On the nature of the dhcp to fcc transition under pressure in Pr and Pr-Th alloys

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Abstract. The results of electrical resistance (R), thermoelectric power (TEP) and X-ray diffraction measurements on praseodymium (Pr) and its alloys with thorium under pressure are reported. The maximum in R vs P curve exhibited by Pr persists only in the dhcp phase of Pr-Th alloy. X-ray measurements confirmed that in the alloys also the maximum in R vs P curve is due to the dhcp → fcc transition. Thus the behaviour of Pr and Pr-Th alloys is different from that of La and its alloys with Ce and Th where the maximum in the R vs P curve is electronic in origin and is exhibited by the dhcp, fcc and dist fcc phases.

Rare earth elements exhibit remarkable similarity in their behaviour and form a system where meaningful interpolations and extrapolations may be made. This is well illustrated by the fact that the structural change with atomic number and with pressure (for individual elements) are part of the structural sequence hcp → Sm-type → dhcp → fcc → dist fcc → collapsed phase (Jayaraman and Sherwood 1964; Grosshans et al 1982; Sikka and Vijayakumar 1986). The light rare earths La, Pr and Nd exhibit a broad maximum in the pressure vs resistance curve at the dhcp → fcc structural transition (King and Harris 1972). Experiments carried out in La have revealed that the anomaly in electrical resistance (maximum) occurs in the pressure-quenched fcc phase (Balster and Witting 1975) in Ce-stabilized fcc phase (King and Harris 1972) and Th stabilized fcc and dist fcc phases (Vijayakumar et al 1985). Also the pressure at which the anomaly occurs is related to the electron density parameter. These observations imply that the resistance anomaly is electronic in origin, resulting from the pressure-induced s to d transition. It will be interesting to see whether Pr, which also undergoes an s–d transition under pressure (Johansson and Rosengren 1975; Duthie and Pettifor 1977) exhibits a similar behaviour.

La exhibits superconductivity at an ambient pressure whereas Pr does not. However Pr-Th alloys exhibit superconductivity even in the Pr-rich region and pressure enhances it further (Huber et al 1982). Thus alloying Pr with Th may bring it closer to the La behaviour and hence Pr-Th alloy is suitable to investigate the extent of similarity or otherwise between La and Pr. Thermoelectric power of Pr and electrical resistance

and X-ray diffraction pattern of Pr-Th alloys were measured under high pressure up to 10 GPa, for this purpose.

The Pr-Th alloy system has the dhcp structure in the Pr-rich and the fcc phase in the Th-rich region with the transition occurring near 20 atom% of Th (Massalaki 1986). For our measurements, single phase $Pr_{1-x} Th_x$ alloys (x-10, 20, 35) were prepared by argon arc melting of an appropriate amount of 99·9% pure Pr and nuclear pure Th. Thin foils cut from the ingot were X-ray analysed. The alloy $Pr_{90} Th_{10}$ was in the dhcp phase and the other two in the fcc phase with no evidence of any other phase.

For electrical resistance and thermoelectric power (TEP) measurements under pressure, a Bridgman anvil set-up with *in situ* Bi pressure calibration was employed (Vijayakumar *et al* 1980). Thin rectangular pieces of sample were used for the measurements. To avoid contamination, samples were handled under dry oil.

The variation of TEP of Pr with pressure is shown in figure 1. There is a sharp increase in TEP at the structural transition at 3·8 GPa. However unlike in La (Vijayakumar 1985), there is no indication that the change in TEP occurs prior to the occurrence of resistance anomaly. Also there is no well-resolved change in TEP prior to or at the fcc-dist fcc transition near 5·5 GPa. The results of electrical resistance measurements are shown in figure 2. Only the alloy in the dhcp phase exhibited a maximum in the R vs P curve. The maximum in R is very broad and centred around 3 GPa, for 10 atom% Th alloy. Thus in Pr the anomaly in R is present only in the dhcp phase and results from the structural transition.

To confirm that the maximum in R vs P curve observed in the dhcp phase alloy is due to the structural transition, high pressure X-ray diffraction measurements were carried out. The energy dispersive X-ray diffraction set-up used consisted of a Syassan-Holzapfel type diamond anvil cell interfaced to a microprocessor-controlled MCA (Sharma *et al* 1986). The dhcp pattern of the alloy changed to an fcc pattern above 3·0 GPa for the alloy of 10% Th confirming that the maximum in R vs P curve is indeed due to the structural transition (figures 3 and 4). In Pr-Th alloys the structural transitions occur at lower pressures because the oversized Th atom compresses the dhcp lattice of Pr.
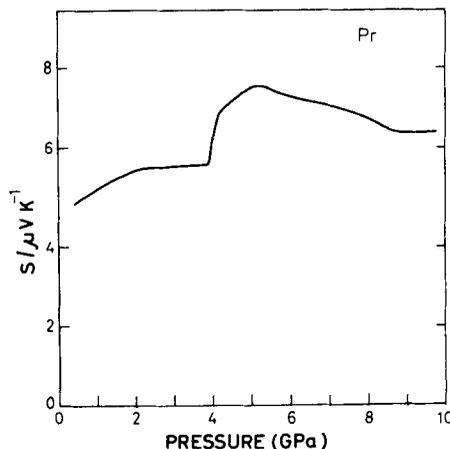

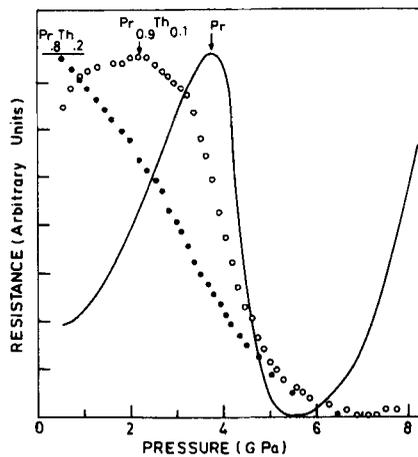**Figure 1.** Thermoelectric power (S) vs pressure curve of Pr.
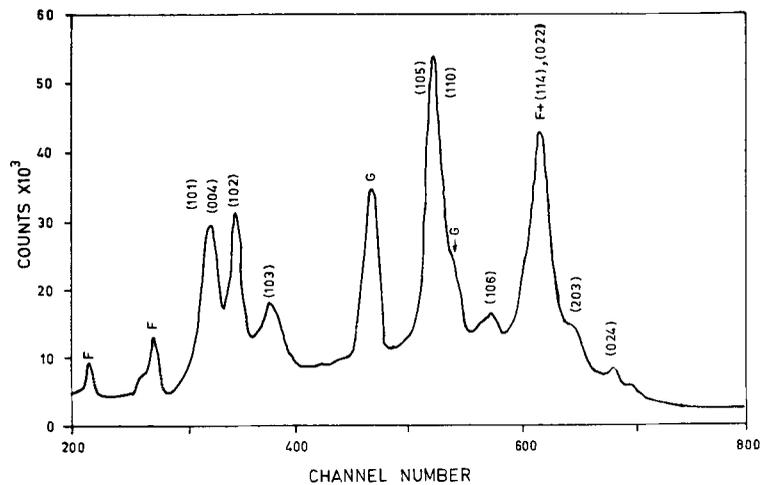
Figure 2. Electrical resistance vs pressure curve of Pr.

Figure 3. Energy-dispersive X-ray diffraction pattern of $Pr_{0.9}Th_{0.1}$ alloy 1 GPa (dhcp phase) (G gasket, F fluorescence).

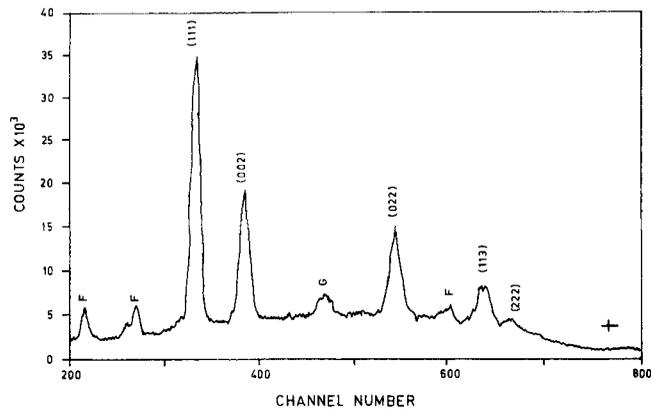**Figure 4.** Energy-dispersive X-ray diffraction pattern of $Pr_{0.9}Th_{0.1}$ just after the transition (fcc phase).

In conclusion, our results show that the electrical resistanc anomaly in Pr is not electronic in origin and is different from that observed in La-Th alloys. The band structure calculations on La (Picket *et al* 1980) indicate that the electronic anomaly near the dhcp fcc structural change in it stems from the fortuitous coincidence of a Fermi surface topology change. There is no evidence for this in Pr (Johansson and Rosengren 1975). Also alloying Pr with Th does not induce a Fermi surface topology change under pressure.

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