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Pressure Dependence of the Kondo Resistance Anomaly and the Pair Breaking Effect in La-Ce Alloys

W. GEY
Physikalisches Institut der Universität Karlsruhe

E. UMLAUF
Zentralinstitut für Tieftemperaturforschung
der Bayerischen Akademie der Wissenschaften, Garching

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The pressure dependence of the pair breaking effect and of the resistance anomaly was measured in LaCe alloys. The results indicate that the maximum in the pressure dependent pair breaking effect is due to a monotonic shift of the Kondo temperature T_k with pressure from values $T_k \ll T_{c0}$ to $T_k \gg T_{c0}$, where T_{c0} is the superconducting transition temperature of pure lanthanum.

Introduction

Measurements of the superconducting transition temperature T_c of La-Ce alloys by Smith[1] have shown that the depression of T_c by paramagnetic impurities of concentration c is pressure dependent. Coqblin and Ratto[2] have explained this effect by assuming a pressure dependent enhancement of the exchange parameter $|J|$, defined by the Hamiltonian $H = -J\boldsymbol{S} \cdot \boldsymbol{\sigma}$ where $\boldsymbol{S}$ and $\boldsymbol{\sigma}$ are the spins of the localized impurity and the conduction electron, respectively. Referring to the theories of Zuckermann[3] and Müller-Hartmann and Zittartz[4], a relative maximum of $\Delta T_c/\Delta c$ has been predicted as a function of pressure[5]. According to these theories $\Delta T_c/\Delta c$ is a function of T_k/T_{c0} (T_k=Kondo Temperature, T_{c0}=superconducting transition temperature of the host metal), and the maximum of $\Delta T_c/\Delta c$ corresponds to a certain value of $T_k/T_{c0} = \vartheta$ which amounts to $\vartheta \simeq 2$ (Ref. [3]) or $\vartheta \simeq 12$ (Ref. [4]). For a Kondo alloy with $T_k \ll T_{c0}$ (at zero pressure) the depression of the transition tempera-

1 Smith, T. F.: Phys. Rev. Letters **17**, 386 (1966).
2 Coqblin, B., Ratto, C. F.: Phys. Rev. Letters **21**, 1065 (1968).
3 Zuckermann, M. J.: Phys. Rev. **168**, 390 (1968).
4 Müller-Hartmann, E., Zittartz, J.: Z. Physik **234**, 58 (1970).
5 Umlauf, E.: In: Sommerschule für Supraleitung. Steibis 5.–10. Oct. 1969, ed. by Universität Köln.

ture $\Delta T_c(p) = T_{c0}(p) - T_c(p)$ is thus expected to have a maximum if the Kondo temperature is shifted monotonically to values $T_k \gg T_{c0}$ by application of pressure. The pressure p_m at the maximum should characterize the Kondo temperature $T_k(p_m) = \vartheta \cdot T_{c0}(p_m)$. Meanwhile Maple *et al.*[6,7] have found such a maximum of $\Delta T_c(p)$ in La-Ce. Their explanation, however, is based on the assumptions that, with gradual application of pressure, ΔT_c first increases as a consequence of an increase in $|J|$ and then decreases because the Ce ion undergoes a transition from a magnetic to nonmagnetic state. These authors already mention the possibility that such a transition may also be caused by the development of a quasi bound state as a consequence of an increase in the Kondo temperature; or that, alternatively, the decrease in ΔT_c may reflect the gradual onset of magnetic order at higher pressure. Although the present understanding of the Kondo effect is still semiquantitative at best, it offers a quite natural explanation of the observed $T_c(p)$ variation. We have thus compiled further experimental information on this problem by measuring the pressure dependence of both the superconducting transition temperature and the resistance anomaly. From the latter a considerable increase of the Kondo temperature with pressure can be deduced.

Experimental Results

First the depression $\Delta T_c(c)$ at zero pressure was measured for several alloys with different Ce concentrations c. The results for the dhcp and the fcc phase are 1.22 ± 0.05 (K/at %) and 1.45 ± 0.05 (K/at %), respectively. From these data the Kondo temperatures can be calculated from the relation

$$\frac{\Delta T_c}{\Delta c} = \frac{1}{8 k_B N(0)} \frac{\pi^2 (S+1/2)^2}{(\ln T_k/12\, T_{c0})^2 + \pi^2 (S+1/2)^2} \cdot \left[1 + \frac{B\left[(\ln T_k/12\, T_{c0})/(S+1/2)\right]}{(S+1/2)^2}\right] \tag{1}$$

which is the main result of the theory of Ref.[4] where also a plot for the correction function B is given. Assuming $N(0) = 2.4\ \mathrm{eV}^{-1}$ (density of states)[8], $S = 1/2$ (spin of the Ce ion), $T_{c0} = 4.9$ K for dhcp La and $T_{c0} = 6$ K for fcc La, we find $T_k = 0.15$ and 0.20 K for the dhcp and the fcc phases, respectively.

It was also attempted to determine the Kondo temperature of a La 1% Ce alloy from resistance measurements down to 0.3 K. For the suppression of superconductivity a magnetic field of 8.5 kG is necessary

6 Maple, M. B., Kim, K. S.: Phys. Rev. Letters **23**, 118 (1969).
7 Maple, M. B., Wittig, J., Kim, K. S.: Phys. Rev. Letters **23**, 1355 (1969).
8 Andres, K.: Phys. Rev. **168**, 708 (1968).

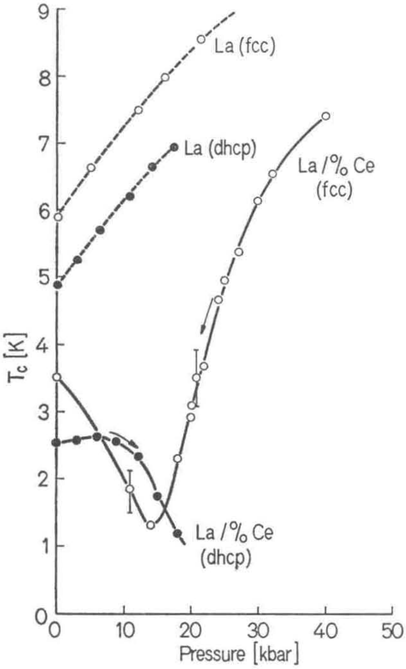

Fig. 1

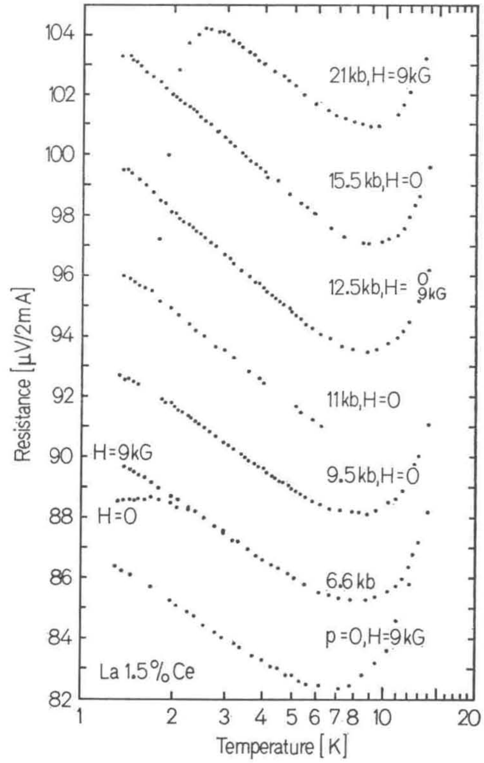

Fig. 2

Fig. 1. Pressure dependence of the superconducting transition temperature of pure La (Maple *et al.*[7]) and of La 1% Ce (present work)

Fig. 2. Variation of the Kondo resistance anomaly in La 1.5% Ce with pressure

for this alloy. We observed that the R vs. $\ln T$ curve already reached a plateau at 0.3 K and that upon further increase of the field to 12 and 15 kG, the plateau changes over into a maximum. The onset of the maximum was shifted to higher temperatures and the level was depressed. So we infer that the resistance curve at low temperatures is strongly influenced by a magnetic field. A determination of T_k by resistance measurements seems in principle, therefore, to be impossible for low concentration LaCe alloys.

The pressure experiments were performed in an apparatus described earlier[9]. Samples with dimensions of $0.02 \times 0.2 \times 2$ mm required for these experiments were prepared by cold rolling. Due to this preparation

9 Buckel, W., Gey, W.: Z. Physik **176**, 336 (1963).

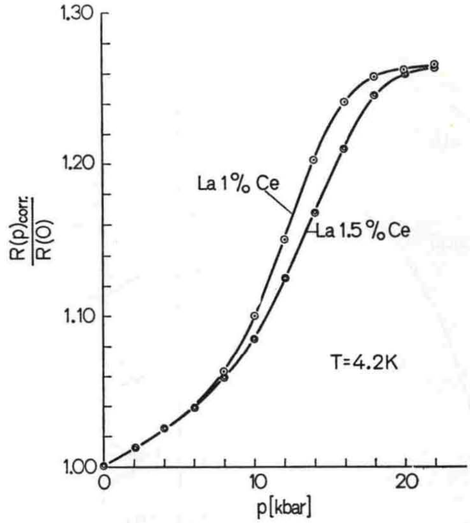

Fig. 3. Pressure dependence of the resistance of La 1% Ce and La 1.5% Ce at 4.2 K

the transition temperature decreases. For pure La Schwidtal[10] has found a decrease of 0.3 K. The LaCe alloys measured in this work showed a considerably greater depression of T_c (approximately 1 K).

Similar discrepancies are known for the effect of pressure on T_c in La[7]. In Fig. 1 we show as an example, the behaviour of $T_c(p)$ of our dhcp La 1% Ce alloy which is pressurized at liquid helium temperature. After an initial increase of T_c, which is due to the increase of T_{c0} for pure La, the growing pair-breaking effect dominates and leads to a drop in T_c which could be recorded up to 18 kbar. Because of the transformation into the fcc phase at ca. 20 kbar, the pressure was increased immediately to 40 kbar; and the sample was then warmed up to room temperature to have the phase transformation as complete as possible. Then T_c was measured with decreasing pressure. In accordance with the measurements of Maple *et al.* the depression of T_c has its maximum at 14 kbar.

To test whether a pressure dependence of the Kondo temperature $T_k(p)$ appears, two procedures have been used. At first the normal resistance $R(T)$ was measured at different pressures. It is found that $R(T)$ always exhibits a minimum near 8 K and then shows a linear increase with $\ln T$ down to 1.5 K, or the lowest temperature to which superconductivity can be suppressed by 9 kG, the maximum field

10 Schwidtal, K.: Z. Physik **169**, 564 (1962).

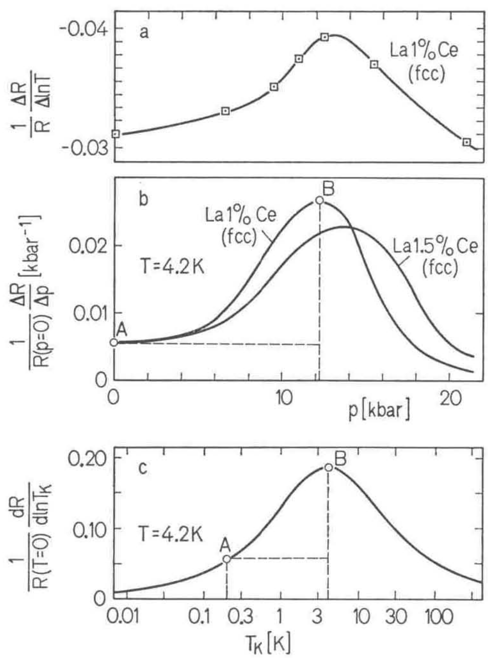

Fig. 4. a) Slope of the low temperature resistivity versus pressure of La 1.5% Ce. b) Differential resistivity increase at a fixed temperature (4.2 K) versus pressure. c) Plot of Eq. (4) differentiated with respect to ln T_k, with $T=4.2$ K

applicable in our pressure device. In Fig. 2 we show data on the 1.5% Ce alloy which has also been transformed to the fcc phase at 40 kbar and 300 K. A characteristic change in slope $\Delta R/\Delta \ln T$ is observed, which is plotted in Fig. 4a*. Its consequences for $T_k(p)$ will be discussed below. Note the maximum at 13 kbar.

The second procedure determining $T_k(p)$ makes use of the drastic increase of the resistance with pressure already seen in Fig. 2. We have investigated this effect for both samples in more detail at a fixed temperature of 4.2 K. The measured resistance curves $R(p)$ contain the pressure dependence of the resistance of the pure La lattice, which consists of a reversible and an irreversible part. These two parts were determined separately by an equivalent experiment on pure La and accounted for in plotting $R(p)/R(0)_{\text{corr}}$ in Fig. 3. Graphic differentiation yields the bell-shaped curves of Fig. 4b with maxima near 12 and 14 kbars, respectively.

* It was verified experimentally that a field of 9 kG has no measurable influence on the slope (Fig. 2, 6.6 and 12.5 kbar).

Discussion

In LaCe alloys the Kondo effect arises from a mixing of the localized $4f$ electron with conduction electron states. The $4f$ level lies a small energy E below the fermi level so that the resonance scattering mechanism dominates the normal exchange scattering. Consequently the effective exchange parameter J_{eff} is negative. According to the Schrieffer-Woolf transformation it is given by

$$J_{\text{eff}} = |V_{kf}|^2/E \tag{2}$$

where V_{kf} is the matrix element of mixing between $4f$ electrons and conduction electrons.

With the application of pressure, the energy difference E becomes smaller and, assuming a nearly constant mixing parameter V_{kf}, the exchange parameter $|J_{\text{eff}}|$ increases. Therefore, when the pair breaking effect is treated only in the Born approximation[2], the depression of the superconducting temperature ΔT_c increases as

$$\Delta T_c = -\frac{c \cdot \pi^2}{8 k_B} N(0)\, S(S+1)\, J_{\text{eff}}^2 . \tag{3}$$

Due to Maple *et al.*[6,7] the $4f$ level eventually overlaps the Fermi level upon further application of pressure, initiating a transition from a magnetic to a nonmagnetic impurity state, which causes a decrease in the pair breaking effect at higher pressures.

In what follows, we will discuss the experimental facts which indicate, in our opinion, that the maximum in ΔT_c follows from the above mentioned theories of Zuckermann or Müller-Hartmann and Zittartz, in which, as a main result, ΔT_c exhibits a maximum by its relationship to T_k/T_{c0} when T_k increases monotonically from values of $T_k \ll T_{c0}$ to $T_k \gg T_{c0}$. For the increase of T_k the same model given above is used (Eq. (2)). However, the transition of the cerium ion from a magnetic to a nonmagnetic state is not needed for this discussion; it may arise at higher pressures.

First we point out that the maximum of ΔT_c is found at about 13 kbar, whereas the resistance anomaly, typical for the Kondo effect, still exists, at least up to 21 kbar, i.e. the Kondo effect is still present (Fig. 2).

For a more detailed discussion of the resistance anomaly we consider Hamann's expression[11]

$$\frac{R(T/T_k)}{R(0)} = \frac{1}{2}\left[1 - \frac{\ln T/T_k}{|(\ln T/T_k)^2 + \pi^2 S(S+1)|^{1/2}}\right]. \tag{4}$$

11 Hamann, D. R.: Phys. Rev. **158**, 570 (1967).

One sees immediately that, at a fixed temperature T_0, the slope of the R vs. $\ln T$ curve goes through a maximum if the Kondo temperature T_k, which is less than T_0 at zero pressure, increases with pressure and finally exceeds T_0. This was observed in our experiments and is shown in Figs. 2 and 4a. Further, under the same conditions, it is easily deduced from Eq. (4) that, at a fixed temperature T_0, the resistance varies monotonically with T_k, showing a turning point when T_k equals T_0. As seen in Fig. 3, such a behaviour was also observed in our experiments for the pressure dependence of $R(p)$ at T_0 (Fig. 3). This correlation again is most naturally explained by a continuous increase of T_k with pressure. To illustrate this, and to compare it with the results of the first procedure given in Fig. 4a, we have plotted both the derivatives of the measured curves, i.e. $1/R(p=0) \cdot \Delta R/\Delta p$ at 4.2 K and of the theoretical function (Eq. (4)), i.e. $1/R(T=0) \cdot dR/d \ln T_k$ at 4.2 K, in Figs. 4b and c, respectively. The maxima in Fig. 4b are again located near 13 kbar.

Comparison with Fig. 4c shows, as marked by points B, that a pressure of approximately 13 kbar has raised the Kondo temperature from 0.2 K (points A) to 4 K. The fact that the $R(p)$ curves do not coincide for both concentrations may be interpreted as due to a stronger interaction between the impurity spins at the higher concentration. In principle, an empirical function $T_k(p)$ can be determined from the theoretical and experimental curves in Fig. 4. However, one sees immediately that a simple relation like $\ln(T_k(p)/T_k(0)) = K \cdot p$, with $K = 0.50 \pm 0.05\ \text{kbar}^{-1}$, holds only in a limited pressure regime (about ± 5 kbar) around the maximum.

If one accepts the Hamann function as describing the resistance anomaly correctly, one then expects a slight curvature in the R versus $\ln T$ dependence, especially for zero pressure and for 21 kbar (Fig. 2). Because of the small temperature interval, bordered by the onset of superconductivity and lattice resistivity, this could not be resolved within experimental accuracy.

In Fig. 5 we summarize our results on the depression $\Delta T_c(p) = T_{c0}(p) - T_c(p)$. One notes that its magnitude is much larger than reported by Maple *et al.* for comparable Ce concentration, indicating a phase mixture or inhomogenity in their "as cast" samples. We mention that the measurements of Maple *et al.* show the largest decrease of $\Delta T_c(p)$ near 25 kbar, which might be interpreted by the transition to a non-magnetic state. However, since *we* see no such kink, it is most likely that it is due to the dhcp-fcc phase change in La. The maximum depression for our La 1% Ce alloy amounts to $\Delta T_{c\,\max} = 6.4$ K*, which is in

* If the depression of the transition temperature due to cold work is taken into account, the $\Delta T_{c\max}$ becomes 5.7 K.

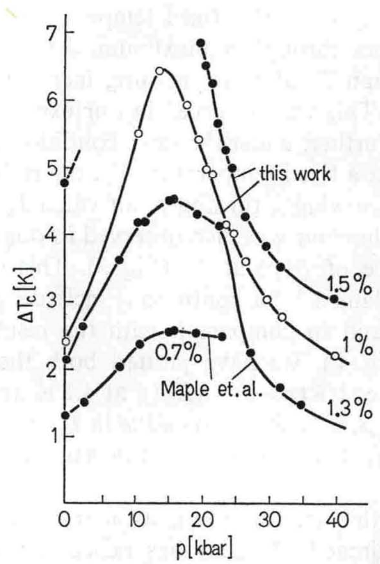

Fig. 5. Depression of the superconducting transition temperature in LaCe alloys under pressure. Numbers denote cerium concentrations. Samples with 1 and 1.5% Ce (this work) were fcc, those of Maple *et al.*[7] "as cast"

remarkable agreement with the theoretical value of 6.05 K, obtained from the formula of Müller-Hartmann and Zittartz[4]

$$\Delta T_{c\,\max} = -\frac{c}{8\,k_B\,N(0)}$$

with $N(0)=2.4\ \mathrm{eV}^{-1}$ [8]. Also the dependence on concentration c is qualitatively obeyed. We wish to mention here that the results of Fig. 1 and 4, according to which $T_k=4$ K and $T_{c0}=7.7$ K at 14 kbar, i.e. $\vartheta \simeq 0.5$ for maximum pair breaking are inconsistent with the theoretical predictions of $\vartheta \simeq 2$ (Zuckermann[3]) and $\vartheta \simeq 12$ (Müller-Hartmann and Zittartz[4]). It must be recalled, however, that the theoretical results hold for very low concentrations only, whereas at 14 kbar the concentration of 1% Ce is close to the critical concentration at which the order parameter vanishes. Here it is noteworthy that, according to a theory of Coqblin and Schrieffer[12], Ce alloys cannot be described exactly by the Hamiltonian $H=J\boldsymbol{S}\cdot\boldsymbol{\sigma}$ because of the strong spin-orbit interaction of the 4 *f* state. Taking this into account, but using the Born approximation only, they obtain for the decrease of T_c nearly the same result as Eq. (3).

12 Coqblin, B., Schrieffer, J. R.: Phys. Rev. **185**, 847 (1969).

To our knowledge the influence of resonance scattering on T_c has not been calculated with this Coqblin-Schrieffer Hamiltonian.

In conclusion, both the maximum in the depression of T_c and the results on the Kondo anomaly under pressure can be reasonably well correlated within existing theories, whereas no details, either experimental or theoretical, are known on the magnetic-nonmagnetic transition of the cerium ion in lanthanum lattices. While the results on the slopes of the R versus $\ln T$ curves may not fully permit an unambigous decision between both ways of interpretation, there is strong evidence from the continuous increase of the resistance in the pressure regime above 14 kbar that the maximum in pair breaking does not characterize the magnetic transition.

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Dr. Edgar Umlauf
Zentralinstitut für Tieftemperaturforschung
der Bayerischen Akademie der Wissenschaften
BRD-8046 Garching, Hochschulgelände
Deutschland

Univ.-Doz. Dr. Wolfgang Gey
Physikalisches Institut
der Universität Karlsruhe
BRD-7500 Karlsruhe, Engesserstr. 7
Deutschland

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