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# KONDO EFFECT IN YCe UNDER PRESSURE

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The decrease of the electrical resistivity minimum in Y 1 at.% Ce with pressure is shown to be due to a monotonic shift of the Kondo anomaly to higher temperatures. At pressures at which the resistivity minimum has practically disappeared (30 kbar), the magnitude of the anomaly does not differ from its zero pressure value. Thus the concept of a magnetic–nonmagnetic transition of the Ce impurities in this pressure regime must be abandoned.

IN AN EARLIER paper we have shown that the Kondo temperature $T_K$ of <u>La</u>Ce increases upon application of pressure.[1] This result was derived from the pressure dependence of the superconducting transition temperature by applying the theory of Müller-Hartmann and Zittartz.[2] It was independently derived from the temperature dependence of the resistance $R$ at different pressures, and the variation of $R$ with pressure at constant temperature, using the calculation of Hamann.[3]

Similar measurements have been reported by other authors, who instead interpreted their results in terms of a magnetic–nonmagnetic transition of the Ce-impurities at pressures at which both the slope $dR/d \ln T$ and the superconducting pair-breaking effect decrease.[4] Particularly the disappearance of the resistance minimum of YCe under pressure has been presented as an argument for the vanishing magnetic moment of the cerium impurities.[5] This explanation has become widely accepted in the literature; review articles have already appeared.[6,7]

We have reinvestigated the pressure dependence of the resistance anomaly of Y 1 at.% Ce. In analogy with the results for <u>La</u>Ce and also for <u>Cu</u>Fe[8] we expected a shift of $T_K$ to higher temperatures with pressure. The experimental results clearly show that this is so. The Kondo temperature is raised from 17 K at zero pressure to approximately 110 K at 30 kbar, while the magnitude of the anomaly, is unchanged. Y 1 at.% Ce is advantageous because of its absence of superconductivity in the pressure regime used and its relatively high Kondo temperature at zero pressure, which permits the use of standard cooling techniques.

The measurements were taken using a piston-cylinder technique in a pair-of-tongs apparatus described earlier.[9] It is sensitive to ± 100 bar at zero pressure and can be cycled repeatedly up to 45 kbar. The use of steatite has proved to be a sufficiently hydrostatic medium.[10] Nevertheless to avoid excessive cold work on the samples, pressure was always applied at room temperature. Samples of pure yttrium (purity 99.9%, residual resistivity ratio $R_{300K}/R_{4K} = 7.8$) and Y 1 at.% Ce ($R_{300K}/R_{4K} = 3.1$) were mounted in series in the pressure cell and fed by the same current of 10.000$_5$mA. Voltages were measured with a Yokogawa Digital Voltmeter with a $\pm 0.1 \mu V$ sensitivity. The YCe alloy was prepared from a master alloy by induction melting on a cooled copper substrate in an atmosphere of high purity argon. Suitable sample sizes were obtained by cutting these slabs with a grinding wheel and polishing by hand to the desired thickness. The resistivity of the materials was determined from larger pieces of the same alloy. The dimensions were determined by means of a travelling microscope and micrometer and controlled by weighing the samples with an electronic microbalance. The resistivities of Y and Y 1 at.% Ce at 4.2 K are 11.8$\mu\Omega$cm and 31.6$\mu\Omega$cm, respectively.

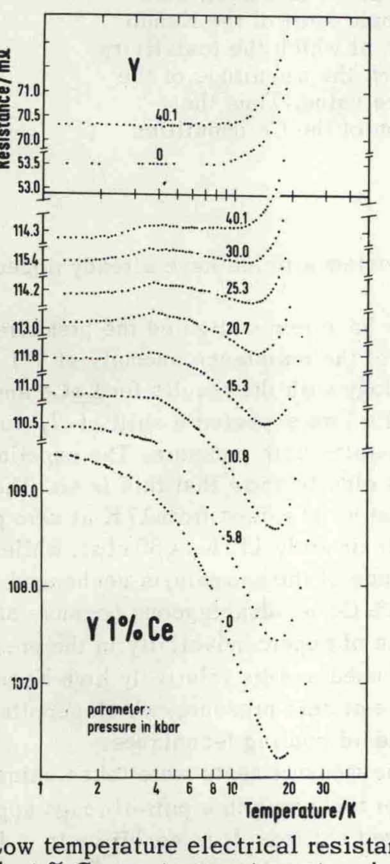


FIG. 1. Low temperature electrical resistance of Y and Y 1 at.% Ce vs. temperature at various pressures.

Figure 1 shows the resistance vs. ln $T$ for both Y and YCe as obtained directly in the low temperature regime. The Y sample shows normal behaviour at all pressures up to 40 kbar with measurable phonon resistivity beginning near 9 K. At low temperatures the phonon dependence is $T^{4.0}$ for all pressures. Only data for 0 and 40 kbar are given. The increase of residual resistivity from 0 to 40 kbar is large because of repeated pressure cycling between these pressures after a continuous run from 0 to 25.3 kbar.

The decrease with pressure of the depth of the resistivity minimum in YCe is qualitatively in accord with the results of Maple and Wittig.[5] The difference in the relative depth for 25 kbar is remarkable and may be due to a different pressure quotation. At zero pressure $\rho$(1K) – $\rho$(10K) is 0.58$\mu\Omega$cm in our measurements in accord with measurements of Sugawara and Yoshida[11] (normalized to 1 at.% Ce) but differing from the corresponding value of about 0.9$\mu\Omega$cm in reference 5. The minimum is shifted with pressure to lower temperatures. It is barely noticable at 30 kbar and has completely disappeared at 40 kbar. These pressure quotations are about half of those of Maple and Wittig. Similar to Y the low temperature resistivity plateau for YCe rises slightly with pressure. The value for 40.1 kbar is low because of a five days annealing at 300 K under this pressure. This indicates imperfections introduced during the application of pressure. Except for the starting zero pressure run, all curves show a kink near 3.8 K with a slightly depressed resistivity below 3.8 K. It is still observed after complete removal of pressure from 25.3 kbar, although the remaining low $T$ part of the curve is practically identical with the starting zero pressure run (not shown). Magnetic ordering upon application of mechanical stress may be suspected.

The gradual disappearance of the resistivity minimum with pressure and its shift to lower temperatures has actually led Maple and Wittig to conclude that the magnetic moment of the Ce impurity vanishes in this pressure regime. In contrast our results show that this is due to an increase of the Kondo temperature. In order to see this it is necessary to isolate the magnetic part of the temperature dependent resistivity from the phonon part at higher temperatures. This can be achieved as follows: near room temperature the magnetic part of the resistance is negligeably small, at least at low pressure, i.e. low Kondo temperatures. Thus the slope of a $R_Y$ vs. $R_{YCe}$-plot near 300 K determines the geometric factor $m$ between both samples. This factor does not change by more than 0.8% for all pressures up to 25.3 kbar. Assuming the constancy of the residual resistance up to room temperature (i.e. Matthiessen's rule) and that the $T$-dependance of the phonon part of the resistance is identical for YCe and Y, one obtains the magnetic resistance anomaly.

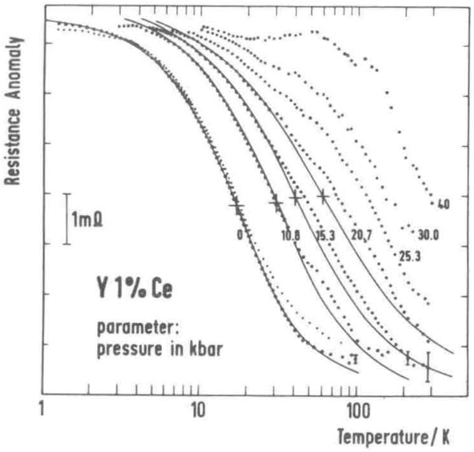


FIG. 2. The magnetic part of the resistance of Y 1 at.% Ce at various pressures and some fitted curves (solid lines) calculated from equation (1).

Figure 2 shows the result of this procedure. The main physical result is that an application of pressure shifts the Kondo anomaly rather drastically to higher temperatures. One notes that for zero pressure[12] the resistance anomaly is rather well described by the Hamann function

$$\rho_m(T) = \tfrac{1}{2}\rho_m(0)\left\{1 - \frac{\ln T/T_K}{[\ln^2 T/T_K + \pi^2 S(S+1)]^{1/2}}\right\} \quad (1)$$

over two decades of temperature (solid line), The magnitude, as determined from the fit, is 7.8mΩ, or 7.1% of the total low temperature resistance. The point of inflection, i.e. the Kondo temperature $T_K$, is located at 17 ± 0.3 K, while the effective spin $S$ is approximately 0.11. It is known from the literature[13] that a fit of Hamann's expression requires considerably small effective spin values than the well known spins resulting from other measurements (0.5 for Ce). The smaller dots represent zero pressure data which were obtained after removal of pressure from 25.3 kbar. With increasing pressure a deviation from the Hamann type behaviour starts to develop above 30 K, which may be due to a deviation from Matthiessen's rule, as suggested by Loram *et al.* for CuFe, AuFe and CuAuFe alloys.[14]

This effect hinders an exact determination of the Kondo temperature, especially at pressures above 25 kbar, where it has become rather large. If this deviation from Matthiessen's rule were due to a single step in the residual resistance, as assumed by Loram *et al.*, then it should be possible to account for it from the data at higher temperatures. However, our 'step' appears to be rather broad. Also, the high temperature data become increasingly uncertain, due to the large phonon parts to be substracted (see error bars). The Hamann fits for higher pressures were thus obtained from the curvature of the data between 8 and 30 K. This regime appears free from disturbances and the data are relatively accurate. It turns out that the fits so obtained are in fair agreement with the high temperature experimental data. The fit parameters are given in the table below. While the

*Table 1. Fit parameters for the calculations of $\rho_m(t)$ from equation (1). Vertical sequence of data in accord with sequence in variation of pressure*

| $p$ (kbar) | $T_K$ (K) | $S$ | $\rho_m(0)$ ($\mu\Omega$cm) |
|---|---|---|---|
| 0 | 17 ± 0.3 | 0.11 | 2.26 |
| 5.8 | 21 ± 1 | 0.14 | 2.44 |
| 10.8 | 31 ± 1 | 0.16 | 2.46 |
| 15.8 | 40 ± 2 | 0.20 | 2.46 |
| 20.7 | 60 ± 3 | 0.25 | 2.44 |
| 25.3 | 80 ± 5 | 0.20 | 2.55 |
| 0 | 17 ± 0.5 | 0.11 | 2.26 |
| 30 | 110 ± 15 | 0.20 | 2.32 |
| 40 | (140 ± 40) | (0.20) | 2.32 |

magnitude of the anomaly $\rho_m(0)$ stays close to 8mΩ (2.3μΩcm) up to 30 kbar the Kondo temperature rises to approximately 110 K. Adjustment of the effective spins is necessary.

It must be emphasized that a transformation of the Ce impurities to a nonmagnetic state should result in a decrease of the resistivity at $T = 0$ of roughly $\rho_m(0)$. This actually does not appear either in our measurements (see Fig. 1) or in those of Maple and Wittig.[5] Sugawara and Yoshida[11] deduce a Kondo temperature $T_K = 40\,\mathrm{K}$ from resistance measurements on YCe applying the formula

$$\rho_m(T) = \rho_m(0)\,[1 - (T/T_K)^2], \qquad (2)$$

but the experimental data are well expressed by equation (2) only below 5 K.

We have also observed the pressure dependance of the anomaly in an isothermal experiment, i.e. we have measured $R(p)$ at constant temperatures. Several pressure runs have been made in small steps up to 44 kbar at 4.2, 70 and 300 K. No indication of a magnetic–nonmagnetic transition has been observed in the high pressure part of the resistivity. However, for all these temperatures there is a maximum in resistivity near 1.5 kbar for Y. Depending on its pressure history, the YCe alloy occasionally exhibited this effect in the two lower temperature runs. We will report on this elsewhere.

The data for 30 and 40 kbar have actually been obtained after this repeated pressure cycling. It was observed that the geometric factor $m$ between the two materials has decreased by 5%, which we attribute to a slight cell deformation at the highest pressures. For 40 kbar $m$ depends in a nonsystematic manner on temperature. Probably slight deformations of the cell occur during warming up at this high pressure. The data for 40 kbar in Fig. 2 must thus be considered with reservation above 40 K. Also, for this pressure the data for the Kondo anomaly quoted in the table become rather inaccurate.

In the theoretical model, first discussed by Coqblin and Ratto[15] for LaCe, the $4f$ level lies a distance $E_f$ below the Fermi energy $E_F$ and the effect of pressure is to shift the $4f$ level up relative to the Fermi level. Calling $V_{kf}$ the maxtrix element of mixing between localized $4f$ electrons and the conduction electrons, the result of the Schrieffer–Wolff transformation[16] for the exchange integral $J$ is:

$$J = 2\,V_{kf}^2/|E_f|. \qquad (3)$$

Equation (3) is valid in the limit of a large Coulomb repulsion integral $U \gg |E_f|$ and in the limit $|E_f| \gg \Delta$, where $\Delta$ is the Hartree–Fock half width of the virtual bound state:

$$\Delta = \pi N(0)\,V_{kf}^2. \qquad (4)$$

Thus the position of the $4f$ level is given by

$$E_f = 2\Delta/\pi N(0)J. \qquad (5)$$

Taking $\Delta = 0.02$ eV,[15] $T_F = 75000\,\mathrm{K}$[17] and $N(0) = 2.15\,\mathrm{eV}^{-1}$,[18] we can calculate $J$ and $E_f$ as a function of pressure from (6)

$$T_k = T_F^{\,1/N(0)J}. \qquad (6)$$

The results given in Table 2 show that at 30 and 40 kbar the energy $|E_f|$ is still about $4\Delta$. Consequently no transformation from a magnetic to a nonmagnetic state is to be expected from this model, within the quoted pressure range.

Plotting $\ln T_k(p)/T_k(0)$ vs. $p$ (with the data from Table 1) a straight line up to 30 kbar is found (the value at 40 kbar lies somewhat below this line) which demonstrates that the assumption of a linear decrease of $|E_f|$ with pressure is justified and $dE_f/dp = 0.0008$ eV/kbar up to 30 kbar.

*Table 2. Values of* $E_f$ *and* J *deduced from the experimental values of* $T_k$ *(with* $N(0) = 2.15\,eV^{-1}$, $T = 75000\,\mathrm{K}$ and $\Delta = 0.02\,\mathrm{eV}$)

| $p$ (kbar) | $\lvert E_f\rvert$ (eV) | $J$ (eV) |
|---|---|---|
| 0 | 0.107 | −0.055 |
| 30 | 0.083 | −0.071 |
| 40 | (0.080) | (−0.074) |

In conclusion, a monotonic shift of $T_k$ and no magnetic–nonmagnetic transition were observed. Such a transition has been inferred by several authors[4–6] from the nonmonotonic depression of the superconducting transition temperature $T_c$ and from the maximum of the slope $|d\rho_m/d\ln T|$ with pressure on LaCe and other Ce-alloys. We note that the described result on YCe strongly supports our earlier results on LaCe alloys.

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Die Abnahme des Minimums im spezifischen elektrischen Widerstand von Y 1 at.% Ce unter Druck ist die Folge einer monotonen Verschiebung der Kondo-Anomalie zu höheren Temperaturen. Im Druckbereich, in dem das Widerstandsminimum praktisch verschwunden ist (30 kbar), unterscheidet sich die Größe der Anomalie nicht von dem Wert bei Druck null. Damit muß das Konzept einer magnetisch–nichtmagnetischen Umwandlung der gelösten Ce-Atome in diesem Druckbereich aufgegeben werden.