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Report:

Despite of the successful extension of the phase diagrams of lanthanide metals into the high-pressure region, the information about low-pressure transformations and high-temperature phases in some of them is still insufficient and unreliable, surprising features of low-pressure transitions between four-layered hexagonal close-packed (dhcp) and three-layered cubic close-packed (fcc) structures in La, Pr and Nd have been reported (see review paper [1]). In these three metals, the dhcp structure is known to be stable at ambient pressure and temperature. The stability domain of the fcc phase however, and the very existence of the dhcp-to-fcc phase transition point on the temperature axis of the phase diagrams of Pr and Nd, have been a matter of a great uncertainty. At ambient pressure the dhcp-to-fcc transformation has been observed only in La [2] while data reported on Pr and Nd are contradictory. On the one hand, most of studies on Pr and Nd confirm the suggestion of Jayaraman [3] that the dhcp-fcc phase transition line ends up in a triple dhcp-bcc-fcc point and does not intersect the temperature axis in the phase diagram of these metals. On the other hand, the observation of the metastable fcc phase at room temperature in Pr and Nd resulted from quenching (splat cooling) in an arc furnace at ambient pressure [4].

We carried out the high-temperature (at ambient pressure) studies of La, Pr and Nd metal concentrating our attention on the region of uncertainty in the phase diagram. We employed two types of set-up for temperature measurements: first, one with a Lincam DT-1500 cell, and, second, one with the ETH-800 furnace. Both arrangements provide the control of an atmosphere in the sample holder (it was an argon of high purity in our case).

The main results obtained in our high-temperature studies on La, Pr and Nd sum up to following:

1. We confirm the existence of the temperature-induced dhcp-to-fcc phase transition at ambient pressure in Pr and Nd. The onset of fcc diffraction peaks in Pr and Nd has been detected at 573 K and 550 K respectively.
2. The dhcp-to-fcc phase transition in Pr and Nd is extremely sluggish and the dhcp phase is stable almost up to the transition to bcc phase in these metals (T_t=1071 K for Pr and T_t=1141 K for Nd).
3. The introduction of temperature gradients (non-equilibrium thermal conditions) accelerates significantly the kinetics of the dhcp-to-fcc phase transition in Pr and Nd.
4. We report an unusual negative thermal expansion of the high-temperature fcc phase of Pr and Nd in the temperature interval of about 200 K, and also a discontinuity in the atomic volume for dhcp phase at higher temperatures (see figs. 1a,b).

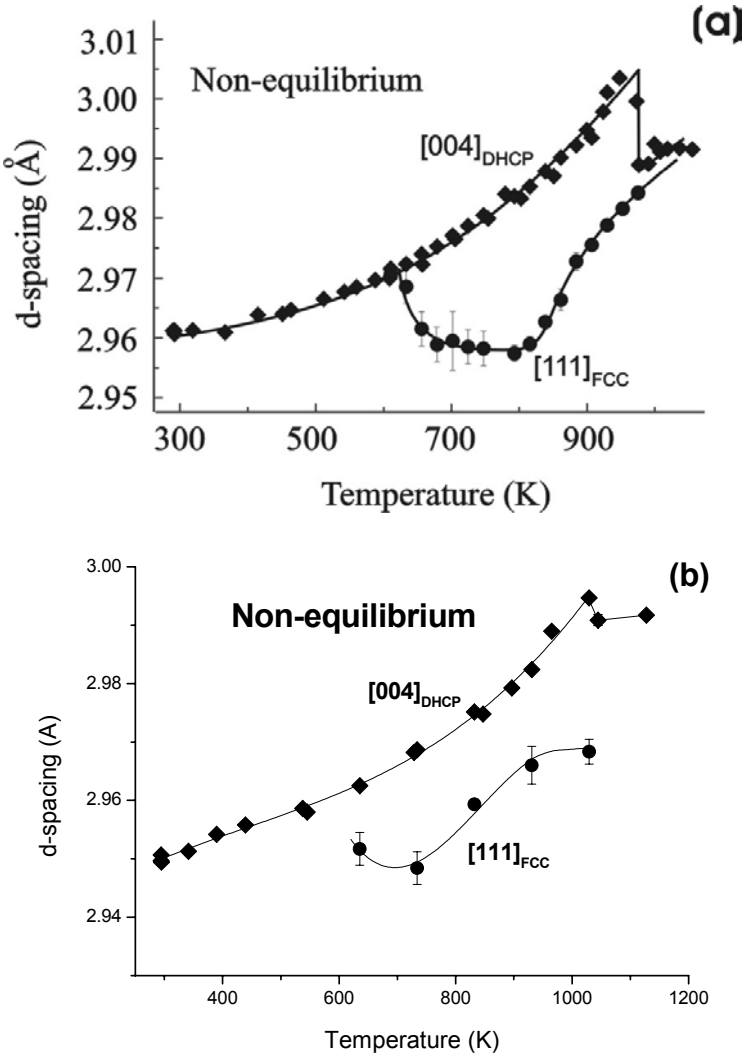

Fig. 1. Linear thermal expansion of (a) Pr and (b) Nd metals. Diamonds correspond to the dhcp phase, and circles to the fcc phase. The interlayer spacing $d_{[111]c}$ between close-packed layers in cubic phase is compared with its hexagonal analog $d_{[004]c}$.

5. For La metal we report the thermal expansion of dhcp and fcc phases (fig. 2). We also report the characteristic features in the X-ray powder diffraction pattern obtained from the dhcp phase of La metal at different temperatures. The peak shifts, the peak asymmetry and the increase in peak broadening for certain reflections could be qualitatively accounted by the general theory of X-ray diffraction by dhcp crystals with stacking faults [5].

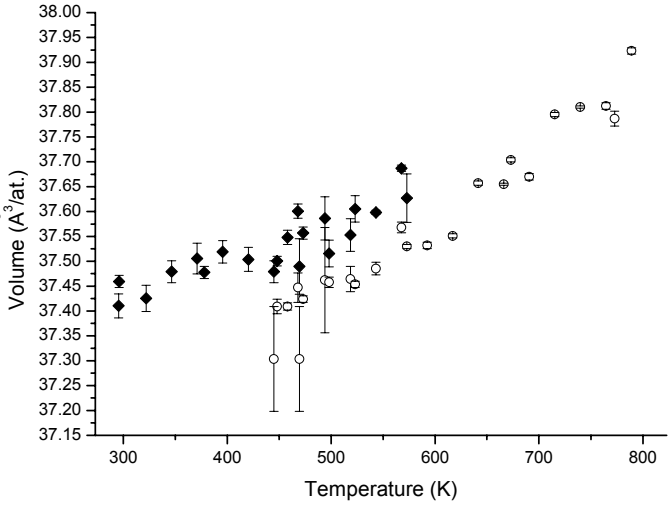

Fig. 2. Temperature dependence of the atomic volume of La metal. Diamonds – dhcp phase; circles – fcc phase.

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