EFFECT OF PRESSURE AND HYDROGENATION ON THE THERMOELECTRIC POWER OF CERIUM COMPOUNDS.

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1. Introduction to the thermoelectric power of Cerium systems.

It is well known that the transport properties are very useful for the study of the electronic structure of different systems. The thermoelectric power has been extensively studied in Cerium, Ytterbium or other anomalous rare-earth systems and also in Uranium or other actinide systems.

Very large values of the thermoelectric power S have been observed in compounds such as $CeAl_3$ (1)(2), $CeCu_2Si_2$ (3) or $YbCu_2Si_2$ (4). A review of many experimental data on the thermopower of Cerium or Ytterbium compounds or alloys can be for example found in ref. (5). At sufficiently high temperatures, S is generally positive in Cerium compounds and negative in Ytterbium compounds. The thermoelectric power S of $CeAl_3$ presents a large positive peak at roughly 60 K (1), but S decreases with decreasing temperature and another positive peak is observed at the very low temperature of 0.1 K after passing through a weak negative minimum at roughly 4 K (2).

The thermoelectric power S=f(T) of Cerium Kondo compounds has been firstly studied theoretically in a "high temperature" model, i.e. for temperatures T larger than the Kondo temperature T_K (6). This model has been performed by using the Coqblin-Schrieffer Hamiltonian (7) and taking into account the crystalline field (CF) effects of the $4f^1$ configuration which were firstly introduced for the calculation

of the electrical resistivity (8). The model of ref. (6) yields a peak at a temperature typically of order $\Delta/3$-$\Delta/6$ where Δ is the overall CF splitting of the $4f^1$ configuration; in fact the preceeding result applies very well to the cubic case with only two levels split by CF effects or to the hexagonal case when the two excited levels are relatively close to each other (6). This model explains well the thermopower of many Ce or Yb compounds.

The thermoelectric power S has been more recently studied theoretically in the "low temperature" model, i.e. for temperatures T smaller than the Kondo temperature T_K (5). Below T_k, the system has a heavy-fermion behavior and is generally well described by a Fermi Liquid behavior with a peak at the Fermi energy in the density of states. It results that S has a positive (negative) peak in Cerium (or Ytterbium) compounds at a temperature roughly $T_K/2$ followed by a change of sign at roughly T_K. The presence of two peaks at roughly $\Delta/3$ and $T_K/2$ is well observed experimentally in compounds like $CeAl_3$ (1)(2) or $CeCu_2Si_2$ (3,9). This theoretical result is clearly considered as well established at present.

2. The Doniach diagram and the effect of pressure.

At first sight, the effect of pressure on Ce systems is to decrease the number n_f of 4f electrons and the opposite effect is observed in Yb systems. The well known case of Cerium metal shows a transition

with pressure from a magnetic f.c.c. γ-phase corresponding to a configuration $4f^1$ to a non magnetic f.c.c. α-phase with an intermediate valence or a number of 4f electrons clearly smaller than 1.

The case of Kondo compounds with n_f almost equal to 1 is well understood within the Doniach diagram shown in Figure 1 (10). The Kondo effect is described by the Hamiltonian $H = J_K \, \mathbf{s_c} \, \mathbf{S_f}$ of interaction between the spins $\mathbf{S_f}$ of the localized 4f electrons and the spins $\mathbf{s_c}$ of the conduction electrons, with a positive exchange integral J_K. The Kondo temperature T_{K0} is proportional to $\exp(-1/\rho J_K)$ and the Néel temperature T_{N0} without Kondo interaction is proportional to $|J_K|^2$. It results that the real Néel temperature T_N is passing through a maximum and tends to zero at the "quantum critical point" Q.
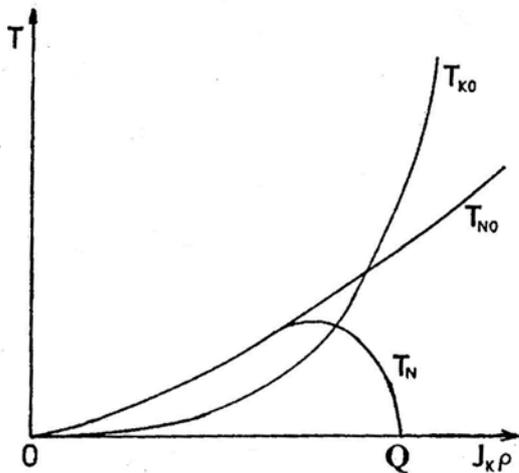

Fig 1. The Doniach diagram

The Doniach diagram (Fig. 1) separates Cerium Kondo compounds in magnetically ordered ones with a weak heavy-fermion behavior for ρJ_K values smaller than the critical value of Q and in non magnetic ones with a large heavy-fermion behavior (11). The effect of pressure is always to increase J_K and eventually to yield a transition from a magnetic order to a non magnetic heavy-fermion behavior.

The variation of the thermopower has been measured experimentally in many Cerium compounds and we present in Figure 2 the temperature dependence of the thermoelectric power of the compound $CeRu_2Ge_2$ under high pressures up to 15.6 GPa (12).

We have presented in ref. (12) a successful theoretical explanation of these results on the basis of the two models presented in refs. (5) and (6). In the classical model for heavy fermions, J_K is given by $J_K = |V_{kf}|^2/|E_f|$, where V_{kf} is the hybridization term between the localized 4f and conduction electrons and E_f is the 4f energy of the ground state with respect to the Fermi level. The detailed variation of the different parameters depends on the different considered models, but it is clear that the quantity J_K increases with pressure. In the model of ref. (12), there are two parameters, the CF splitting Δ which is taken constant with pressure and equal to $\Delta = 0.07$ eV and the quantity $\Gamma = \pi |V_{kf}|^2/W$, where W is the half-width of the conduction band. In our model, Γ varies from 0.06 eV to 0.2 eV from normal pressure to the high pressure of 15 GPa.
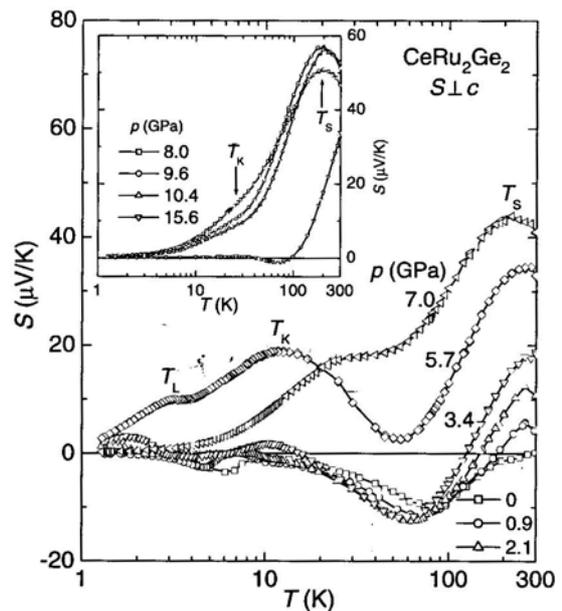

Fig 2. The pressure dependence of the thermoelectric power of $CeRu_2Ge_2$ (12).

We can account for the increase of S with pressure from a small value with two positive peaks separated by a negative minimum to finally a large positive value with only a positive maximum corresponding to roughly $\Delta/3$. Detailed of the different models can be found in refs (5,6,12,13).

3. The effect of hydrogenation.

An important research effort has been done to study the hydrogenation-induced changes of the properties of Cerium compounds and in fact hydrogenation gives different and even opposite effects in different cases.
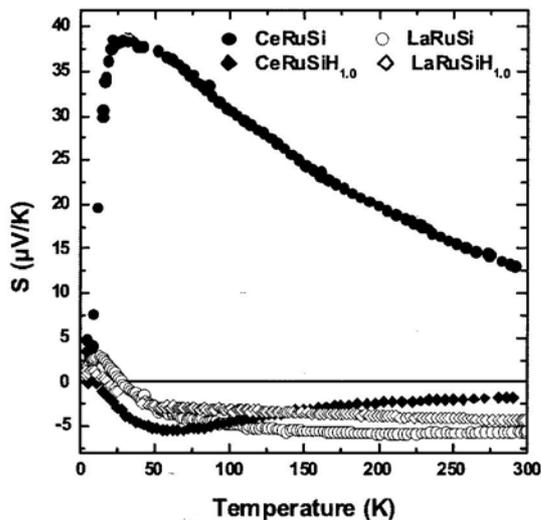

Fig 3. Temperature dependence of the thermoelectric power for CeRuSi, LaRuSi and their hydrides (14).

First, we present the case of the compound CeRuSi and the hydrogenated CeRuSiH$_{1.0}$ one (14). Figure 3 shows the thermoelectric power of these two compounds and their equivalent compounds with Lanthanum.

CeRuSi is a moderate heavy-fermion compound which has an electronic specific constant $\gamma=220$ mJ/mol K^2 and does not order magnetically at low temperature. On the opposite, the hydride CeRuSiH has a smaller value $\gamma=26$ mJ/mol K^2 and orders magnetically with two antiferromagnetic transitions at T$_{N1}=7.5$ K and T$_{N2}=3.1$ K, as evidenced by magnetization, specific heat measurements (14) and neutron powder diffraction (15). We see clearly that the hydrogenation has here an effect opposite to the effect of pressure and corresponds in the Doniach diagram to a decrease of the effective value of J$_K$ which gives a change from an heavy fermion behavior above the point Q of Figure 1 to a magnetically ordered system below this point Q.

We can analyze the data of S=f(T) again on the basis of the previously explained theoretical models. The thermoelectric power of CeRuSi has a maximum at a temperature roughly equal to half the value $\Delta = 45$ K of the crystal field splitting deduced from the resistivity measurements (14). In fact, S of CeRuSi looks like that of CeAl$_3$, which is, however, a much stronger heavy-fermion compound, and can be well accounted for by the previous calculation for T>T$_K$ (6).

On the other hand, the thermoelectric powers of the three compounds CeRuSiH, LaRuSi and LaRuSiH are negative and very small, of the order of only 5 μV/K. The thermoelectric power of CeRuSiH is very small but has a broad peak at roughly 60 K, which can yield a value of Δ typically of the order of 150-300 K, in rough agreement with the analysis of the electrical resistivity data (14).

Thus, the magnetic change of the compound CeRuSi under hydrogenation corresponds to a cell expansion or to an effect opposite to the application of pressure and the analysis of the thermoelectric power is in agreement with the theoretical model describing both the Kondo and CF effects.

But, in fact, the hydrogenation can have a completely opposite effect. Hydrogen insertion in CeCoSi and CeCoGe compounds leads to the transition from an antiferromagnetic order to a non magnetic spin fluctuation behavior and it appears that the presence of a strong Ce-H bonding

induces an intermediate valence state for CeCoSiH (16). In the temperature range 4.2–300 K, S of this hydride is always positive but presents a minimum at low temperature (S = 8 µV/ K near 30–35 K) and a broad peak at high temperature (S = 22 µV/K around 110 K). This behaviour can be qualitatively understood in terms of the model described in ref. (6).

4. Conclusions.

Thus, we have very briefly reviewed the effect of pressure and hydrogenation on Cerium compounds. The effect of pressure is clear and leads to an increase of J_K, yielding for example a transition from an antiferromagnetic order to a non magnetic heavy-fermion compound, as observed in $CeRu_2Ge_2$ and in many other Cerium compounds. On the other hand, the effect of hydrogenation is not so clear, as previously explained, but we can say that hydrogen insertion in the compound CeRuSi gives an expansion of the lattice and has consequently an effect opposite to that of pressure.

References.

(1) P. B. Van Aken, H. J. Van Daal and K. H. J. Buschow, Phys. Lett. **49A**, 201 (1974)
(2) D. Jaccard and J. Flouquet, Helv. Phys. Acta, **60**, 108 (1987)
(3) G. Sparn, W. Lieke, U. Gottwick, F. Steglich and N. Grewe, J. Mag. Mag. Mater. **47-48**, 521 (1985)
(4) K. Alami-Yadri, H. Wilhelm and D. Jaccard, Physica B **259-261**, 157 (1999).
(5) V. Zlatic, B. Horvatic, I. Milat, B. Coqblin, G. Czcholl and C. Grenzebach, Phys. Rev B **68**, 104432 (2003)
(6) A K. Bhattacharjee and B. Coqblin, Phys. Rev. B **13**, 3441 (1976).
(7) B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).
(8) B. Cornut and B. Coqblin, Phys. Rev. B **5**, 4541 (1972)
(9) D. Jaccard, J. M. Mignot, B. Bellarbi, A. Benoit, H. F. Braun and J. Sierro, J. Mag. Mag. Mater. **47-48**, 23 (1985)
(10) S. Doniach, in *Valence Instabilities and Related Narrow-band phenomena*, ed. by R.D. Parks, Plenum Press (1976) p.168.
(11) B. Coqblin, in *Lectures on the Physics of highly correlated electron systems X*, Salerno (October 2005), AIP Proceedings, **846**, pp. 3-93 (2006).
(12) H. Wilhelm, D. Jaccard, V. Zlatic, R. Monnier, B. Delley and B. Coqblin, J. Phys. : Condens. Matter **17**, S823 (2005).
(13) V. Zlatic and R. Monnier, Phys. Rev B **71**, 165109 (2005).
(14) B. Chevalier, E. Gaudin, S. Tencé, B. Malaman, J. Rodriguez Fernandez, G. André and B. Coqblin, Phys. Rev B **77**, 014414 (2008).
(15) S. Tencé, G. André, E. Gaudin and B. Chevalier, J. Phys.: Condens. Matter **20**, 255239 (2008).
(16) B. Chevalier, S. F. Matar, M. Ménétrier, J. Sanchez Marcos, J. Rodriguez Fernandez, J. Phys.: Condens. Matter **18**, 6045 (2006).