Thermoelectric power of cerium at high pressures

T G RAMESH, A S RESHAMWALA and S RAMASESHAN

Materials Science Division, National Aeronautical Laboratory, Bangalore 560017

Abstract. The electronic phase transition in cerium occurring near 7 kbar pressure at room temperature which is attributed to the 4f-5d electron promotion has been studied using thermoelectric power as a tool. The important results that have emerged out of this work are: (a) the relatively large variation in the absolute thermoelectric power of γ-cerium (normal fcc phase) with pressure prior to the phase transition (in contrast to the rather small resistivity change with pressure in this region); (b) a sharp decrease in the thermoelectric power accompanying the iso-structural γ-α phase transition; and (c) the continuous decrease in the thermoelectric power of α-cerium (collapsed fcc phase) with pressure, ultimately changing sign at higher pressures. An explanation based on the "virtual bound state" model is proposed to account for these results.

1. Introduction

The phase diagram of cerium is presented in figure 1 (Jayaraman 1965). At room temperature and atmospheric pressure, a well-annealed sample of cerium has the fcc structure (γ-phase) whereas a cold worked specimen is a mixture of the γ-phase and the β-phase which has a double hexagonal close packed structure. However, in this work we will be mainly interested in the pressure behaviour of the γ-phase. Lawson and Tang (1949) from their high pressure x-ray diffraction work established that the phase transformation near 7 kbar pressure at room temperature involves only a decrease in the lattice parameter without any change in symmetry. That the iso-structural γ-α transition is associated with the 4f-5d electron promotion was suggested by Zachariasen (quoted by Lawson and Tang 1949) and independently by Pauling (quoted by Schuch and Sturdivant 1950).

The γ-phase is paramagnetic with the Ce^{3+} ion cores carrying a magnetic moment corresponding to a total angular momentum of $J = 5/2$. The α-phase is assumed to comprise of Ce^{4+} ion cores with four conduction electrons per atom. Hall effect measurements on the γ and α phases (Gschneidner and Smoluchowski 1963) support the view that there is a definite change in the valency accompanying the transition. The α-phase is non-magnetic as the delocalisation of 4f electrons destroys the magnetic moment of the ion cores. This has been confirmed from neutron diffraction studies by Wilkinson et al (1961).

An extremely interesting feature of the cerium phase diagram (figure 1) is the termination of the γ-α phase boundary at a critical point. Beecroft and Swenson (1960) from their measurements on the lattice parameter decrease at various tempe-
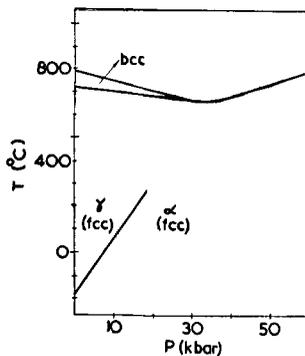
P—1

Figure 1. Phase diagram of cerium (Jayaraman 1965).

ratures suggested that the discontinuity should disappear near 20 kbar pressure and 630 K. Jayaraman (1965) confirmed this and from his studies on the resistivity variation of cerium with pressure at various temperatures established the existence of a critical point for the γ-α transition at about 550 K and 17·5 kbar pressure.

On the theoretical side Blandin *et al* (1965) have discussed the problem of the stability of the magnetic moments at high pressures. Their theory based on the "virtual bound state" model of Friedel (1956) or the equivalent "localised magnetic states" description of Anderson (1961) could account for the main features of the phase transition. Ramirez and Falicov (1971) have proposed an alternative mechanism wherein the Coulomb repulsion between the localised 4f electrons and the conduction electrons derived from the 6s–5d band is taken to be the driving force for the phase transition. Recently Alascio *et al* (1973) have extended the Ramirez-Falicov theory to include the effects associated with the hybridization of the localized 4f states with the conduction band. Their model could account for the Curie behaviour observed in the γ-phase and also for the magnitudes of the electronic specific heat, magnetic susceptibility and fractional valency of the α-phase.

The object of this paper is to report some new data on the variation of the absolute thermoelectric power of cerium with pressure. We present here our experimental results up to 20 kbar pressure in the temperature range 20-100° C. It is shown that these results can be accounted on the basis of the "virtual bound state" model of Friedel (1956).

2. Experimental

A teflon cell technique for the measurement of the absolute thermoelectric power of solid and liquid metals in the temperature range 0–250° C and up to 40 kbar pressure has been developed by Reshamwala and Ramesh (1974). The main features of this technique are (*a*) generation of truly hydrostatic pressure on the sample, (*b*) creation of a steady temperature gradient along the length of the sample, and (*c*) easy adaptability to solid or liquid metals.

Figure 2 presents the geometry of the thermo-power cell used in the present experiment. The specimen in bar form was pierced into the centre of a teflon disc and the assembly is inserted into a teflon cell container filled with silicone fluid. The teflon cell container, when used in conjunction with a piston cylinder device,
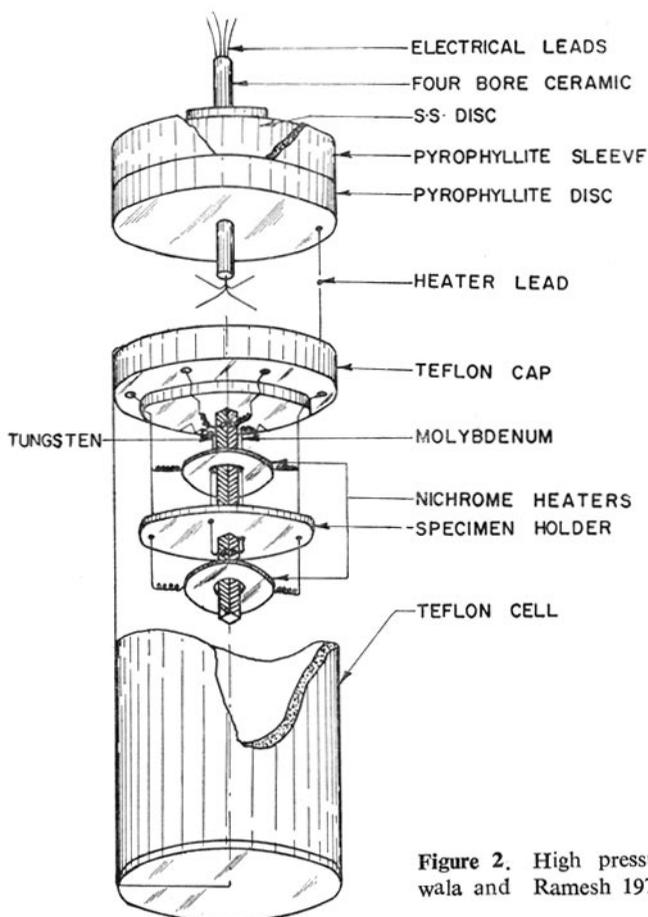
Figure 2. High pressure thermo-power cell (Resham-wala and Ramesh 1974).

acts as a pressure chamber where pressure is generated *in situ* by the advancing piston. The teflon disc effectively partitions the pressure chamber for the purpose of establishing a steady temperature gradient along the sample length by minimising convection mixing of the silicone fluid. The two compartments of the teflon cell container were heated differentially by two heaters of different resistances connected in parallel. It is also possible to operate the two heaters independently if required. This design of the thermo-power cell allows one to maintain temperature gradients from 0·5° to 10° C along the length of the specimen. Two sets of thermocouple probes, namely chromel-alumel and molybdenum-tungsten wires, were used in the present experiment. The thermocouple wires were either spot welded or crimpled on to the sample. These wires are taken out from the high pressure to the atmospheric pressure region using a procedure described by Jayaraman *et al* (1967).

The experimental method of measuring the thermo-power at high pressures has been discussed earlier (Reshamwala and Ramesh 1974). Briefly, the method consists in measuring the Seebeck e.m.f. $\triangle E$ developed in a thermocouple circuit consisting of the specimen and one of the thermocouple probes, say chromel, when a temperature gradient $\triangle T$ is maintained between the ends of the specimen. The

absolute thermo-power of cerium, Q_{ce}, is given by the relation

$$Q_{chromel} - Q_{cerium} = \triangle E / \triangle T . \tag{1}$$

The temperature difference $\triangle T$ can be measured accurately using the relation

$$\triangle T = \frac{\triangle E_{chromel-cerium} - \triangle E_{Alumel-cerium}}{Q_{chromel} - Q_{Alumel}} \tag{2}$$

The pressure effect on the chromel-alumel thermocouple is small (Bundy 1961) and hence is not corrected for in this work. However the effect of pressure on molybdenum-tungsten couple is considerable and has been taken into account using the data of Reshamwala and Ramesh (1974).

The thermoelectric voltages given in equations (1) and (2) were measured using a dc nanovoltmeter (Keithley Instruments Model 140). The measurements were taken under isobaric conditions at various temperatures of the specimen. The cerium metal used in these experiments was of high purity obtained from Research Chemicals, Inc (USA). In view of the possibility of both the γ (fcc) and β (dhcp) phases being present, the structure of the starting material was checked. X-ray diffractometer record confirmed that the starting material was completely γ-phase (fcc).

3. Results

Figure 3 presents the thermo-power variation with temperature at various pressures. The data points on these graphs were obtained using two different thermocouple probes, namely, chromel-alumel and molybdenum-tungsten wires. The
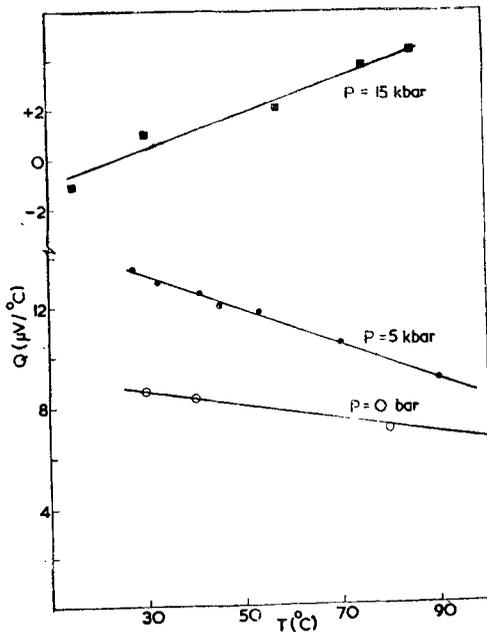

Figure 3. Variation of the thermo-power of cerium with temperature in the γ and α-phases.
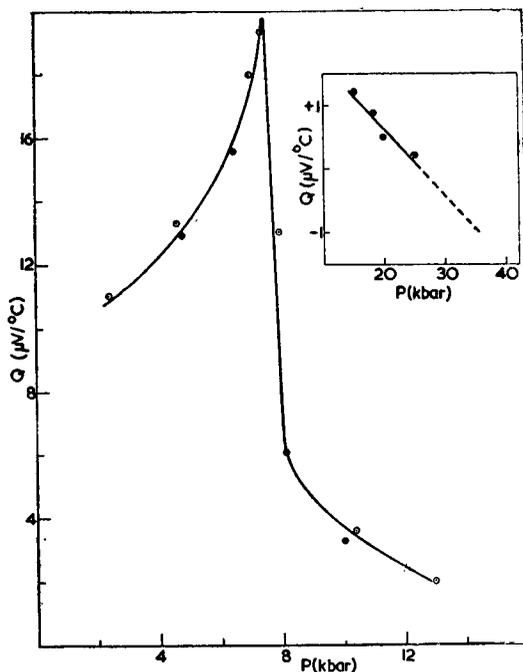
Figure 4. Thermoelectric power *versus* pressure graph for cerium metal at 30°C. ● — Data points obtained using molybdenum-tungsten thermocouple. ☉ —Data points obtained using chromel-alumel thermocouple.

experimental results in the α-phase region and at high pressures were derived mostly using the Mo — W thermocouple. This was necessitated by the much smaller magnitude of Q_{ce} ($\sim 0\cdot5\,\mu V/°C$) as compared with either $Q_{chromel}$ ($\sim +22\,\mu V/°C$) or Q_{Alumel} ($\sim -18\,\mu V/°C$). In the γ-phase region, $(dQ/dT)_p$ is negative and its magnitude becomes larger at higher pressures. It is interesting that in the α-phase, $(dQ/dT)_p$ changes sign. Further Q_{ce} also changes sign from positive to negative values at lower temperatures.

Figure 4 shows the behaviour of the thermoelectric power of cerium as a function of pressure at constant mean temperature of 30° C. The salient features of the experimental curve are briefly summarised below:

(i) In the γ-phase region, the pressure variation of the thermoelectric power is rather large leading to a cusp-like behaviour prior to the phase transition. This remarkable variation in the thermoelectric power from nearly $7\,\mu V/°C$ at atmospheric pressure to about $20\,\mu V/°$ C near the phase transition is in sharp contrast with the resistivity variation in the same region (Jayaraman 1965).

(ii) The first order γ-α phase transition associated with the delocalisation of 4f electrons manifests as a sharp decrease in the magnitude of the thermoelectric power of cerium.

(iii) In the α-phase region, there is a continuous decrease in the magnitude of the thermoelectric power with pressure leading to a change of sign at higher pressures. The pressure coefficient of thermoelectric power in this region is of the order of $-(0\cdot27)\,\mu V/°$ C kbar. The inset in figure 4 containing the pressure behaviour in the α-phase suggests that near 40 kbar pressure the value for Q_{ce} would be of the order of $-1\,\mu V/°$ C at 30° C.

4. Discussion

The electron diffusion thermoelectric power is given, quite generally, by the expression (McDonald 1962)

$$Q = -\frac{\pi^2 k^2 T}{3e}\left[\frac{d}{dE}\log n\,(E) + \frac{d}{dE}\log v^2\,(E) + \frac{d}{dE}\log \tau\,(E)\right]_{E_F} \tag{3}$$

Here e is the absolute magnitude of the elementary charge. $\tau(E)$ and $n\,(E)$ represent the relaxation time and the density of states evaluated at energy E respectively.

The pressure behaviour of the thermoelectric power of cerium metal can be understood on the basis of the Friedel-Anderson model (Friedel 1956, Anderson 1961) for localised magnetic states in metals. According to the model developed for γ-cerium, the six-fold degenerate 4f level ($J = 5/2$) is split by the intra-atomic Coulomb interaction and exchange such that one state lies below and the other five are above the Fermi level. The effect of pressure is to move the lower occupied 4f level towards the Fermi level and at the γ-α phase transition, this level shifts abruptly to a position above the Fermi level. Thus in the α-phase all the six sub-levels of the $J = 5/2$ state are above the Fermi level.

The thermoelectric power of γ-cerium even at atmospheric pressure is relatively large and positive of the order of $+ 7\,\mu V/^\circ C$ as compared with the value for the other rare earth metals which is of the order of $- 2\,\mu V/^\circ C$ at 300 K (Born *et al* 1961). This, we believe, is related to the proximity of the 4f state relative to the Fermi energy. The existence of a resonant state overlapping with the conduction band and lying just below the Fermi level has the effect of contributing an extra density of states at the Fermi level in addition to the regular band structure associated with the 6s-5d band. This extra density of states factor is given by the expression (Blandin *et al* 1965)

$$\rho_t\,(E) = \frac{1}{\pi}\frac{\triangle}{(E - E_t)^2 + \triangle^2} \tag{4}$$

where $\triangle$ represents the width of the virtual level and E_t corresponds to the renormalised energy of the 4f state lying below the Fermi level. It is clear from equations (3) and (4) that the virtual 4f level makes a contribution to the thermoelectric power which is proportional to $\left[\dfrac{d\,\rho_t\,(E)}{dE}\right]_{E_F}$

where

$$\left[\frac{d\rho_t\,(E)}{dE}\right]_{E_F} = -\frac{2}{\pi}\frac{\triangle\,(E_F - E_t)}{[(E_F - E_t)^2 + \triangle^2]^2} \tag{5}$$

The level width $\triangle$ is extremely small and is estimated from various studied to be around 10^{-2} eV (Huber and Maple 1970). Assuming $E_F - E_t \gg \triangle$, we have

$$\left[\frac{d\rho_t\,(E)}{dE}\right]_{E_F} \simeq -\frac{2}{\pi}\frac{\triangle}{(E_F - E_t)^3} \tag{6}$$

The contribution to the thermoelectric power due to the presence of the virtual level is given by

$$Q' \simeq \frac{2\pi k^2 T}{3e} \cdot \frac{1}{n\,(E)} \cdot \frac{\triangle}{(E_F - E_t)^3} \tag{7}$$

We note here that Q' is very sensitive to the position of the 4f state relative to the Fermi level and can even change sign. For $E_F - E_t \sim 0 \cdot 2$ eV and $n(E) \sim 2$ states/eV per atom, one gets $Q' \sim + 4\,\mu V/°C$. When $E_F - E_t \sim 0 \cdot 1$ eV, the magnitude of Q' is large of the order of $+ 20\ \mu V/° C$.

The pressure variation of the thermoelectric power of γ-cerium with regard to both magnitude and sign finds an explanation on the basis of the relation (7). In the entire γ-phase region of the phase diagram (figure 1), $(E_F - E_t)$ is positive so that Q' is positive and its magnitude becomes large with increasing pressure. The contribution to the thermoelectric power from the regular band structure of the 6s–5d band can be either positive or negative depending on the energy dependence of the electron relaxation time and the normal density of states at the Fermi level. We assume that as far as the pressure variation is concerned, the major contribution to the thermoelectric power comes from the Q' term. Due to lack of experimental data on the variation of the parameter $(E_F - E_t)$ with pressure, it is not possible to make a quantitative prediction of the thermoelectric behaviour of cerium under pressure. However, the large variation observed in the thermopower of γ-cerium especially as the transition pressure is approached can be understood as arising due to the increasing contribution of Q' towards the thermoelectric power.

The drastic decrease in the thermo-power accompanying the phase transition at 7 kbar pressure is mainly due to the delocalisation of the 4f electrons resulting in an enhancement of the conduction electron concentration. According to Thomson's point of view (McDonald 1962), the thermoelectric power can be thought of, crudely, as the electronic specific heat per conduction electron. Although the electronic specific heat constant in the α-phase is large due to the enhanced density of states at the Fermi level (Gschneidner 1965) this effect is masked by the additional contribution of nearly an electron per Ce atom to the conduction band.

The progressive decrease in the magnitude of Q_{ce} with pressure in the α-phase region can be explained by assuming that all the six sublevels of the 4f state, although they are located above the Fermi level, can still influence the transport properties. Based on a considerable amount of experimental evidence like the Hall effect measurements on γ and α-cerium (Gschneidner 1965) and the magnetic susceptibility measurements at high pressures (MacPherson *et al* 1971), a view that α-cerium is not really a four-valent metal has emerged. It is estimated that, on the average, about $0 \cdot 3$ electrons per Ce atom retain f character in the α-phase close to the phase transition. The effect of increasing pressure is to reduce this f character so that only near 40–50 kbar region cerium can be considered to be a true four-valent metal. We propose that the progressive decrease in the thermoelectric power of α-cerium leading to a change of sign near 20 kbar pressure as additional evidence in support of the fractional valency model for α-cerium described above. It may also be noted that in the entire α-phase region the contribution Q' is negative and accounts, qualitatively, for the change of sign in the thermo-power observed near 20 kbar pressure.

5. Conclusions

The thermoelectric behaviour of cerium metal has been studied in the temperature range 20–100° C and up to 25 kbar pressure. The main features of the experi-

mental thermoelectric power *versus* pressure graph have been qualitatively explained on the basis of the Friedel-Anderson model developed for cerium. The experimental results presented in this paper correspond to the first order γ-α phase transition. On the basis of the theoretical model, it appears that above the critical point where the position of the 4f level can be varied continuously as a function of lattice parameter, measurement of the thermoelectric power would be of great interest.

6. Acknowledgements

References

Alascio B, Lopez A and Olmedo C F E 1973 *J. Phys. F.* **3** 1324
Anderson P W 1961 *Phys. Rev.* **124** 41
Beecroft R l and Swenson C A 1960 *J. Phys. Chem. Solids* **15** 234
Blandin A Coqblin B and Friedel J 1965 in *Physics of solids at high pressures*, ed C T Tomizuka and R M Emrick (Academic Press, New York) p 233
Born H J Legvoild S and Spedding F H 1961 *J. Appl. Phys.* **32** 2543
Bundy F P 1961 *J. Appl. Phys.* **32** 483
Friedel J 1956 *Can. J. Phys.* **34** 1190
Gschneidner K A and Smoluchowski R 1963 *J. Less-common Metals* **5** 374
Gschneidner K A 1965 *Rare-earth Research* III, ed L Eyring (Gordon and Breach)
Huber J G and Maple M B 1970 *J. Low-temp. Phys.* **3** 537
Jayaraman A 1965 *Phys. Rev.* **137** 179
Jayaraman A, Hutson A R, McFee J H, Coriell A S and Maines R G 1967 *Rev. Sci. Instrum.* **38** 44
Lawson A W and Tang T Y 1949 *Phys. Rev.* **76** 301
McDonald D K C 1962 *Thermoelectricity* (John Wiley & Sons, New York) p 12
MacPherson M R, Everett G E, Wohlleben D and Maple N B 1971 *Phys. Rev. Lett.* **26** 20
Ramirez R and Falicov L M 1971 *Phys. Rev. B* **3** 2425
Reshamwala A S and Ramesh T G 1974 *J. Sci. Instrum. E* **7** 133
Schuch A F and Sturdivant J H 1950 *J. Chem. Phys.* **19** 145
Wilkinson M K, Child H R, MacHargue C J, Koeller W C and Wollan E D 1961 *Phys. Rev.* **122** 1409