spin-orbit-split 4 f states are located at 1.2 – 1.4 and 2.5 – 2.7 eV below the Fermi level at normal pressure.

The theoretical situation can be summarized as follows :

— The metal-insulator transition appearing around 15 kbar can be explained by classical crossing of s, p, d bands, without involving any 4 f band [17]. Recent band calculations [21] and recent experiments on ytterbium-barium alloys [22] are in good agreement with the preceding explanation. The presence of a 4 f band just at the gap edge in semiconducting ytterbium [2] is not necessary and not very probable because of the position of the 4 f level at normal pressure.

— The question of magnetism is more puzzling. From the position of the 4 f level at normal pressure and the variation of atomic volume with pressure, we can conclude that ytterbium will become magnetic at very high pressures. The presence of a 4 f level at a little more than 1 eV indicates that ytterbium is certainly different from strontium and barium. A theoretical model [2] has located the appearance of magne-

tism at the f. c. c.  $\leftrightarrow$  b. c. c. transition, because of the similarity with the  $\alpha \leftrightarrow \gamma$  transition in cerium : no experimental evidence of this fact has been yet found [17].

The recent experiments of Bucher et al. are difficult to understand in the framework of resonant scattering, because they conclude to the existence of localized magnetism with only 0.8 % 4 f holes, while cerium becomes magnetic with at least a third of 4 f electrons.

#### V. Alloys with cerium and ytterbium impurities.

— The alloys with cerium and ytterbium impurities can be classified according to the position of the narrow 4 f level relative to the Fermi level [23].

1. MAGNETIC CERIUM ALLOYS. — When the 4 f level is below the Fermi level, the corresponding cerium alloy is magnetic. It can be described by the s-f exchange Hamiltonian (1) with a  $\Gamma$  value given by :

$$\Gamma = \Gamma_1 + \Gamma_2 \quad (9)$$

$\Gamma_1$  comes from the normal exchange scattering mechanism and is small, positive and almost pressure independent, while  $\Gamma_2$  comes from the resonant scattering mechanism and is negative and given by the Schrieffer-Wolff transformation :

$$\Gamma_2 = - \frac{2 V_{kf}^2}{|\varepsilon|} \quad (10)$$

$\varepsilon (\varepsilon < 0)$  is the distance from the 4 f level to the Fermi level.  $|\Gamma_2|$  increases with pressure, because  $|\varepsilon|$  decreases. The formula (10) is valid when  $\varepsilon$  is not too small ( $|\varepsilon| > \Delta$ ).

The Kondo effect exists if  $\Gamma$  is negative, i. e. for  $|\Gamma_2| > \Gamma_1$ . The other properties are proportional to  $\Gamma^2$ , such as the variation of the superconducting transition temperature  $T_c$  with the concentration  $c$  of cerium impurities which is given by :

$$\frac{dT_c}{dc} = - \frac{\pi^2}{8} n_c(E_F) S(S+1) \Gamma^2 \quad (11)$$

$n_c(E_F)$  is the density of states for electrons which participate to the superconductivity mechanism.

The magnetic cerium alloys which a  $|\varepsilon|$  value not too small ( $|\varepsilon| > \Delta$ ) can then be divided in two groups :

— The magnetic alloys which have no Kondo effect :  $\Gamma$  is positive and  $|\Gamma_2| < \Gamma_1$ . In principle,  $|\varepsilon|$  is larger than  $|\varepsilon_c|$  such as :  $\varepsilon_c = - 2 V_{kf}^2 / \Gamma_1$ .  $\varepsilon_c$  can be estimated to be roughly 0.1 eV. The cerium alloys behave as normal non-Kondo magnetic rare-earth alloys with an almost 4 f<sup>1</sup> configuration : this is the case of MgCe [24], AgCe [25] and AuCe [25, 26] alloys. However, although there is no Kondo effect because of a positive  $\Gamma$  value, the resonant scattering effect is not always negligible and its effect can be seen on some peculiarly sensitive properties such as thermoelectric power because of its rough proportionality to  $1/\Delta$ . This is the case of AgCe and AuCe alloys which have « giant » and negative thermoelectric powers [25]. From the experimental values of Gainon et al. [25] and from the classical theory of virtual bound states applied to the thermoelectric power, we

can conclude to a value  $\varepsilon = -0.11$  eV in  $\text{AuCe}$  and  $\varepsilon = -0.15$  eV in  $\text{AgCe}$ , assuming  $\Delta = 0.02$  eV. By applying pressure,  $\text{AuCe}$  and  $\text{AgCe}$  would have a Kondo effect as  $\text{LaCe}$  at normal pressure.

— The magnetic alloys which have a Kondo effect :  $\Gamma$  is negative and  $|\Gamma_2| > \Gamma_1$  :  $|\varepsilon|$  is smaller than  $|\varepsilon_c|$ . This is the case of  $\text{YCe}$ ,  $\text{LaCe}$ ,  $\text{LaAl}_2\text{Ce}$ ,  $\text{La}_3\text{InCe}$  which have already been studied in detail [23]. The spin disorder resistivity and the value of  $-dT_c/dc$  are larger in these cerium alloys than for the normal rare-earth alloys.  $-dT_c/dc$  increases rapidly with pressure in superconducting alloys, for example from 170 °K at 0 kbar to 320 °K at 10 kbar in  $\text{LaCe}$ . This increase is explained by formulae (9), (10) and (11) because  $|\varepsilon|$  decreases with pressure [27]. We can deduce the value of  $\varepsilon$  from experimental  $-dT_c/dc$ .  $\varepsilon$  is  $-0.04$  eV to  $-0.05$  eV in superconducting  $\text{LaCe}$ ,  $\text{LaAl}_2\text{Ce}$  and  $\text{La}_3\text{InCe}$  and  $|\varepsilon|$  decreases by 0.01 eV under a 10 kbar pressure.

2. TRANSITION FROM MAGNETISM TO NON MAGNETISM IN CERIUM ALLOYS. — When the 4f level goes from a position below the Fermi level to another one above the Fermi level with pressure, the alloys go from a magnetic state to a non magnetic state : that is the case of  $\text{LaCe}$  and  $\text{YCe}$  alloys at very high pressure, as recently seen by Maple et al. [28].

In  $\text{La-Ce}$  alloys, the value of  $-dT_c/dc$  increases firstly rapidly, then reaches a maximum near 15 kbar, then decreases continuously till 125 kbar, with a rapid decrease near 25-30 kbar [28] (Fig. 4). The slope  $|dR/d \ln T|$  of the Kondo resistivity increases firstly

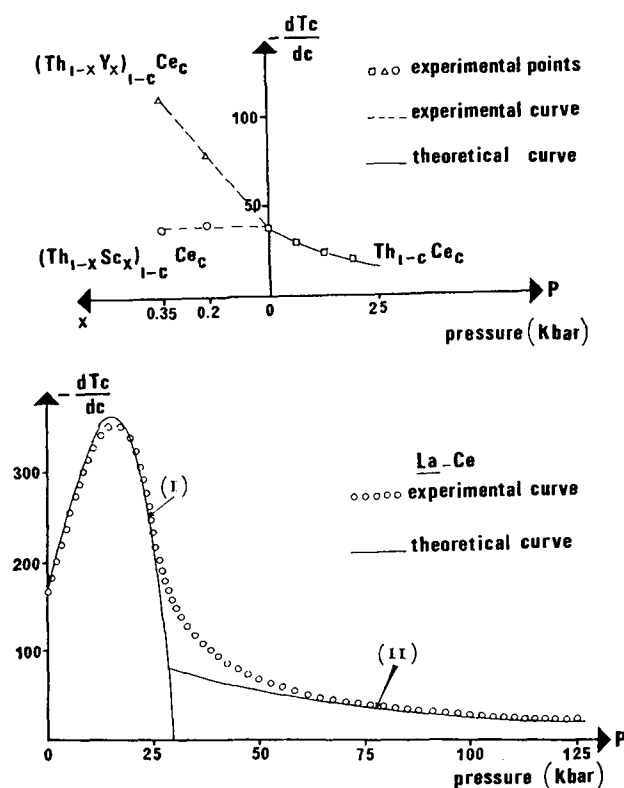


FIG. 4. — Plot of  $-dT_c/dc$  for La, Th, Th-Y, Th-Sc based alloys with cerium impurities ( $T_c$  is the superconducting temperature and  $c$  the cerium concentration).

and reaches also a maximum near 15 kbar, while the temperature of the resistivity minimum increases only by a very small factor [29] (Fig. 5a).

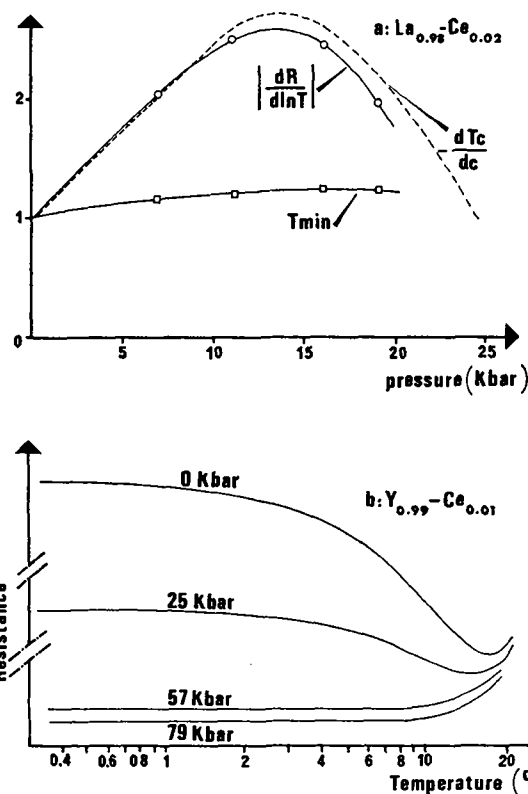


FIG. 5a. — Plot of  $|dR/d \ln T|$ ,  $T_{min}$  and  $-dT_c/dc$  (normalized to zero pressure value) for  $\text{La}_{0.98}\text{Ce}_{0.02}$  alloys as a function of pressure.

b. — Resistance (in arbitrary units) of  $\text{Y}_{0.99}\text{Ce}_{0.01}$  alloys for different pressures, as a function of temperature.

In  $\text{Y-Ce}$  alloys, on the first results of Maple [30], we can see a resistivity minimum still present at 25 kbar, while it has completely disappeared at 57 and 79 kbar (Fig. 5b).

In  $\text{La-Ce}$  alloys, the transition from magnetism to non magnetism can be located at around 30 kbar from the figure 4. In absence of really good theory for the magnetic transition, we present here the classical theories for the magnetic domain below 30 kbar and for the non magnetic domain above 30 kbar, in order to see the discrepancy between the experiment and these classical theories.

Below the magnetic transition, the phase-shift  $\delta_v$  of the occupied 4f level varies rapidly with  $\varepsilon$  as  $\varepsilon$  tends to zero. So, in addition to the s-f exchange Hamiltonian (1), we take the direct potential scattering Hamiltonian which gives  $\delta_v$ . One effect of the potential scattering term is to renormalize the  $\Gamma_2$  value (10) in an effective  $\tilde{\Gamma}_2$  value [31, 32] given by :

$$\tilde{\Gamma}_2 = \Gamma_2 \cos^2 \delta_v = \frac{2 V_{kf}^2}{\varepsilon} \frac{\varepsilon^2}{\varepsilon^2 + \Delta^2} = -\frac{2 V_{kf}^2 |\varepsilon|}{\varepsilon^2 + \Delta^2}. \quad (12)$$

Above the magnetic transition, we use the non magnetic resonant states theory as presented in section II.3. For each cerium impurity, the number of 4f

electrons and the 4f density of states are given by (3) and (4) as a function of the distance  $E$  from the non magnetic 4f level to the Fermi level.

This description of the magnetic transition is very rough, because we use two different models in the two domains: ionic model in the magnetic domain and Hartree-Fock model in the non magnetic domain. The use of Hamiltonian (1) for  $\varepsilon$  tending to zero is in principle not justified, because the spin  $S$  cannot be defined.  $E$  and  $\varepsilon$  cannot be linked with each other. In principle, the real theory would be to see how the non magnetic 4f state is split in different 4f levels at the magnetic transition.

In spite of all these principle questions, we present here the main results of these models:

— For  $p < 30$  kbar, the value of  $-dT_c/dc$  is given by the equation (11) with the  $\tilde{T}_2$  value of (12), instead of  $T_2$ . This gives the theoretical curve (I) of the figure 4, by taking a linear variation of  $\varepsilon$  with pressure from  $\varepsilon = -2\Delta$  at normal pressure to  $\varepsilon = 0$  at 30 kbar. So,  $-dT_c/dc$  is maximum at 15 kbar corresponding to  $\varepsilon = -\Delta$ . We use  $S = \frac{1}{2}$  even when  $\varepsilon$  tends to zero. A justification of the preceding procedure can be found in the fact that the Kondo temperature is smaller than  $T_c$  in La-Ce alloys.

For  $p > 30$  kbar,  $T_c$  is given by the Ratto-Blandin [33] formula:

$$\ln \frac{T_c}{T_{c0}} = -c \cdot \alpha \frac{n_f(E_F)}{n_s(E_F)} \left\{ 1 + \alpha \frac{n_f(E_f) U_{eff}}{7} \right\}. \quad (13)$$

The formula (13) gives the theoretical curve (II) of the figure 4 by taking a linear variation of  $E$  with pressure from  $E = 5.2\Delta$  at 30 kbar to  $E = 9\Delta$  at 125 kbar.

The two models give two curves in very good agreement with experiment far from the magnetic transition. At the magnetic transition, they give a sudden change of slope, instead of a smooth experimental variation. It is well known that the Kondo magnetic transition is smooth, in contrast to the predictions of « classical pre-Kondo » theories.

— The slope of the Kondo resistivity [32] in the magnetic region is proportional to  $\tilde{T}_2^3 \cos 2\delta_v$ , if we take into account only the resonant scattering term; this gives a maximum a little below  $\varepsilon = -\Delta$  and a zero value at  $\varepsilon = -\Delta$ . The present analysis is complicated by the  $\Gamma_1$  term. However, we can also find a maximum in the slope of Kondo resistivity near  $\varepsilon = -\Delta$ , which is in good qualitative agreement with the resistivity curves of figure 5a. Further investigations are in progress and will be published soon [34].

In the non magnetic domain, there is no resistivity minimum, as it can be seen in the curves of the figure 5b for Y-Ce alloys at 57 and 79 kbar.

— The temperature of the resistivity minimum  $T_{min}$  is proportional to the power 1/5 of the slope of the Kondo resistivity, which gives a very small increase of  $T_{min}$  between  $\varepsilon = -2\Delta$  and  $\varepsilon = -\Delta$ , in good qualitative agreement with the results of the figure 5a.

— The plateau of the Kondo resistivity in the magnetic domain [32] is proportional to

$$\cos^2 \delta_v = \varepsilon^2 / (\varepsilon^2 + \Delta^2),$$

which decreases rapidly when  $\varepsilon$  tends to zero. In the non magnetic domain, the residual resistivity at low temperatures is proportional to  $\Delta^2 / (\Delta^2 + E^2)$ , which decreases when  $E$  increases with pressure. Detailed measurements of the resistivity at low temperatures would be very instructive, in order to see, as for  $-dT_c/dc$ , the discrepancy at the magnetic transition between experiment and classical theories.

So, the magnetic transition is a continuous one with a progressive increase of the magnetic moment. Another example of a continuous transition will be found in  $(Au_xAg_{1-x})_{1-c}Yb_c$  alloys.

3. NON MAGNETIC ALLOYS. — When the 4f level is above the Fermi level, the alloys are non magnetic and can be described by the non magnetic resonant states theory. The number of 4f electrons is given by (3), the density of states by (4) and, in the case of superconducting alloys,  $T_c$  is given by (13).

When the 4f level is sufficiently close, the effect of 4f states can be important; this effect decreases with pressure. That is the case of La-Ce alloys at high pressures, as already explained, and also the case of Th-Ce alloys [35]:  $-dT_c/dc$  decreases with pressure from the experiments of Huber and Maple (Fig. 4). The theoretical curve of figure 4 is obtained by use of (13) and with taking the same linear variation of  $E$  with pressure as in non magnetic La-Ce alloys:  $E = 6\Delta$  at  $p = 0$  and  $E = 7\Delta$  at  $p = 25$  kbar. So, the zero pressure of Th-Ce alloys corresponds roughly to the 50 kbar pressure of La-Ce alloys. We can conclude that Th-Ce alloys are « close to be magnetic ». But, the best prove of the proximity of magnetism in Th-Ce alloys comes from the ternary system  $(Th_{1-x}Y_x)_{1-c}Ce_c$ :  $-dT_c/dc$  increases rapidly with the concentration of yttrium [35]. When  $x$  is 0.35, the alloys are almost becoming magnetic, as La-Ce at 35 kbar. The increase of  $x$  is the same as the decrease of pressure in La-Ce alloys, because the 4f level goes nearer the Fermi level in the two cases. So, the  $Th_{1-x}Y_xCe$  system can be described by moving the 4f level from a position  $\varepsilon \simeq -2\Delta$  in YCe to a position  $E \simeq 6\Delta$  in ThCe. Further experiments would be very interesting at higher concentrations in yttrium, in order to find the same curves as in La-Ce alloys for  $|dR/d \ln T|$  and  $-dT_c/dc$ .

On the other hand, dilution of scandium in thorium [35] does not modify the  $-dT_c/dc$  value of cerium impurities, which seems to indicate that Sc-Ce is non magnetic as Th-Ce.

At last, when the 4f level is far away and above the Fermi level, the resonant scattering term is negligible and cerium alloys behave as normal non magnetic alloys: that is probably the case of InCe and SnCe [36].

4. GOLD-SILVER BASED ALLOYS WITH YTTERBIUM IMPURITIES. — One system which summarizes all the preceding cases is the  $(Au_xAg_{1-x})_{1-c}Yb_c$  alloys [37, 38]. Ytterbium impurity is not magnetic in silver and magnetic in gold. The magnetic moment increase continuously from 0 to the  $Yb^{+++}$  value, when  $x$

goes from 0 to 0.1, and then it remains constant with  $x$  [37]. The resistivity minimum exists when  $x$  is between 0.1 and 0.3 [38]. When  $x$  increases the 4f level of ytterbium impurity increases relative to the Fermi level. When  $x = 0$ , the 4f level is just below the Fermi level and  $\text{AgYb}$  is close to be magnetic,  $x = 0.1$  corresponds to the magnetic transition,  $x = 0.3$  corresponds to the  $\varepsilon_c$  value of disappearance of the Kondo effect and from  $x = 0.3$  to  $x = 1$  we find again the ionic model for  $\text{Yb}^{+++}$  impurities. To go from  $\text{AgYb}$  to  $\text{AuYb}$  makes the 4f level move by roughly 0.5 eV, if we take  $\varepsilon_c \approx 0.1$  eV.

All the properties of cerium and ytterbium alloys can be accounted by a movement of the 4f level relative to the Fermi level. The real movement is the reverse movement of the Fermi level relative to a fixed 4f level [2]. So, the question arises whether it is possible to predict the position of the 4f level of cerium impurities in a given matrix. We can find an empirical rule which is that the Fermi level moves according to the valency of the matrix. Hosts with a valency smaller than 3 (Au, Ag, Mg) give a 4f level below the Fermi level; hosts with a valency 3 (Y, La,  $\text{LaAl}_2$ ,  $\text{La}_3\text{In}$ ) give a 4f level closer to it. Hosts with a valency 4 (Th, Sn) give non magnetic alloys. But, Sc and In (valency 3) are probably not magnetic, and especially, ytterbium has a completely different behaviour in the two monovalent gold and silver metals. So, this empirical law is not always checked and we have probably to find a rule involving details of the band structure of the host.

**VI. Kondo effect in cerium alloys.**— We have used here the Hamiltonian (1) and not the classical Hamiltonian for rare-earths [1]:

$$H = -\Gamma(g_J - 1) \mathbf{s} \cdot \mathbf{j} \quad (14)$$

$\mathbf{j}$  is the total angular momentum of the configuration ( $j = \frac{5}{2}$  for cerium). (14) gives some puzzling results for

the Kondo effect, because of the  $(g_J - 1)$  factor which is negative for cerium and positive for ytterbium. The situation has been clarified by the derivation of a new Hamiltonian by the Schrieffer-Wolff transformation for the 4f<sup>1</sup> configuration of cerium (or the 4f<sup>13</sup> configuration of ytterbium). This Hamiltonian can be written [39]:

$$H = -\frac{\Gamma}{2} \sum_{k,k',M,M'} C_{k'M'}^+ C_{kM} \left\{ C_M^+ C_{M'} - \frac{\delta_{MM'}}{2j+1} \sum_{M''} n_{M''} \right\} \quad (15)$$

$\Gamma$  is given by (10) and  $M$  designs the  $j_z$  — component of the given  $j$  value.

The Hamiltonian (15) is deeply different from (1) and describes spin and orbit exchange scattering. In contrast to the  $\mathbf{s} \cdot \mathbf{j}$  exchange model, the change  $\Delta M = M' - M$  in the magnetic quantum numbers can be equal to 0,  $\pm 1$ ,  $\pm 2 \dots \pm 2j$  and is not limited to 0 or  $\pm 1$  as it is for the  $\mathbf{s} \cdot \mathbf{j}$  Hamiltonian. (15) gives a good description of the Kondo effect which exists only for negative  $\Gamma$  values as for the Hamiltonian (1). The values of the superconducting temperature and the spin disorder resistivity are similar to those obtained with (1), with only a change of coefficient [39]: thus the preceding use of (1) is justified.

If there is a crystalline field effect, the Hamiltonians (1) and (15) are deeply different, because all the levels of the ground state are always coupled by (15), while it is not always the case for (1) as pointed out recently by Maranzana [40]. For example, if the ground state is  $M = \pm \frac{5}{2}$  as in Maranzana paper [40] and if it is well apart from the excited states, there is no Kondo effect with (1) and there is a Kondo effect with (15). A full paper will be published soon on the effect of crystalline field effect in cerium alloys [41].

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