Intern. J. Magnetism, 1971, Vol. 1, pp. 333–340

MAGNETIC–NONMAGNETIC TRANSITIONS IN ALLOYS WITH CERIUM IMPURITIES

B. COQBLIN
Laboratoire de Physique des Solides† Faculté des Sciences, 91 Orsay, France

M. B. MAPLE‡ and G. TOULOUSE¶
University of California, San Diego, La Jolla, California 92 037, U.S.A.

(*Received* 17 *February* 1971)

The continuous transition of dilute metallic alloys from magnetic to nonmagnetic behaviour has been recently observed experimentally in alloys containing Cerium impurities. A brief review of these experiments, which include measurements of the resistivity and of the depression of the superconducting temperature under applied pressure, is presented in connection with the predictions of a phenomenological model. The parameters needed to fit the existing data are consistent with those obtained in pure Ce or in other Ce alloys.

I EXPERIMENTAL INTRODUCTION

It is well-known that cerium, either as a pure metal or an impurity dissolved in a non magnetic matrix, exhibits peculiar properties related to the proximity of the Ce 4f level to the Fermi level E_F.[1,2] Alloys with cerium impurities have been extensively studied in previous years[2,3] and their properties depend strongly on the relative position of the Ce 4f level and E_F; they are non magnetic when the 4f level is above E_F, and magnetic when it is below. From experiments by Smith[4] on the pressure dependence of the superconducting transition temperature T_c of **La**Ce alloys, it has been estimated[5] that the Ce 4f level lies a few hundredths of an eV below E_F at normal pressure and moves towards E_F by a hundredth of eV under a pressure of 10 kbar. Hence, **La**Ce as well as **Y**Ce have been suggested[5] as promising candidates for an experimental study of the transition from magnetism to nonmagnetism at feasibly higher pressures.

A minimum in the variation of T_c with pressure was first observed in the $(\mathbf{La}Ce)_3In$ system and interpreted as signalling the onset of a magnetic–nonmagnetic transition.[6] In these alloys, for a given concentration c of magnetic cerium impurities, the depression of T_c, $\Delta T_c \equiv T_{c_0} - T_c$ where T_{c_0} is the transition temperature of the matrix, initially increases strongly with pressure and then goes through a maximum at higher pressure. Recently, Maple *et al.*[7] have measured the variation of T_c with pressure in **La**Ce alloys to 140 kbar. They observed that T_c of pure lanthanum increases monotonically to 12°K at 140 kbar, while, for example, T_c of a $La_{0.987}Ce_{0.013}$ alloy first decreases with pressure and then goes through a minimum at 15 kbar. This behaviour is so pronounced in a $La_{0.98}Ce_{0.02}$ alloy, that there is a 'normal gap' between 5 and 15 kbar on the pressure axis where the sample is not superconducting above the lowest temperature (0.35°K) accessible to the experiment. Hence, ΔT_c shows a maximum as a function of pressure. In figure 1, we have plotted $\Delta T_c/c$ for the $La_{0.987}Ce_{0.013}$ alloy versus pressure to 140 kbar. The depression of T_c at high pressure ($\gtrsim$ 100 kbar) is more than an order of magnitude smaller than at the maximum depression at 15 kbar. Moreover, the shape of the T_c versus c curve changes with pressure, as seen in Figure 2. At low pressures, it is nearly linear with a small negative curvature, while at high pressures the curvature becomes positive and is strongest at roughly 30 kbar. From Figure 1, the magnitude of the depression of T_c is typical of a magnetic impurity (like other rare-earth impurities) at low pressure (below $\sim$ 30 kbar), while it is typical

† Laboratoire associé au C.N.R.S.

‡ Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under Grant No. AF-AFOSR-631-67-A.

¶ Permanent address: Laboratoire de Physique des Solides—Faculté des Sciences—91—Orsay—France.

of a nonmagnetic impurity at very high pressure (above $\sim$ 100 kbar).

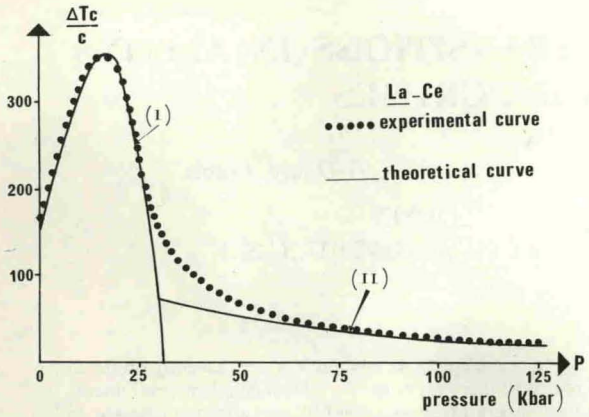

FIGURE 1 Depression of the superconducting transition temperature $\Delta T_c/c$ of a **La**Ce (1.3 at. % Ce) alloy versus pressure to 140 kbar (reference 7) compared to the theoretical curves (I and II) discussed in the text.

The preceding variation of ΔT_c (or $-\mathrm{d}T_c/\mathrm{d}c$), characteristic of the pressure induced magnetic–nonmagnetic transition in **La**Ce alloys, can also be obtained in a ternary alloy by varying the composition of the matrix.[8] This is shown in Figure 3. To the right we have plotted $(-\mathrm{d}T_c/\mathrm{d}c)_{c=0}$ vs pressure for **Th**Ce alloys[9,10] which decreases with pressure in much the same manner as for **La**Ce alloys at very high pressure; to the left we have plotted the same quantity as a function of the relative composition of the matrix, i.e., the yttrium concentration x in ternary $(\mathrm{Th}_{1-x}\mathrm{Y}_x)_{1-c}\mathrm{Ce}_c$ alloys.[8] The variation of $(-\mathrm{d}T_c/\mathrm{d}c)_{c=0}$ with x is similar to that which occurs with decreasing pressure in nonmagnetic **La**Ce alloys.

The electrical resistivity is another quantity which is expected to show a remarkable variation in the vicinity of the magnetic–nonmagnetic transition. Figure 4 shows the slope of the Kondo resistivity $|\mathrm{d}R_m/\mathrm{d}\ln T|$ (normalized to the value at zero pressure) in the temperature range where R_m is linear in $\ln T$, and the temperature of the resistivity minimum $T_{\min}$ (also normalized to the zero pressure value) vs pressure to 18 kbar for a $\mathrm{La}_{0.98}\mathrm{Ce}_{0.02}$ alloy.[11] In the same figure ΔT_c, determined from resistive transitions on the same sample when the alloy is superconducting or extrapolated when it is no longer superconducting, is shown for comparison. Experimentally, $|\mathrm{d}R_m/\mathrm{d}\ln T|$ and ΔT_c have a maximum at nearly the same pressure, while $T_{\min}$

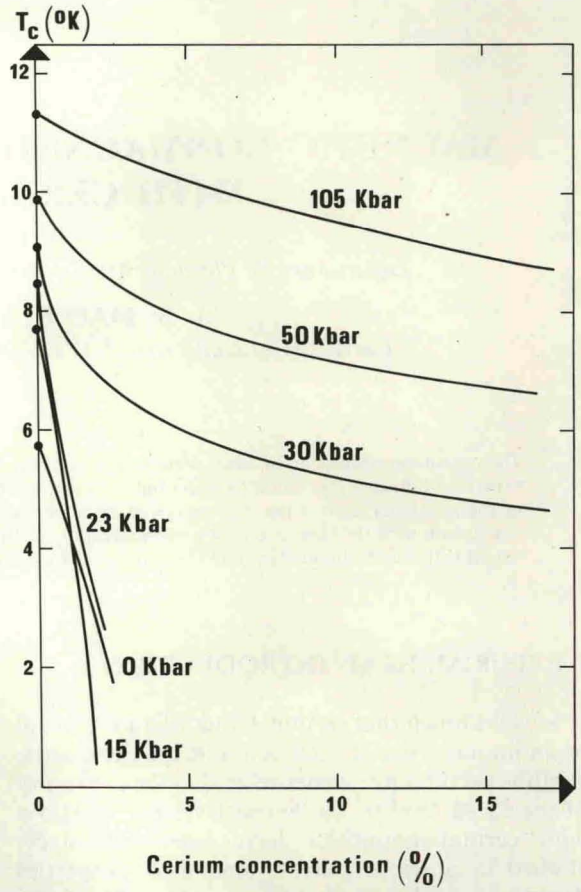

FIGURE 2 Isobaric concentration dependence of the superconducting transition temperature T_c in the **La**Ce system (reference 7).

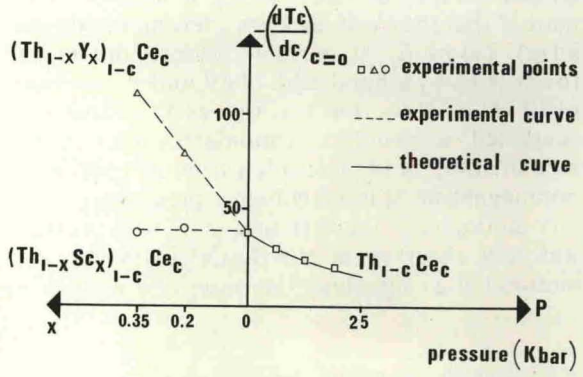

FIGURE 3 Initial depression of the superconducting transition temperature $(\mathrm{d}T_c/\mathrm{d}c)_{c=0}$ versus pressure in the $\mathrm{Th}_{1-c}\mathrm{Ce}_c$ system, and matrix composition x in the $(\mathrm{Th}_{1-x}\mathrm{Y}_x)_{1-c}\mathrm{Ce}_c$ and $(\mathrm{Th}_{1-x}\mathrm{Sc}_x)_{1-c}\mathrm{Ce}_c$ systems (reference 8).

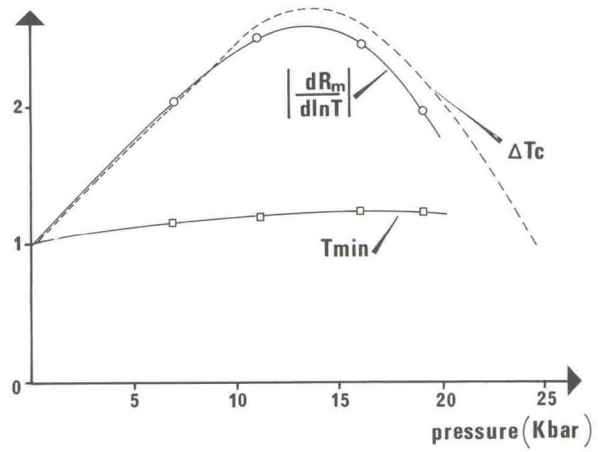

FIGURE 4 $|dR_m/d \ln T|$, ΔT_c and T_{min} for a **La**Ce (2 at. % Ce) alloy (normalized to their respective values at normal pressure) to 18 kbar (reference 11).

increases slowly with pressure. Shown in Figure 5 is the resistivity vs temperature curve of an $Y_{0.99}Ce_{0.01}$ alloy at different pressures.[12] The resistivity minimum, present at low pressure, disappears completely at high pressure.

II THE THEORETICAL MODEL

It is well recognized that in the dilute alloy limit no sharp transition is expected, either as a function of temperature or pressure. The meaning of magnetic or nonmagnetic impurity states is then relative and qualitative. Keeping this in mind, we can *grosso modo* characterize three typical regions (on a T,p plane for example):

(i) a high temperature $T > T_k$ (T_k = Kondo temperature) magnetic region;
(ii) a low temperature $T < T_k$ nonmagnetic (or condensed magnetic) region; and
(iii) a normal nonmagnetic region.

Hence we see that a magnetic–nonmagnetic transition can occur in two typical ways: (i) → (ii) and (i) → (iii).

In the first case, it will be convenient to use throughout a Kondo Hamiltonian with some assumed or adjusted dependence of T_k on the pressure.

In this paper, we explore the second case. The resistivity experiments on **La**Ce up to 18 kbar indicate that T_k remains very small in this pressure range and that the exchange integral exhibits a maximum near 15 kbar instead of a monotonically

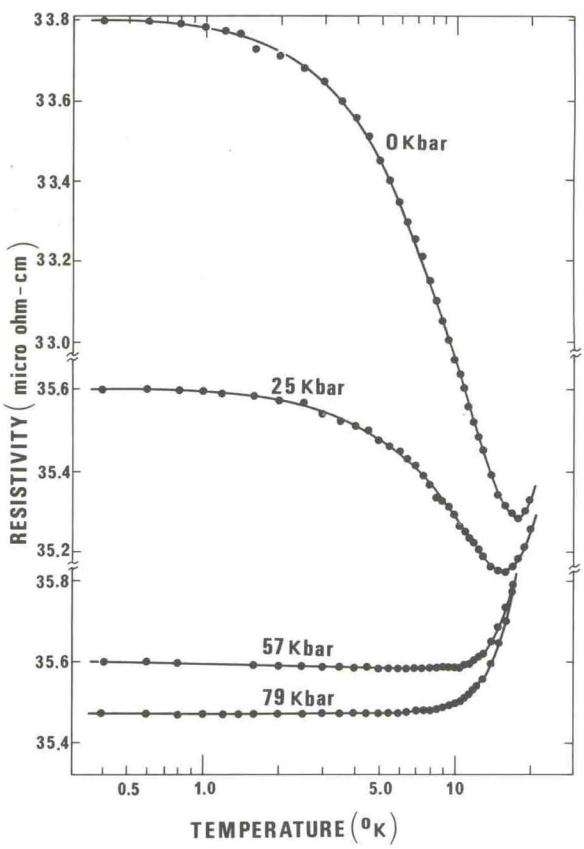

FIGURE 5 Resistivity versus temperature of **Y**Ce (1 at. % Ce) at various pressure up to 79 kbar (reference 12).

increasing variation as a function of pressure. In the absence of susceptibility and specific heat measurements, we have to rely on these indications from the resistivity to discriminate between cases 1 and 2 because the variation of T_c will be qualitatively similar in both instances.

We assume that the effect of pressure is to shift linearly the energy E_{4f} of the 4f level upwards with respect to the Fermi level E_F. In the absence of a good solution of the Anderson Hamiltonian throughout the region where the impurity level crosses the Fermi level, we attack this region from the left (low pressures, $E_{4f} < E_F$) and from the right (high pressures, $E_{4f} > E_F$). The aim is to see how far we can go from each side and to see how the parameters needed to fit the data compare with those obtained in pure Ce or in other Ce alloys. The results obtained show a rather good degree of self-consistency; further experiments on these alloys will tell if the model encompasses the essential features.

In the magnetic domain below p_c ($\simeq$ 30 kbar), the 4f level is below E_F and the Anderson Hamiltonian can be reduced to an exchange Hamiltonian

$$\mathcal{H} = -\Gamma \boldsymbol{s} \cdot \boldsymbol{S} \tag{1}$$

describing the interaction between the conduction electron spin density $\boldsymbol{s}$ at the impurity site and the localized electron spin $\boldsymbol{S}$. The interaction constant, as previously described,[3,5] is the sum of the two terms:

$$\Gamma = \Gamma_1 + \Gamma_2 \tag{2}$$

Γ_1 comes from the normal exchange scattering mechanism and is small, positive and nearly pressure independent. We make here the reasonable approximation that Γ_1 is constant in the rare-earth series and take the value deduced for gadolinium impurities for which Γ_2 is nearly zero. Γ_2 arises from the resonant scattering mechanism, is negative, and can be obtained from the Schrieffer–Wolff transformation[13]

$$\Gamma_2^0 \simeq -\frac{2V_{kf}^2}{|\varepsilon|} \tag{3}$$

V_{kf} is the matrix element of mixing and $\varepsilon(\varepsilon < 0)$ is the energy separating the 4f level and E_F. Formula (3) is no longer valid when $|\varepsilon|$ becomes very small, i.e. $|\varepsilon|$ smaller than Δ. As ε approaches zero, the the phase-shift δ_v of the occupied 4f level varies rapidly with ε. Thus in the region of very small ε, we have to take into account the direct scattering Hamiltonian which gives the ε dependent phase-shift δ_v.[14,15] One effect of the direct scattering term is to renormalize Γ_2^0 into an effective Γ_2 approximately given by

$$\Gamma_2 = \Gamma_2^0 \cos^2\delta_v = \frac{2V_{kf}^2}{\varepsilon}\frac{\varepsilon^2}{\varepsilon^2 + \Delta^2} = -\frac{2V_{kf}^2|\varepsilon|}{\varepsilon^2 + \Delta^2} \tag{4}$$

Γ_2 has a maximum when $\varepsilon = -\Delta$ and is zero when $\varepsilon = 0$. We apply this ionic model until $\varepsilon = 0$ although, obviously, the nearer we approach the transition, the less valid the ionic model and, in turn, the less valid formulas (2) and (4).

In the nonmagnetic domain above p_c, the 4f level is above E_F at a distance E and we use the nonmagnetic resonant states theory within the Hartree–Fock approximation. E is much larger than the half-width Δ in the nonmagnetic domain because the Coulomb repulsion is very much larger than E and Δ in rare-earth metals. The total 4f density of states for the two spin directions is:

$$n_f(E_F) = \frac{\xi}{\pi\Delta}\left(\frac{\Delta}{E}\right)^2 \tag{5}$$

and the total number of 4f electrons N is given by

$$N = \frac{\xi}{\pi}\frac{\Delta}{E} = \sqrt{\frac{\xi\Delta n_f(E_F)}{\pi}} \tag{6}$$

ξ is the degeneracy of the nonmagnetic 4f state which is equal to 14 if we do not take into account spin–orbit coupling. On the other hand, if the spin–orbit coupling is large relative to Δ, as is usually the case in rare-earths, the 4f level is split in a $j = 5/2$ and a $j = 7/2$ state. For cerium, the ground state is $j = 5/2$ and we can consider it the only occupied state, so that ξ is equal to 6.

III RESULTS

(1°) *Depression of the superconducting transition temperature.*

We calculate $-dT_c/dc$ in the magnetic domain ($T > T_k$). At low concentration $-dT_c/dc$ is given by the Abrikosov–Gor'kov formula:[16]

$$-\left(\frac{dT_c}{dc}\right)_{c=0} = \frac{\pi^2}{4} n_s(E_F)\, S(S+1)\Gamma^2 \tag{7}$$

with Γ given by (2) and (4):

$$\Gamma = \Gamma_1 + 2\Gamma_0 \frac{\Delta\varepsilon}{\varepsilon^2 + \Delta^2} \tag{8}$$

where

$$\Gamma_0 = \frac{2}{\pi n_s(E_F)} \tag{9}$$

We take the value $n_s(E_F) = 4.4$ states/eV atom for the density of states of the sd band of pure lanthanum (for two spin directions) deduced from specific heat measurements. Thus, $\Gamma_1 = 0.028$ eV is deduced from experiments on **La**Gd[5] where $\Gamma_2 \sim 0$, $\Gamma_0 = +0.145$ eV and we assume, as usual,[1] $\Delta = 0.02$ eV.

We further assume a linear variation of ε with pressure of 0.02 eV per 15 kbar and choose p_c equal to 32 kbar. Thus $\varepsilon = -(32/15)\Delta = -0.0427$ eV at normal pressure. Using these values and equations (7), (8) and (9) we plot the theoretical curve (labeled (I)) in Figure 1. Hence, by assuming a reasonable

value of ε at normal pressure, we can fit the experimental curve quite well, in particular the position of the maximum, between 0 and 27 kbar, where 27 kbar corresponds to $\varepsilon = -\Delta/3$. However, between $\varepsilon = -\Delta/3$ and $\varepsilon = 0$ (near the magnetic–nonmagnetic transition) the theoretical curve departs from the experimental curve. The occurrence of the maximum in the depression of T_c can be explained by expression (4), whereas it cannot be explained by the Schrieffer–Wolff formula (3).

In the nonmagnetic domain, we use the Ratto–Blandin theory[17] which does not take into account spin fluctuations. The Ratto–Blandin expression (in the previous notation) is given by

$$\ln \frac{T_c}{T_{c_0}} = -c\alpha \frac{n_f(E_F)}{n_s(E_F)} \left(1 + \alpha \frac{n_f(E_F)\, U_{\text{eff}}}{\xi}\right) \qquad (10)$$

where T_{c_0} is the superconducting transition temperature of pure lanthanum (which varies with pressure), and α is a parameter given by

$$\alpha = \ln \frac{1.14\,\omega_D}{T_c} \text{ for } E \gg \Delta, \omega_D \qquad (11)$$

In the limiting case of small concentration and $E \gg \Delta$, we obtain:

$$-\left(\frac{dT_c}{dc}\right)_{c=0} = \left(\frac{\alpha \xi T_{c_0}}{\pi \Delta n_s(E_F)}\right) \left(\frac{\Delta}{E}\right)^2 \left(1 + \frac{2\alpha}{\pi}\frac{\Delta}{E}\right) \qquad (12)$$

Curve (II) plotted in Figure 1 has been obtained using expression (12) with the following two sets of parameters:

—either $\xi = 6$, i.e. the large spin–orbit coupling limit, by taking a linear variation of E versus pressure with $E = 6\Delta$ at $p = 125$ kbar and $E = 3{\cdot}675\ \Delta$ at $p_c = 32$ kbar. This corresponds to a change of E by $\Delta = 0.02$ eV for a pressure of 40 kbar. The total number of 4f electrons, N, varies from 0.32 at 125 kbar to 0.52 at $p_c = 32$ kbar.

—or $\xi = 14$, i.e. the zero spin–orbit coupling limit, by taking a linear variation of E versus pressure with $E = 9\Delta$ at $p = 125$ kbar and $E = 5.28\Delta$ at $p_c = 32$ kbar. This implies a change of E by $\Delta = 0.02$ eV for a pressure of 25 kbar. N varies from 0.5 at 125 kbar to 0.85 at p_c. The relevant case is probably the large spin–orbit coupling limit which, incidentally, corresponds to the smallest values of N.

Above 50–60 kbar, the agreement between experiment and the theoretical curve (II) is very good, without taking into account spin fluctuations. However, when we approach p_c from high pressures, the theoretical curve (II) deviates markedly from experiment. An expression which takes into account correctly the spin fluctuations will certainly improve the agreement between experiment and theory in the pressure range p_c to 50–60 kbar, although even without such an expression, the Ratto–Blandin formula gives a reasonable qualitative explanation demonstrating unambiguously the nonmagnetic character of cerium impurities above p_c.

Around p_c, we are unable to describe the magnetic–nonmagnetic transition, nor can we link the variables ε and E to each other. Thus, although we can accurately describe the pressure dependdence of the depression of T_c at pressures sufficiently far from p_c, our description of the magnetic transition in the vicinity of p_c is rather crude.

T_c as a function of Ce concentration for the nonmagnetic **Th**Ce system has recently been measured between 0 and 18 kbar.[9,10] Although it has been shown[10] that the T_c versus c curves may be *quantitatively* described by a recent extension of the Ratto–Blandin theory due to Kaiser,[18] we consider here only the low concentration limit where the depression of T_c is linear in c for which the Ratto–Blandin theory is adequate. Using equation (10) or (12), we obtain the theoretical curve for $-(dT_c/dc)_{c=0}$ versus pressure in Figure 3 which agrees well with the experimental data using again the following two sets of parameters:

—either $\xi = 6$, by taking a linear variation of E versus pressure with $E = 4.3\Delta$ at 0 kbar and $E = 5\Delta$ at 18 kbar. This corresponds to a change of E by $\Delta = 0.02$ eV for a pressure of 26 kbar. N varies from 0.44 at 0 kbar to 0.38 at 18 kbar;

—or $\xi = 14$, by taking a linear variation of E versus pressure with $E = 6{\cdot}2\Delta$ at 0 kbar and $E = 7.1\Delta$ at 18 kbar. This implies a change of E by $\Delta = 0.02$ eV for a pressure of 20 kbar. N varies from 0.72 at 0 kbar to 0.63 at 18 kbar.

The variation of $-(dT_c/dc)_{c=0}$ versus pressure in **Th**Ce alloys is explained by the same argument as for **La**Ce alloys with a change of E with pressure of the same order. By comparison with the **La**Ce system, zero pressure for **Th**Ce alloys corresponds roughly to 50 kbar for **La**Ce alloys. Noting that Ce impurities are magnetic in Y, the ternary alloy system $(Th_{1-x}Y_x)_{1-c}Ce_c$ should exhibit the same variation of $-(dT_c/dc)_{c=0}$ with increasing x as with decreasing pressure in **La**Ce alloys. This has been observed recently by Huber and Maple[8] as shown

in Figure 3. $-(dT_c/dc)_{c=0}$ increases with x and has the same value for $x = 0.35$ as for **La**Ce at 35 kbar. By again increasing x to 0.70 (where the $Th_{1-x}Y_x$ alloys are no longer superconducting), one should be able to generate a curve similar to that of Figure 1 to roughly the maximum.

Another example is the ternary alloy system $(Th_{1-x}Sc_x)_{1-c}Ce_c$ where $-(dT_c/dc)_{c=0}$ is roughly independent of x to $x = 0.35$.[8] This indicates that E does not change with matrix composition in this concentration range. It is interesting to note that **Sc**Ce alloys are nonmagnetic as shown by recent magnetic susceptibility experiments.[19]

Finally, the extreme sensitivity of $-dT_c/dc$ to the relative position of the $4f$ level and E_F makes it a very good tool for studying magnetic–nonmagnetic transitions in dilute alloys.

(2°) *Resistivity*

The second result concerns the occurrence of the Kondo effect and the variation of the slope of the Kondo resistivity in the magnetic domain. In the nonmagnetic domain, far from the transition, there is obviously no resistivity minimum and the slope $dR_m/d \ln T$ is positive.

In the magnetic region, above the Kondo temperature, the magnetic resistivity is given (in the usual notation) by:[15]

$$R_m = \frac{m_0 c}{\pi z N e^2 \hbar \rho}\left(2\sin^2\delta_v + 2\pi^2\rho^2\Gamma^2\cos 2\delta_v S(S+1) + 8\pi^2\Gamma^3\rho^3 S(S+1)\cos 2\delta_v \ln\frac{k_B T}{D}\right)$$

Since Γ and δ_v vary with pressure, while ρ and S are assumed to be constant, the slope of the resistivity is conveniently written as:

$$\frac{dR_m}{d\ln(k_B T/D)} = \alpha c \Gamma^3 \cos 2\delta_v \qquad (14)$$

where α is independent of pressure and given by:

$$\alpha = \frac{8 m_0 \pi S(S+1)}{z N e^2 \hbar \rho} \qquad (15)$$

Expression (14) becomes:

$$\frac{dR_m}{d\ln(k_B T/D)} = \alpha c {\Gamma_1}^3 z \qquad (16)$$

with:

$$z = \left(1 + \frac{2\Gamma_0}{\Gamma_1}\frac{x}{1+x^2}\right)^3 \frac{x^2-1}{x^2+1} \qquad (17)$$

as a function of $x = \varepsilon/\Delta$; while $(dT_c/dc)_{c=0}$ is given by

$$-\left(\frac{dT_c}{dc}\right)_{c=0} = -\frac{\pi^2}{4} n_s(E_F) S(S+1) {\Gamma_1}^2 y \qquad (18)$$

with

$$y = -\left(1 + \frac{2\Gamma_0}{\Gamma_1}\frac{x}{1+x^2}\right)^2 \qquad (19)$$

The two parameters y and z are plotted in Figure 6 as function of x for $\Gamma_1 = 0.028$ eV and $\Gamma_0 = 0.145$ eV. z and y are negative and increase in absolute value when x increases by negative values, z has a minimum around $x \cong -1.5$ and a maximum around $x \cong -0.6$, while y has only a minimum at $x = -1$. y is always negative and has two zero values at $x_1 = -(2\Gamma_0/\Gamma_1)$ and $x_2 = (-\Gamma_1/2\Gamma_0)$; z has three zero values at x_1, x_2 and -1. Thus z is negative in the present case

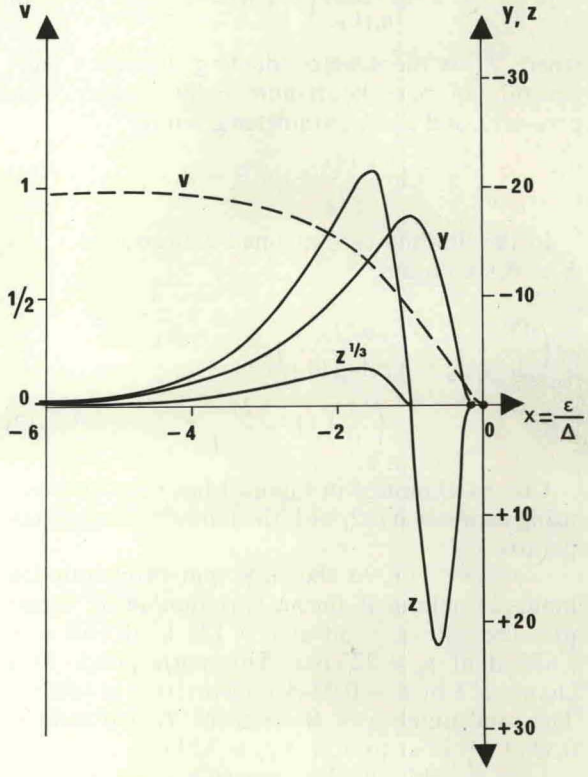

FIGURE 6 The functions y, z, $z^{\frac{1}{3}}$ and v versus the parameter $x = \varepsilon/\Delta$ for $2\Gamma_0/\Gamma_1 = 10.4$.

from $x_1 \cong -10.4$ to $x = -1$; z is positive from $x = -1$ to $x_2 \cong -0.1$, and the Kondo effect has in principle disappeared in this region.

If we compare the dependence of $dR_m/d \ln k_B T$ on pressure given theoretically by expression (16) with experiment (Figure 4), we see that quantitative agreement is relatively poor. Qualitatively, we observe a maximum in $|dR_m/d \ln T|$ for $La_{0.98}Ce_{0.02}$ at roughly 13 kbar, a little lower in pressure than the maximum of ΔT_c for the same alloy. The occurrence of a maximum in $|dR_m/d \ln T|$ is a very good qualitative check of formulas (8) and (16), although the maximum does not appear at precisely the right position, i.e., the maximum in $|dR_m/d \ln T|$ occurs at $\varepsilon = -1.5\Delta$, whereas the maximum of $-(dT_c/dc)_{c=0}$ occurs at $\varepsilon = -\Delta$. Moreover, $|dR_m|d \ln T|$ is not zero when $-(dT_c/dc)_{c=0}$ is a maximum as predicted by the theory, but it is suggestive that, at the 18 kbar limit of present experiments, $|dR_m/d \ln T|$ begins to decrease more rapidly than ΔT_c. Further experiments at higher pressure on $R_m(T)$ would be interesting to clarify this point in relation to the theoretical curves of Figure 6. The curves of resistivity versus temperature in the $Y_{0.99}Ce_{0.01}$ alloy (Figure 5) are obviously in qualitative agreement with the theoretical results; the Kondo effect disappears at high pressure when the 4f level goes above E_F. The nonmagnetic nature of Ce impurities in **Y**Ce alloys at high pressures is also consistent with the rather small depression of T_c (~ 0.5°K/at. % Ce) above 100 kbar.[12]

The total temperature dependent contribution to the resistivity is given by

$$R = \beta T^n + R_m \tag{20}$$

so that the temperature of the resistivity minimum is

$$T_{\min} = \left(\frac{\alpha c}{\eta \beta k_B} \Gamma_1^3 \right)^{1/n} z^{1/n} \tag{21}$$

where $n \cong 3$ for La[20] and $\cong 4$ for Y.[21]

The function $z^{\frac{1}{3}}$ is plotted in Figure 6 and is obviously significant only when z is positive. Again, there is good qualitative agreement between theoretical calculations and experiment on $La_{0.98}Ce_{0.02}$ for which $T_{\min}$ increases very slowly with pressure. For an $Y_{0.99}Ce_{0.01}$ alloy, Figure 5 shows that $T_{\min}$ is roughly constant between 0 and 25 kbar, in qualitative agreement with formula (21).

(3°) *Low temperature resistivity*

We have argued above that the present experimental results are probably in the regime $T > T_k$. Our model predicts that the low temperature ($T < T_k$) resistivity plateau should decrease with pressure ($p < p_c$) according to the formula[15]

$$R_m = \frac{2m_0 c}{\pi z N e^2 \hbar \rho} \cos^2 \delta_v = \frac{2m_0 c}{\pi z N e^2 \hbar \rho} \frac{x^2}{1 + x^2} \tag{22}$$

the function $v = \dfrac{x^2}{1 + x^2}$ is plotted in Figure 6.

For $p > p_c$, in the nonmagnetic domain, the residual resistivity should decrease according to the Friedel formula

$$R_m = \frac{2\pi c}{z k_F} \xi \sin^2 \delta_f = \frac{2\pi c}{z k_F} \xi \frac{\Delta^2}{E^2 + \Delta^2} \tag{23}$$

Resistivity experiments conducted at low temperatures would therefore provide a good check on this model which predicts a decrease of R_m with increasing pressure and a typical transition pressure in the 30 kbar range.

Another very desirable experimental quantity would be the susceptibility with a change from a Curie–Weiss law in the magnetic domain to an exchange enhanced Pauli behavior in the nonmagnetic domain.

IV. CONCLUDING REMARKS

Some interesting aspects of this problem remain to be discussed. The first concerns the shape of the variation of T_c versus impurity concentration. In Figure 2, the isobaric curves of T_c versus c are plotted for different pressures. At low pressures (below 15 kbar), the curvature is slightly negative as predicted by the Abrikosov–Gor'kov theory. At 23 kbar, the curvature is slightly positive while at higher pressures, the positive curvature becomes quite pronounced. At very high pressure (105 kbar), the curvature although still positive, is less apparent due to the decrease of the initial slope $-(dT_c/dc)_{c=0}$ with pressure. The same type of curvature is exhibited by **Th**Ce, $(Th_{1-x}Sc_x)_{1-c}Ce_c$ and $(Th_{1-x}Y_x)_{1-c}Ce_c$ alloys (Figure 7) as well as **Th**U[22] and **Al**Mn[23] alloys. All these alloys are nonmagnetic or only weakly magnetic.[24]

Another remark concerns Hamiltonian (1). For the case of magnetic cerium impurities, a new Hamiltonian[25] has been recently derived for the

resonant scattering term Γ_2 but not for the normal scattering term Γ_1. For this reason we have relied on Hamiltonian (1). Nonetheless, the main results of the present paper are basically conserved with the new Hamiltonian, particularly the variation of z, y and v with x (or pressure) given by formulas (17), (19) and (22).

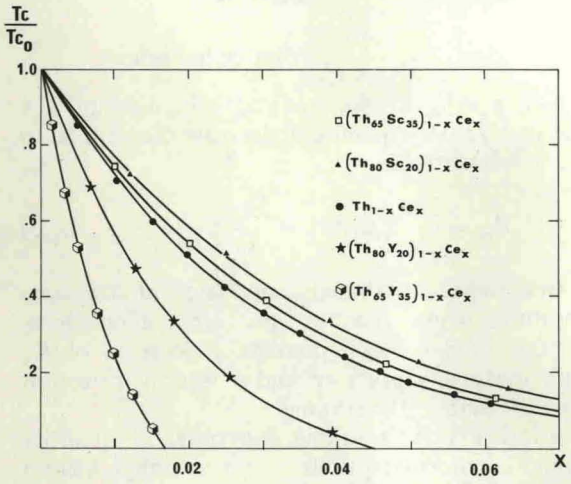

FIGURE 7 T_c/T_{c_0} versus Ce concentration c in $(Th_{1-x}Y_x)_{1-c}$ Ce_c and in $(Th_{1-x}Sc_x)_{1-c}Ce_c$ alloys (reference 8).

In the nonmagnetic domain, we have presented both zero and large spin–orbit coupling limits. Large spin–orbit coupling is probably appropriate, although without direct measurements, we have preferred to consider both limits.

A drawback of the theory for the nonmagnetic domain is the absence of a formula for T_c taking into account correctly the spin fluctuations. The effect of spin fluctuations is probably not very important far away from the magnetic–nonmagnetic transition, i.e., above 50–60 kbar, but close to the transition, a better theory of exchange enhancement would certainly improve agreement between experiment and theory.

In summary, we have developed a model for the first observation of the smooth and continuous transition of a dilute metallic alloy from magnetic to nonmagnetic behavior.

REFERENCES

1. B. Coqblin and A. Blandin, *Adv. in Physics*, **17**, 281 (1968); and references cited therein.
2. M. B. Maple, Ph.D. Thesis, Univ. of California, San Diego, (1969); and references cited therein.
3. B. Coqblin, *Proceedings of the International Conference on Magnetism*, Grenoble, France (September 14–19, 1970), to be published.
4. T. F. Smith, *Phys. Rev. Letters*, **17**, 386, (1966).
5. B. Coqblin and C. F. Ratto, *Phys. Rev. Letters*, **21**, 1065, (1968).
6. M. B. Maple and K. S. Kim, *Phys. Rev. Letters*, **23**, 118, (1969).
7. M. B. Maple, J. Wittig and K. S. Kim, *Phys. Rev. Letters*, **23**, 1375, (1969).
8. J. G. Huber and M. B. Maple, to be published.
9. M. B. Maple, J. G. Huber and K. S. Kim, *Solid State Comm.*, **8**, 981 (1970).
10. J. G. Huber and M. B. Maple, *J. Low Temp. Physics*, **3**, 537, (1970).
11. K. S. Kim and M. B. Maple, *Phys. Rev.* **2** B, 4696 (1970).
12. J. Wittig and M. B. Maple, to be published.
13. J. R. Schrieffer and P. A. Wolff, *Phys. Rev.*, **149**, 491, (1966).
14. G. Toulouse and B. Coqblin, *Solid State Comm.*, **7**, 853, (1969).
15. J. Kondo, *Solid State Physics* (Academic Press, New York, 1969) Vol. XXIII.
16. A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. i Teor. Fiz.*, **39**, 1781 (1960); *Soviet Phys., J.E.T.P.*, **12**, 1243, (1961).
17. C. F. Ratto and A. Blandin, *Phys. Rev.*, **156**, 513, (1967).
18. A. B. Kaiser, *J. Phys.*, C **3**, 409, (1970).
19. L. I. Isaacs, D. J. Lam and F. Y. Fradin, to be published in Proceedings of Magnetism and Magnetic Materials Conference (Miami, Nov. 1970).
20. T. Sugawara and H. Eguchi, *J, Phys. Soc. Japan*, **21**, 725, (1966).
21. T. Sugawara, *J, Phys. Soc. Japan*, **20**, 2252, (1965).
22. M. B. Maple, J. G. Huber, B. R. Coles and A. C. Lawson, *J. Low Temp. Physics*, **3**, 137, (1970).
23. J. G. Huber and M. B. Maple, *Solid State Comm.* **8**, 1987 (1970).
24. See also E. Müller-Hartmann and J. Zittartz, *Phys. Rev. Lett.* **26**, 428 (1971) and W. Gey and E. Umlauf *Z. Physik* **242**, 241 (1971).
25. B. Coqblin and J. R. Schrieffer, *Phys. Rev.*, **185**, 847, (1969).

DIFFERENT EFFECT OF CERIUM AND GADOLINIUM IMPURITIES ON THE PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF LANTHANUM*

B. Coqblin and C. F. Ratto†
Laboratoire de Physique des Solides, Faculté des Sciences, Orsay, France
(Received 1 July 1968)

The different effect of cerium and gadolinium impurities on the pressure dependence of the superconducting transition temperature of lanthanum is due to different electronic structures of the rare-earth impurity. The ionic model explains the properties of gadolinium alloys, while the resonant scattering theory explains those of cerium alloys.

The superconducting transition temperature T_c for solid solutions of cerium and gadolinium in lanthanum has been recently measured as a function of pressure.[1] The plot of T_c versus the impurity concentration c at different pressures gives straight lines (at least for small concentration) shown in Fig. 1. Their slope is almost independent of the pressure in La:Gd ($dT_c/dc = -400°K$), while it is strongly varying with pressure in La:Ce: $dT_c/dc = -170°K$ at normal pressure, $-240°K$ at 5 kbar, and $-320°K$ at 10 kbar.

Moreover, the La:Ce alloys show a resistivity minimum at very low temperatures, while the La:Gd alloys do not show it.[2]

The theoretical explanation of these experiments comes from the model recently developed for rare-earth metals and alloys[3] and from the Schrieffer-Wolff transformation.[4] If one writes the interaction Hamiltonian between the localized spins $\vec{S}$ on impurity sites and the spins of conduction electrons $\vec{s}$,

$$H = -J\vec{s}\cdot\vec{S}, \tag{1}$$

there are in fact two mechanisms contributing to the value of J: (1) There always exists the normal exchange-scattering mechanism.[5] It gives a positive and almost pressure-independent value J_1 for J.[1] (2) Moreover, when the energy level of $4f$ electrons coming from the rare-earth impurity is close enough to the Fermi level, there is an important mixing between localized $4f$ electrons and conduction electrons. The interaction (1) is produced by a mechanism of resonant scattering of the conduction electrons by the localized potential of the $4f$ electrons. Here we call E the distance between the $4f$ energy level and the Fermi level and V_{kf} the matrix element of mixing between localized $4f$ electrons and conduction electrons. Schrieffer and Wolff[4] have shown that, in the limit of small V_{kf} and large Coulomb repulsion integral U, the resonant scattering mechanism leads to an interaction given by (1) with a value J_2 for J:

$$J_2 = -2V_{kf}^2/E. \tag{2}$$

The second-order (in V_{kf}) formula (2) is valid when U is much larger than E and when E is not too small compared with V_{kf}. This expression is approximately still valid for cerium impurities, because V_{kf} is of the order of some hundredths of an eV, U of the order of several eV, and the $4f$ level lies some hundreths of an eV to $\frac{1}{10}$ eV below the Fermi level.[3]

The expression (1) is very appropriate for the study of the superconducting transition temperature in rare-earth alloys, but causes some concern for the study of the Kondo effect. A complete study of the Kondo effect in rare-earth alloys has been recently done by use of the Schrieffer-Wolff transformation and will be reported elsewhere,[6] but this work does not change the main physical conclusions of the present paper.

In general, the two mechanisms described here

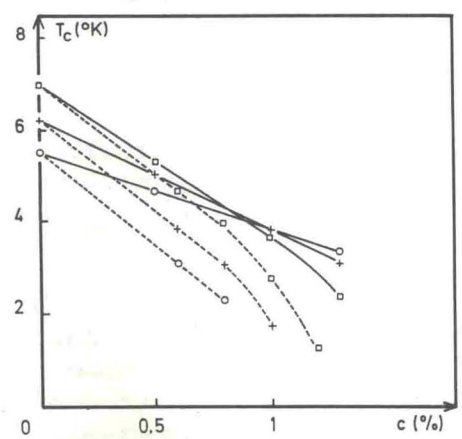

FIG. 1. Superconducting transition temperature versus impurity concentration at different pressures (after T. F. Smith). Dashed curve, La:Gd alloys; solid curve, La:Ce alloys. Circles, normal pressure; plus signs, 5-kbar pressure; squares, 10-kbar pressure.

contribute to the value of J:

$$J = J_1 + J_2. \tag{3}$$

The difference of behavior between La:Gd and La:Ce alloys is explained by the following argument:

(1) In La:Gd alloys, the gadolinium impurities behave as ions and the resonant scattering mechanism is negligible. J, equal to J_1, is positive and pressure independent. Its positive value is checked by the absence of a resistivity minimum at low temperatures.

(2) In La:Ce alloys, a $4f$ level is close to the Fermi level and the resonant scattering mechanism is more important than the normal exchange-scattering mechanism. The total J value is negative, which is checked by the presence of a resistivity minimum at low temperatures. Moreover, the Fermi level decreases and the $4f$ energy level does not change, when the pressure is applied.[3] E decreases and $|J|$ increases with the pressure.

The variation of the superconducting temperature with the concentration c of magnetic impurities is given by[7]

$$\frac{dT_c}{dc} = -\frac{\pi^2}{8}\frac{n(E_F)}{k_B}S(S+1)J^2, \tag{4}$$

where $n(E_F)$ is the density of states at the Fermi level of the conduction band for one spin direction.

The value of the density of states of the conduction band for pure lanthanum, deduced from specific heat data,[8] is $n(E_F) = 2.4$ states/eV atom. In fact, the conduction band is composed of both a $6s$ band and a narrow $5d$ band. Band calculations on yttrium,[9] which is similar to lanthanum, have shown that the d electrons contribute greatly to the total density of states. Furthermore, both $6s$ and $5d$ electrons participate to the superconductivity mechanism, but with different densities of states and different effective masses. One can surmise that the density of states coming into the formula (4) is certainly lowered from the 2.4 states/eV atom value. However, it is not possible to compute it exactly, in the absence of both a two-band calculation for superconductivity and also precise data on the band structure of lanthanum. So here we take two limiting cases: The first value is the total density of states $n(E_F) = 2.4$ states/eV atom, which gives a lower limit for $|J|$. The second value is a typical free-electron density of states $n(E_F) = 0.5$ states/eV atom, which gives an upper limit for $|J|$.

Here, we have made the reasonable assumption of keeping $n(E_F)$ constant with pressure. In fact, the relative variation of $n(E_F)$, as well as the relative variation of the value J_{Gd} of J for La:Gd alloys, is negligible compared with the relative variation of the value J_{Ce} of J for La:Ce alloys. So, the approximation of taking $n(E_F)$ constant with pressure is consistent with the preceding theoretical analysis. A study of the pressure dependence of the normal and superconducting properties of pure lanthanum is actually in progress and will be reported elsewhere.[10]

The calculation, by use of the expression (4), gives the following results: (1) For La:Gd alloys, J_{Gd} is constant with pressure, as expected, and of the order of 1/20 eV, in good agreement with previous calculations.[5] (2) For La:Ce alloys, J_{Ce} is negative and of the order of 0.1-0.2 eV. This anomalously large value J for cerium impurities is in good agreement with all the preceding calculations on rare-earth alloys.[2,11] In order to determine the position E of the $4f$ level in La:Ce alloys and its variation dE between the normal pressure and 10 kbar, we take J_1 equal to the constant value J_{Gd} and we express E as a function of the Hartree-Fock half-width Δ of the virtual bound state[3]:

$$\Delta = \pi n(E_F) V_{kf}^2. \tag{5}$$

Thus, the position of the $4f$ level is

$$\frac{E}{\Delta} = \frac{2}{n(E_F)|J_2|}. \tag{6}$$

Table I gives the different values of J, E, and dE, taking the half-width $\Delta = 0.02$ eV.[3] The values found for E, of the order of 0.05-0.1 eV, and dE, of the order of some 0.01 eV, are of just the same order of magnitude as previously obtained values for cerium.[3]

Thus, the simple argument developed here gives a fairly good explanation of the difference of behavior between La:Ce and La:Gd alloys. It is not possible to extrapolate the calculation to higher pressures, because the second-order calculation in V_{kf} of the Schrieffer-Wolff transformation is no longer valid, when E becomes very small.

However, we can suggest that these experiments should be continued at higher pressures in La:Ce alloys, in order to observe the disappearance of magnetism and the Kondo effect and also a completely different behavior of T_c. Another

Table I. Values (in eV) of the exchange integral J for La:Ce and La:Gd alloys, of the position E of the $4f$ level, and its variation dE under a 10 kbar pressure in La:Ce alloys. Calculations are done with two densities of states, $n(E_F)=2.4$ and 0.5 states/eV atom, and with a half-width $\Delta=0.02$ eV. (Between brackets the pressures p are expressed in kbar.)

	$J_{Gd}=J_1$ (eV)	$J_{Ce}(p=0)$ (eV)	$J_{Ce}(p=10)$ (eV)	$E(p=0)$ (eV)	$E(p=10)$ (eV)	$dE=E(p=0)-E(p=10)$ (eV)
$n(E_F)=2.4$ states/eV atom	0.03	−0.08	−0.11	0.05	0.04	0.01
$n(E_F)=0.5$ states/eV atom	0.06	−0.18	−0.24	0.11	0.085	0.025

similar system, the Y:Ce alloys,[11] which are not superconductors, would also be very interesting to study at very high pressures. Both La:Ce and Y:Ce alloys show a Kondo effect and are good candidates to study experimentally the transition from magnetism to nonmagnetism at very high pressures when E becomes zero. This study would relate directly to all the recent theoretical developments on the Kondo effect.

We gratefully acknowledge discussions with Professor A. Blandin.

*Work part of thesis for degree of Doctorat d'Etat, to be submitted by C. F. Ratto to the Faculté des Sciences d'Orsay.

†On leave of absence from the Istituto di Fisica dell' Università, Genova, Italy. Partially supported by Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Rome, Italy.

[1]T. F. Smith, Phys. Rev. Letters 17, 386 (1966).

[2]T. Sugawara and H. Eguchi, J. Phys. Soc. Japan 21, 725 (1966).

[3]B. Coqblin, thesis, Orsay, 1967 (unpublished); B. Coqblin and A. Blandin, Advan. Phys. 17, 281 (1968).

[4]J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966); J. R. Schrieffer, J. Appl. Phys. 38, 1143 (1967).

[5]P. G. de Gennes, J. Phys. Radium 23, 510 (1962).

[6]B. Coqblin and J. R. Schrieffer, to be publsihed.

[7]A. A. Abrikosov and L. P. Gorkhov, Zh. Eksperim. i Teor. Fiz. 41, 569 (1961) [translation: Soviet Phys. −JETP 12, 1243 (1961)]; S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).

[8]K. Andres, Phys. Rev. 168, 708 (1968).

[9]T. L. Loucks, Phys. Rev. 144, 504 (1966).

[10]B. Coqblin and C. F. Ratto, to be published.

[11]T. Sugawara, J. Phys. Soc. Japan 20, 2252 (1965)