Characteristics of the phase transitions of La and Pr under hydrostatic pressures up to 9 GPa and temperatures up to 700 K: Electrical resistivities and thermoelectric powers

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We have investigated the behavior of the electrical resistivity and differential thermoelectric power of La and Pr for the phase transitions HCP↔FCC↔distorted FCC under hydrostatic conditions up to pressures of 9 GPa and temperatures up to 700 K. Analogous behavior of the critical coefficients of La and Pr under pressure near room temperature attests to the lack of influence of the 4*f* electrons of Pr on its kinetic properties. It is found that hysteresis in the transition twinned HCP↔FCC decreases with temperature and goes to zero near 1.0 GPa and 610 K. There is no hysteresis in the phase transition FCC↔distorted FCC when it occurs at room temperature.

INTRODUCTION

Lanthanum and praseodymium belong to the rare-earth series of metals. In this series, the following succession of changes in crystal structure occurs under pressure: HCP→Sm type→twinned HCP→FCC.[1] These crystal structures differ in the location of the hexagonal close-packed atomic layers, and can be transformed into one another with help of layer translation. An empirical *P-T* diagram has been constructed for the trivalent metals from Lu to La (Ref. 2). It is now considered established that the structural transformations are related to $s\rightarrow d$ electronic transitions in the metals.[3–5]

The generalized *P-T* diagram for La and Pr lies in a region of very high pressures and temperatures. Lanthanum undergoes a twinned HCP→FCC transition at atmospheric pressure and a temperature of 583 K.[6] Contrary to expectations,[2] Pr does not undergo such a transition at high temperatures under atmospheric pressure.[7,8] At room temperature, the transition twinned HCP→FCC is observed under quasi-hydrostatic conditions for La at 2 GPa and for Pr at ~4 GPa (Refs. 7,8). For higher pressures (6–8 GPa) a transformation FCC→distorted FCC (Refs. 12–14) is observed in La (Ref. 9) and Pr (Ref. 11), whose nature is explained by peculiarities of the electron and phonon spectra of the metals.[15–17] The formation of a weakly-distorted FCC structure was investigated in Refs. 18 and 19 as a function of hybridization of the electrons in the metals. In Ref. 20 it was noted that for "order 2 1/2" transitions large anomalies in the thermoelectric power are expected.

In order to study the *P-T* diagram and the character of the phase transition in La and Pr, we measured the electrical resistivity and thermoelectric power of our samples.

EXPERIMENT

We have described earlier our method of measuring the kinetic coefficients of metals under conditions of high hydrostatic pressure and temperature.[21] In these experiments polycrystalline samples of La and Pr were used, with dimensions $6\times1\times0.5$ mm^3. Using a mass spectrometer, we recorded the following rare-earth element inpurities in our samples: in metallic lanthanum, 0.07% Pr, 0.09% Nd, 0.004% Gd, and all the rest <0.001%; in metallic praseodymium, 0.002% La, all the rest <0.001%. For the samples of praseodymium, the ratio of electrical resistivities $R_{293\text{ K}}/R_{4.2\text{ K}}$ equalled 31. The accuracy of the results presented here was estimated to be ±50 bar and ±0.01 μV/K for pressure and coefficient of thermoelectric power respectively; the measurement errors for the relative electrical resistivity were less than ±0.07%. The hydrostatic pressure was generated in a "Toroid" chamber.

RESULTS AND DISCUSSIONS

1. The transitions twinned HCP↔FCC and FCC↔distorted FCC at room temperature

In Figs. 1 and 2 we show how the kinetic coefficients, i.e., the electrical resistivity and differential thermoelectric power, depend on hydrostatic pressure, obtained near room temperature for La and Pr. In La at room temperature the transformation twinned HCP→FCC under hydrostatic conditions (Fig. 1a) begins at 2.05 GPa and takes place primarily over a range of pressures up to 2.6 GPa. The decrease in electrical resistivity at the transition amounts to 14.7%. The reverse transformation FCC→twinned HCP begins at a pressure of 1.05 GPa and is "stretched out" down to atmospheric pressure.[23] For Pr (Fig. 1b) the initial values of the pressure for the direct and inverse transformations at room temperature are 4.0 and 2.9 GPa respectively. The transformation FCC→twinned HCP is complete for pressures above 2 GPa. Observation of this phase in Pr under normal conditions is unlikely after high-temperature sintering.[24] The results of cycling samples (Figs. 1a and 1b) in pressure and holding them for a time at intermediate transition points showed that the transformation twinned HCP→FCC in La and Pr had martensitic character, corresponding to a diffusionless phase transition mechanism at room temperature. The peculiarities in the thermoelectric power in Ref. 25 are clearly connected with the kinetics of the structural transition twinned HCP→FCC and with complexities associated with the method of measurement of thermoelectric power under nonhydrostatic conditions.

At room temperature and under hydrostatic conditions the transformation FCC→distorted FCC in the case of La (Figs. 1a, 2a) takes place over a wide range of pressure, from 7.6 to 8.25 GPa. For increasing pressure this transition is

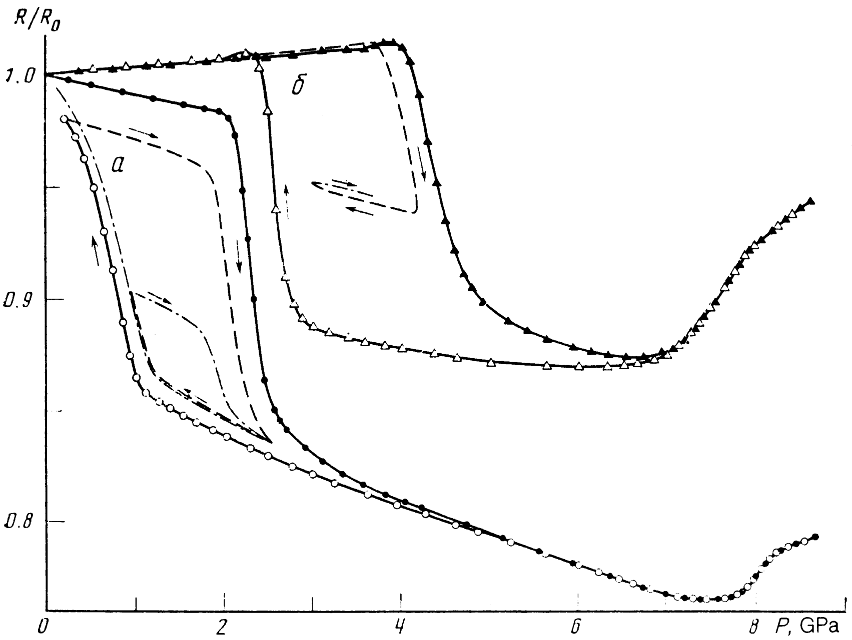

FIG. 1. Dependence of the relative electrical resistance on hydrostatic pressure: a—lanthanum, $T = 19$ °C, and b—praseodymium, $T = 20$ °C, respectively. ●,▲—for increasing and ○,△—for decreasing pressure. The dashed and dotted-dashed curves are from consecutive partial cycling of the transition twinned HCP↔FCC in the metals.

accompanied by an increase in the electrical resistivity by 2.8% and by a small (~0.35 μV/K) decrease in the thermoelectric power coefficient. Cycling the transition FCC↔distorted FCC over the pressure range 7–8.5 GPa results in complete overlap of the experimental curves. Measurement of the electrical resistivity of Pr for the transition FCC → distorted FCC (Fig. 1b) yields a somewhat larger value than for La, amounting to 5.4% over the pressure range from 7.0 to 7.9 GPa. The variation in the differential thermoelectric power of Pr over the transition is insignificant (Fig. 2b) and cannot provide any confirmation of the postulated electron-topological character of the transition under study.[17,20]

Figures 1 and 2 demonstrate the completely analogous behaviors of the electrical resistivity and thermoelectric power of La and Pr as functions of pressure, which allows us to treat Pr as a d-metal over the investigated range of pressure up to 9 GPa, similar to lanthanum.

2. The transformation twinned HCP↔FCC of Pr for temperatures above room temperature

In Fig. 3 we present isotherms for the relative electrical resistivity in samples of Pr from room temperature up to 620 K, obtained as the pressure is increased and decreased. As the temperature increases, the phase transitions are shifted toward the low-pressure side and exhibit hysteresis. This hysteresis reduces to zero for the 620 K isotherm and for the electrical resistivity isobar corresponding to a pressure of 0.96 GPa (Fig. 4). Note that the temperature scales shown in Fig. 4 for the various isobars are shifted relative to each other.

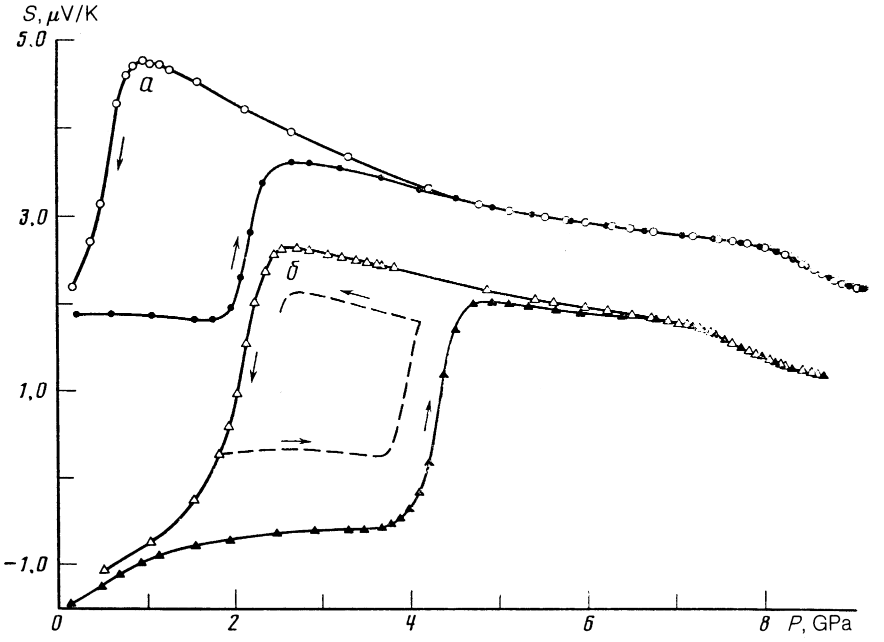

FIG. 2. Dependence of the absolute differential thermoelectric power on hydrostatic pressure: a—lanthanum, $T = 32$ °C, and b—praseodymium, $T = 27$ °C, respectively. ●,▲—for increasing and ○,△—for decreasing pressure. The dashed curve is data from partially inducing the transition twinned HCP↔FCC in Pr.

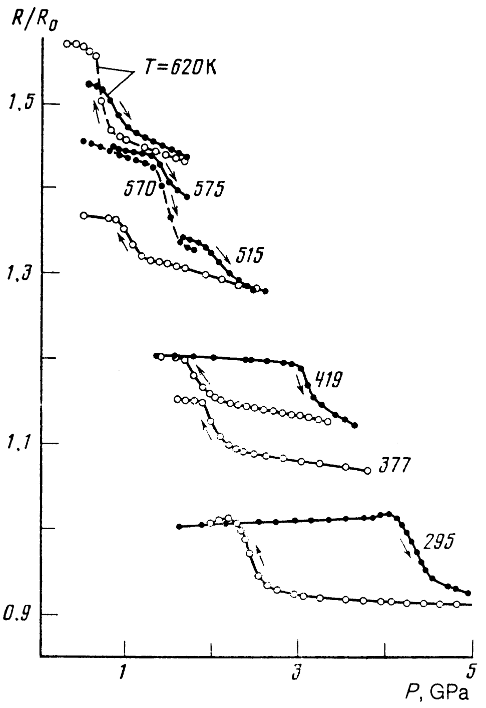

FIG. 3. Isotherms of the relative electrical resistance of praseodymium in the region of the transition twinned HCP↔FCC; ●,○ are for increasing and decreasing pressure, respectively.

In Fig. 5 we present the phase transition diagrams for the twinned HCP→FCC and FCC→twinned HCP phases of Pr, obtained under isothermal and isobaric conditions of investigation. In the range of temperatures up to 600 K the slopes of the lines for the direct transition twinned HCP→FCC wholly coincide with the slope of the direct transition for La (Ref. 26) and amount to ∼ − 100 K/GPa. The generalized phase diagram[2] over this range of temperature, in essence, provides confirmation of this. However, it is clear from Fig. 5 that the line for the inverse transformation FCC→twinned HCP for temperatures starting at 500 K undergoes a more abrupt rise than the line for the direct transition twinned HCP→FCC. As a result of the steepening of the slope of the inverse transition line FCC→twinned HCP for temperatures above 500 K, the hysteresis of the phase transition decreases and in the region of 1.0 GPa and 610 K it is reduced to zero. We argue that this feature explains the absence of any crossing of the temperature axis by the phase transition line for twinned HCP→FCC in Pr.

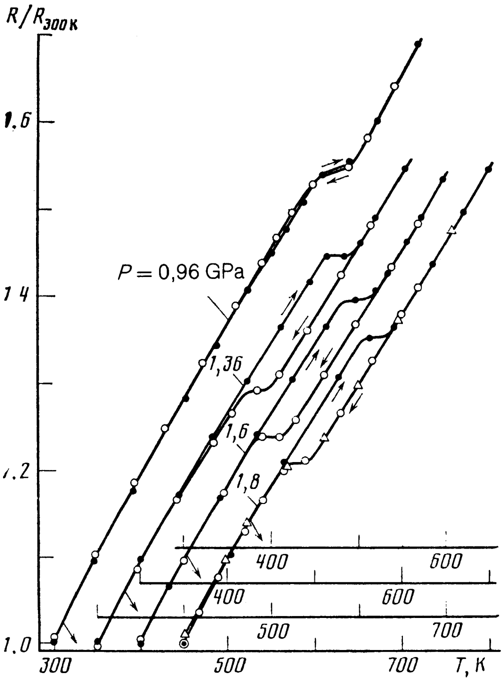

FIG. 4. Isobars of the relative electrical resistance of praseodymium for the transition twinned HCP↔FCC. ●,○ are for increasing and decreasing temperature, respectively; ▲—is data from repeated cycling at low temperature and at 1.8 GPa.

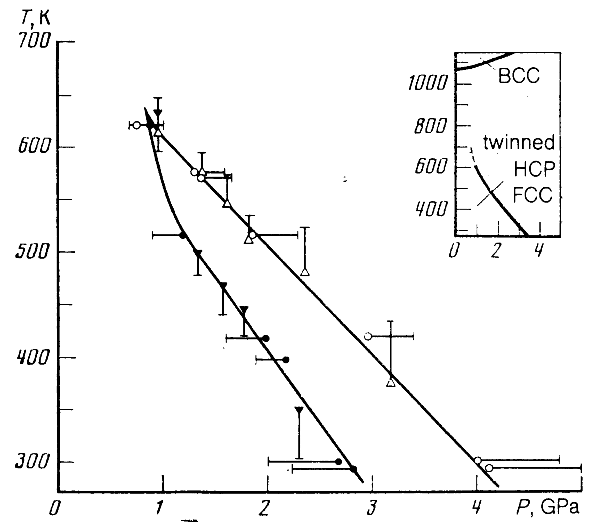

FIG. 5. *P-T* diagram of the phase transition twinned HCP↔FCC in Pr under hydrostatic conditions: ○ or △ and ● or ▼ are the beginnings of the direct and inverse phase transitions respectively for increasing and decreasing pressure or temperature. The error bars show the experimentally-observed extension of the transition. In the inset we show a fragment of the assumed equilibrium *P-T* diagram of Pr.

In Refs. 27, 28 it was assumed that the equilibrium line for the transition twinned HCP→FCC in Pr forms a triple point with the BCC phase at pressures ∼0.8 GPa. The inset to Fig. 5 shows the postulated *P-T* phase diagram for Pr, where the transition line to the BCC phase of the metal is taken from Ref. 27. The equilibrium transformation line for twinned HCP→FCC along which the hysteresis reduces to zero can be connected with the jump point on the line of transformation to the high-temperature BCC phase. The changes in volume and entropy for these phases of Pr for the transformation twinned HCP→FCC are unknown. Based on available x-ray, radiographic data from studies of La[29] and Nd,[30] we can assume that the jump in volume for the transformation twinned HCP→FCC in Pr at room temperature is small, and amounts to some fraction of a percent. As the temperature increases, the jumps in volume and entropy for the transitions under study apparently decrease. If we regard as firmly established the hypothesis that over all ranges of investigated temperature the original phase of Pr has the twinned HCP structure while the high-pressure phase has FCC structure, then a transition of the first kind with hysteresis reducing to zero in the high temperature region and with small changes in volume and entropy is interesting to study in its own right, since it may be close to a transition of the second kind. In the opposite case, the high temperature phase transition in Pr could be a transition of the second kind in which one of the phases (the original or high-pressure phase) possesses symmetry elements of the crystal lattice which form a subgroup of the symmetry elements of the other phase. The results we have obtained can serve as a basis for a search for analogous features in the phase transitions HCP → Sm type → twinned HCP → FCC in other lanthanides.

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