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THEORY OF THE EFFECT OF IMPURITIES ON THE α-γ TRANSITION IN CERIUM

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A B S T R A C T

The Ramirez-Falicov model for the α-γ transition in Ce has been extended to describe Ce-rare earths dilute alloys. Changes in the transition temperatures and pressures predicted by the model, are in good agreement with existing experiments. The most important effect of the impurities is to lower the transition temperature, the effect being more marked for divalent impurities, The assumption that in this way an ordering (Néel) temperature can be reached, leads to the prediction of a phase diagram for these alloys similar to that found for Cr doped V_2O_3.

I-INTRODUCTION:

The phase diagram of the Ce below room temperature shows several transformations. The initially high temperature annealed Ce, when cooled to room temperature yields the fcc paramagnetic γ phase. Further cooling produces a partial transformation of the γ phase to the dhcp β form. Under still further cooling the remaining γ phase transformes to a collapsed fcc α phase.

Present theoretical understanding of this behaviour is based on the idea that the α phase consists of Ce^{4+} ion cores and four conduction electrons per atom; this Ce^{4+} ion, being isoelectronic to the Xe atom is non-magnetic, with zero total angular momentum. The γ phase is assumed to be formed by Ce^{3+} ions and three conduction electrons per atom. The Ce^{3+} ion is magnetic and has a total angular momentum $J = 5/2$.

Pauling[1] and Zachariasen[2] suggested that the α-γ transformation corresponds to an electronic transition from the 4f level to the conduction band. Recently, Ramirez and Falicov(R F)[3] have proposed a mechanism for the transition in which the Coulomb repulsion between 4f localized and band electrons acts as the driving force. Assuming a linear pressure dependence for the parameters they were able to explain the main features of the α-γ transformation. Since the(RF)mechanism depends strongly on the number of localized states, the model could be tested by replacing a few Ce atoms by other atoms as similar to Ce as possible, with their localized f states far enough from the Fermi energy in such a way that it is impossible to change

its occupation for all interesting temperatures. In this sense one can think of Th, La, Pr and other rare earths as impurities. This test is more relevant since there exists a bulk of experimental information on the effect of impurities on the α-γ transition[4-8]. These experiments show that addition of a few per cent of trivalent rare earths impurities lowers the transition temperature substantially, while the effect of divalent impurities is even more marked.

We present here an axtension of the RF model to include the effect of impurities. In this way it is seen that a generalization of the RF Hamiltonian, treated within the mean field approximation, can account for the main experimental results on alloys, with the noticeable exceptionof La. A possible explanation of this could be that for La the assumption that the valency of impurities is not changed at the transition is not valid.

In section IV we include a speculative discussion based on the hypothesis that by alloying for instance with Yb, the transition temperature can be lowered to the point where the spins in the γ phase may order. In this case, one would have a phase diagram for Ce alloys quite analogous to that of the V_2O_3 system where a low temperature antiferromagnetic phase is known to exist.[9] If our speculations can be experimentally verified it would turn out that Ce and the V_2O_3 system

have a completely analogous behaviour. This similarity has first been pointed out by Rice and McWhan [9] for the high temperature transformation.

II-MODEL HAMILTONIAN FOR Ce ALLOYS.

If we assume that alloying Ce with other rare earths or similar atoms, does not change appreciably the position of the localized 4f levels and the band states in the host we can write the following Hamiltonian for Ce alloys

$$H = \sum_{k\sigma} \varepsilon_k C^{\dagger}_{k\sigma} C_{k\sigma} + \Lambda \sum_{im} b^{\dagger}_{im} b_{im} + \Lambda' \sum_{i'm'} b^{\dagger}_{i'm'} b_{i'm'} \tag{2.1}$$

$$+ G \sum_{i\sigma m} C^{\dagger}_{i\sigma} C_{i\sigma} b^{\dagger}_{im} b_{im} + G \sum_{i'\sigma m'} C^{\dagger}_{i'\sigma} C_{i'\sigma} b^{\dagger}_{i'm'} b_{i'm'}$$

Here $C^{\dagger}_{k\sigma}$ creates an electron with spin σ in a band state of energy ε_k; $b^{\dagger}_{im}$ creates an electron in a localized 4f state at a Ce atom at site i, with total angular momentum in the z direction m., $b^{\dagger}_{i'm'}$ creates an electron in a localized state at an impurity site, G is the Coulomb interaction between an electron in the band and an electron in a localized state in Ce and G' is the Coulomb interaction between an electron in the band and an electron localized at an impurity site. $C^{\dagger}_{j}$ creates an electron in the Wannier state at site i associated with the band. The localized states are assumed to be highly correlated ionic-like 4f orbitals, with a well defined total angular momentum.

Within the framework of the rigid band model and in the mean field approximation we have for the energy

$$E = \int_0^\infty d\varepsilon\, D(\varepsilon)\, n(\varepsilon) + c\,\Delta\, N_0\, n + x\,\Delta'\, N_0\, n' + c\, G\, N_c\, n + x\, G\, N_c\, (\theta + n') \tag{2.2}$$

Where $D(\varepsilon)$ is the density of states in the band, $n(\varepsilon)$ the one electron distribution function, N_0 the number of lattice sites, c the Ce concentration, n the number of electrons (≤ 1) localized at a 4f level in a Ce atom and n' the corresponding quantity for the impurities. x = 1-c, is the impurity concentration. N_c is the total number of conduction electrons given by

$$N_c = \int_0^\infty d\varepsilon\, D(\varepsilon)\, n(\varepsilon) \tag{2.3}$$

In Eq. (2.2) θ accounts for the occupation of a second localized f level in a divalent impurity, which we assume to lie well below the conduction band. $\theta = 1$ for divalent impurities and $\theta = 0$ for the other cases.

In what follows we shall assume that $n' = 1$ for all rare-earth impurities and $n' = 0$ for Th.

Within the same approximation the entropy is given by

$$S = -\int_0^\infty d\varepsilon\, D(\varepsilon) \{ n(\varepsilon) \ln n(\varepsilon) + [1 - n(\varepsilon)] \ln(1-n(\varepsilon)) \}$$

$$- N_o c \{ n \ln n + (1-n)\ln(1-n) - n \ln(2J+1) \} \qquad (2.4)$$

where the first term gives the entropy of the band electrons while the second term corresponds to the Ce ions.

In (2.4) J is the total angular momentum of the localized electrons in these ions.

To obtain the equilibrium values for $n(\varepsilon)$ and n we must minimize $F = E - T S$ subject to the constraint

$$N_c + c N_o n = 4 c N_o + n x N_o \qquad (2.5)$$

where n is the valency of the impurities.

From the above given expressions for the interval energy and entropy, by eliminating the number of conduction electrons N_c, we can write the following expression for the free energy per atom in temperature units.

$$F = \frac{1}{2\alpha}\left[c\,(4-n) + \eta x\right]^2 + c\,n\,\Delta + c\,n\,G\,[c(4-n)+\eta x] + x\,G\,(4-\eta)\,[c(4-n)+\eta x] \qquad (3.1)$$
$$+ c\,T[\,n\,\ln n + (1-n)\,\ln(1-n)] - cT\,n\,\ln(2J+1) + \text{const.}$$

In deriving (3.1) we have assumed a constant density of states $D(\varepsilon) = \alpha N_o$, and neglected the entropy of the band electrons.[10] We may write the free energy per Ce atom in the following form

$$F = E\,n - B\,n^2 + T\,\{n\,\ln n + (1-n)\ln(1-n) - n\,\ln(2J+1)\,\} + \text{const.} \qquad (3.2)$$

Where

$$E = E_o - E_1\,x \qquad (3.3a)$$

$$B = B_o\,(1-x) \qquad (3.3b)$$

$$B_o = G - \frac{1}{2\alpha} \qquad (3.3c)$$

$$E_1 = 2(4-\eta)B_o \qquad (3.3d)$$

$$E_o = \Delta + 4\left(G - \frac{1}{\alpha}\right) \qquad (3.3e)$$

E_o is the distance from the Fermi level to the localized 4f state in Ce.

The extremal condition on F with respect to n leads to

$$n=\frac{1}{\frac{1}{2J+1}\exp\left(E-2Bn\right)T^{-1}\ |+\ 1}=f(n) \tag{3.4}$$

This equation has in general one, two or three solutions [10]. As discussed in reference [10], the transition takes place when $n=\frac{1}{2}$ is a solution of (3.4), i.e.

$$T_t=\frac{E-B}{\ln 6} \tag{3.5}$$

taking explicitly $J=\frac{5}{2}$ for Ce^{3+} ions.

The critical transition, defined by the condition that $\frac{dn}{dT}$ is infinite, occurs at

$$T_c=\frac{B}{2} \tag{3.6}$$

One may expect small changes in the parameters Δ, G, and α. with increasing pressure. Since E and B are defined as differences between comparable quantities they will be sensitive to this changes. [3]. One can reproduce the observed α-γtransition line for pure Ce by assuming a linear pressure dependence of E and B. In Ref. (8) the linear dependence of B for V_2O_3 has been adjusted using experimental data on the variation of the critical parameters with impurity concentration. Since no such data exist for Ce alloys, we shall only

Take E as pressure dependent keeping W constant. This can be seen to be equivalent to the assumption made by Ramirez and Falicov in ref. (3). Taking

$$E = E_0 - E_1 x + \gamma p$$

and adjusting T_t to the experimental p-T diagram of pure Ce we get $\gamma = 42.53$ K/kbar which is in good agreement with the value used by RF.

Using the values $T_c = 579^\circ K$, $T_t(p=o) = 116^\circ K$ and $D(\varepsilon) = N_o \alpha \pm \frac{No}{7892}\ ^\circ K^{-1}$ for pure Ce we obtain

$G = 5106^\circ K$

$\Delta = 12510^\circ K$

Equation (3.5) allows us to draw phase diagrams for Ce R alloys, where R designates a rare earth generically. These are depicted in Fig. 1 and show that in general the transition pressures will increase and transition temperatures will decrease as a result of alloying, in agreement with the experiments by Gschneider et al [7] in Pr, Dy and Lu.

The calculated transition temperatures for the 2%/at. concentrations at zero pressure are $T_o^{3+} \simeq 103\ ^\circ K$ for trivalent impurities and $T_o^{2+} \simeq 77^\circ K$ for the divalent ones, in good agreement with the values reported by Miner et al. [8] We assume that Eu and Yb are divalent [8] while the other rare earths (with the

[illegible] at all temperatures and pressures of interest. If Eu becomes trivalent in the α phase and remains so when going back to the γ phase the results are consistent with those of Ref [8]. (c.f. Fig 2 in that work). For La impurities, the procedure used here would predict transition temperatures and pressures in contradiction with the results of both Refs [7] and [8], whether La were assumed to be a magnetic or non-magnetic impurity in Ce.

It would be desirable to have direct experimental information (for instance such as provided by NMR) regarding possible changes in the occupation of the 4f level of La in the range of pressure not too far from the transition values

Ce-Th alloys.

Since Th is tetravalent when disolved in Ce, we have $E = E_o$, independent of impurity concentration; B is still given by (3.3b) Transition temperatures and pressures are obtained from(3.5) as above, and the model predicts that T_t at zero pressure increases linearly with x. Experiments of Ref. [6] show an hysteresis effect. (T_t increases with x in cooling and decrases in heating) so direct comparison is not possible. However, our formulae give a maximum concentration of Th , x = 38% /at. above which there is no more

first order transition, which, considering the crudness of the model is in reasonable agreement with the results of Ref. [4] (c.f., fig 3), which indicate a critical concentration of about 30%.

IV-POSSIBILITY OF A MAGNETIC TRANSITION IN Ce ALLOYS.

Rice and Mc Whan[9] have suggested that the the α-γ transition in Ce is equivalent to the metal-insulator transition in $(V_{1-x}Cr_x)_2O_3$ except that in this system all the conduction electrons become localized, whereas in Ce, just one of the conduction electrons in the α-phase is trapped in the 4f state. This fact is implicit in the equivalence between the RF model and the model for metal-insulator transitions previously proposed by Falicov and Kimball[11]. The phase diagram for $(V_{1-x}\ Cr_x)_2\ O_3$ shows a second first order transition at lower temperatures from the metallic to an antiferromagnetic insulating state.[12]

Recently Falicov, Goncalves da Silva and Huberman[13] and Alascio, López and Grunfeld[10] have independently succeeded in constructing very similar models in which it is shown that if the insulating phase orders magnetically below a certain temperature T_N, the second transition is a natural consequence of the the thermodynamics of these models, provided the entropy of the metallic phase is large enough.

A similar low temperature behaviour has not been found in pure Ce, because the paramagnetic

γ phase [illegible] before reaching the ordering temperature.

As we have seen in the previous sections, divalent impurities have a strong effect in lowering the α-γ transition teperature. The assumption that in this way an ordering(Néel) temperature can be reached, plus a thermodynamical analysis similar to that given above, leads to the prediction of a phase diagram for these alloys similar to that of V_2O_3 doped with Cr.

Making the additional assumptions that the exchange interactions of the impurities can be neglected and that the spin entropy of the α phase can be disregarded, we have the following expression for the magnetic free energy of the ordered γ phase per Ce atom in the molecular field approximation[10]

$$F_n = -(1-x)T_N^0 n^2 \frac{3J}{2(J+1)} m^2 - T n \ln(2J+1) + T n \int_0^m B_J^{-1}(m')\, dm' \qquad (4.1)$$

where T_N^o is the hypothetical Néel temperature for pure Ce (not to be confused with the Néel temperature of the β phase), m the reduced sublattice magnetization and $B_J^{-1}(m)$ the inverse Brillouin function.

Variation of the total free energy with respect to n and m leads to the following equations to determine the equilibrium values

$$m = B_J\left(\frac{3J}{J+1}\, n\, \frac{m}{t}\right) \tag{4.2}$$

and

$$n = \frac{1}{\frac{1}{q}\exp(E-B'n)/T+1} \tag{4.3}$$

where $t=\frac{T}{T_N}$, $(T_N=(1-x)T_N^o)$ is the reduced temperature and

$$q = \frac{1}{2J+1}\exp -\int_o^m B_J^{-1}(m')\, dm' \tag{4.4}$$

$$B' = B + \frac{3J}{2(J+1)}\, T_N\, m^2$$

The implications of Eqs. (4.2) and (4.3) on the transition have been discussed in Ref. [10]

At T=0, the free energy reduces to the internal energy of the system

$$U = E\, n - B\, n^2 - \frac{15}{14}\, n^2\, m^2\, T_N \tag{4.5}$$

For the ground state we must therefore have

$$m = 1$$

$$n = \begin{cases} 0 \text{ for } E-B' > 0 \\ 1 \text{ for } E-B' < 0 \end{cases} \tag{4.6}$$

The transition takes place then at E=B', which using (3.3) yields the following relation between the transition pressure at T=0 and the other parameters

$$p_o = \frac{15}{14} T_N + B\ (1+3x) - E \qquad (4.7)$$

Above this critical pressure the metallic state (α - phase) is stable at T=0.

Equation (3.5) shows that for the 6% Yb alloys the transition occurs along the line

$$T = \vartheta\, p$$

with ϑ = 23.74 K/kbar.

Taking the hypothetical Néel temperature T_N =10°K, we have for the transition pressure at T = 0, p_o = 0.26 kbar and at T_N, p_N =0.42 kbar.

Numerical solution of Eq..(4.2) and (4.3) allows us to draw the phase diagram shown in Fig. 2. This shows the possibility of a transition from the magnetically ordered phase(MO) to the α phase taking place on increasing pressure. The transition from the α phase to the MO phase on increasing temperature is consequente of our neglect of the entropy in the α phase. This assumption could be modified by taking into account the entropy of impurities which should be more easily disordered in the α phase than

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in the γ phase. Also the non-integral valency[14] and the high susceptibility[15] of α -Ce (probably resulting from f-s hybridization) are not explained in this simple model and could contribute to the entropy. Both effects would tend to give the line separating the MO and α phase a finite negative slope. The possibility of structural changes at T_N derived from magnetoelastic terms as pointed out by Falicov et al.[13] should not be ruled out. Work on the effect of f-s hybridization on the properties of the α-phase and on the α-γ transformation in pure Ce is presently in progress, and will be the subject of a forthcoming paper.

The existence of the ordered β phase should not be a hindrance to the experimental verification of the type of transition that we have discussed here. Determination of the phase diagram of the alloys would not only increase the understanding of the behaviour of Ce metal but should also shed light on the validity of the ideas underlying the models proposed for the phase diagram of $(V_{1-x}Cr_x)_2O_3$

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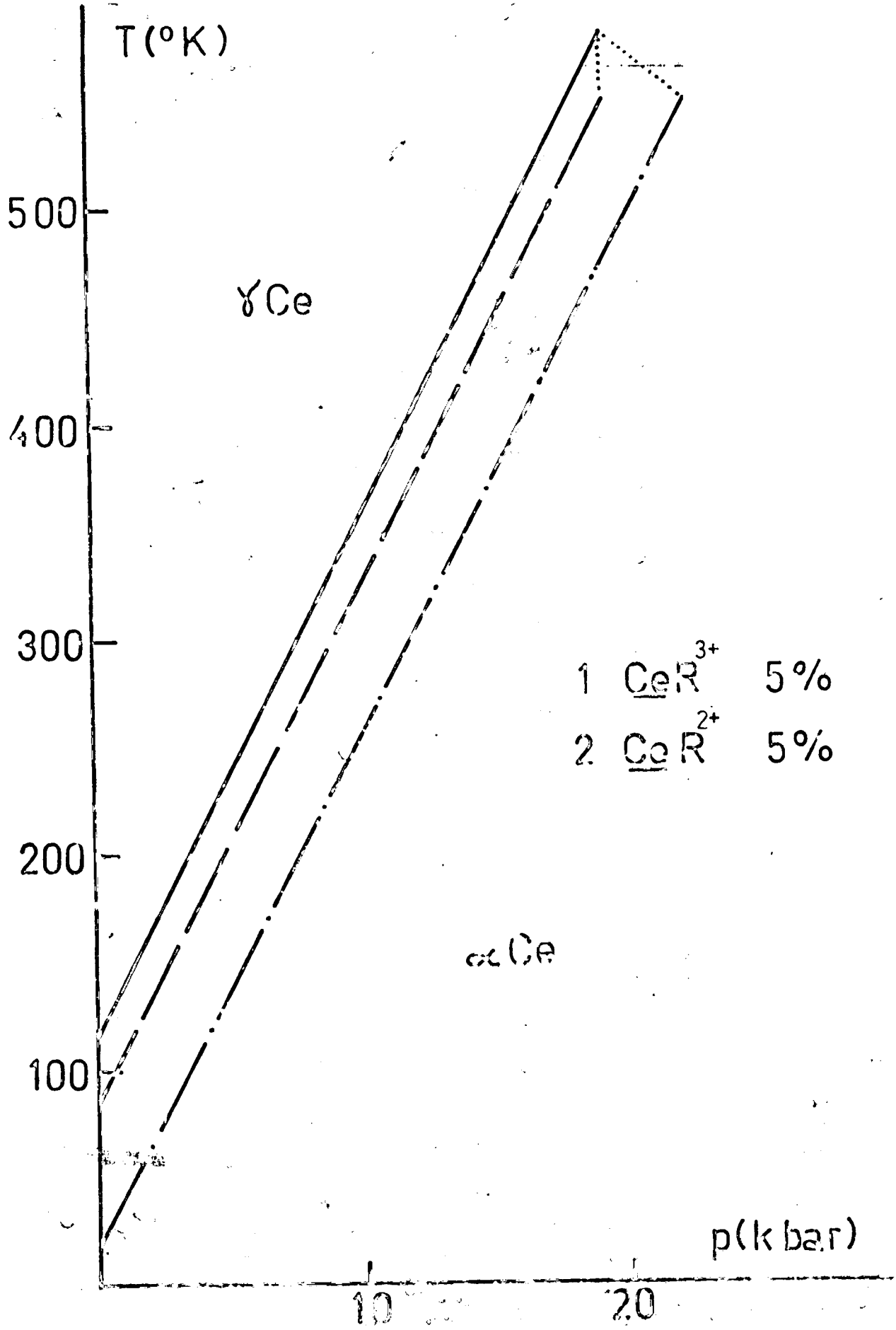
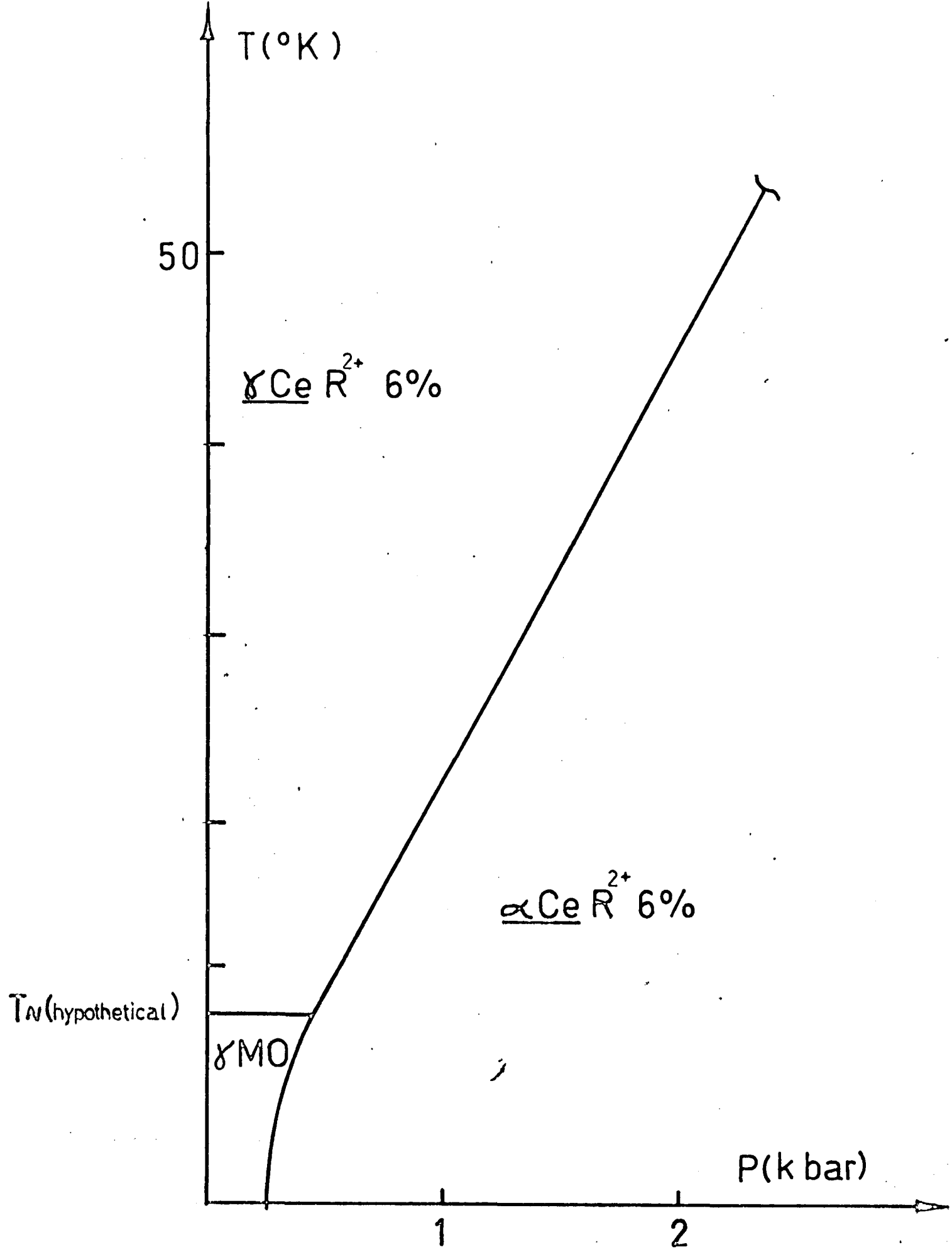
Figure Captions

Figure 1. Phase diagram for Ce alloys. Full line corresponds to pure Ce. Dashed line corresponds to alloying with a trivalent impurity. Dashed-dotted line is an an alloy with a divalent impurity.

Figure 2. Low temperature phase diagram for Ce alloyed with a divalent rare earth such as Yb. AO is themagnetically ordered phase.


T(°K)
500
400
300
200
100
γCe
αCe
1 CeR3+ 5%
2 CeR2+ 5%
p(k bar)
10
20


T(°K)
50
γCe R2+ 6%
αCe R2+ 6%
TN(hypothetical)
γMO
P(k bar)
1
2