

Conversions between double-hcp and fcc lattices in neodymium at high pressures and temperatures

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The high-temperature region (up to 800 K) of the phase transition between the double hcp (dhcp) lattice and the fcc lattice in neodymium has been studied by measuring the behavior of the electrical resistance during hydrostatic compression. For the first time, data have been obtained on the behavior of the differential thermal emf of Nd under hydrostatic compression up to 9 GPa near room temperature. A transition from the dhcp phase to a high-pressure phase occurs in the pressure interval 7.0–8.5 GPa in Nd at room temperature. The inverse transition occurs at 6.0–4.5 GPa. A singularity has been found in the behavior of the hysteresis of the dhcp↔hcp phase transition on the high-temperature part of the P - T diagram of Nd. Above 500 K, the hysteresis of the transition gradually decreases, vanishing near the point 2.0 GPa, 750 K. The results reveal similarities between the P - T phase diagrams of Nd and Pr. The results apparently also furnish evidence that the behavior observed here in high-temperature phase transitions between close-packed structures in compressed rare earth metals is of a universal nature.

INTRODUCTION

In the family of rare earth metals, neodymium (Nd) is the closest analog of praseodymium (Pr) in terms of its physical and chemical properties. We recently found that at temperatures above 600 K the hysteresis of the phase transition between the double hcp (dhcp) lattice and the fcc lattice on the P - T diagram of Pr vanishes. One might therefore expect to find a similar feature in the dhcp↔fcc transition in metallic Nd.

The phase diagram of Nd and its physical properties under compression have been studied on very few occasions.¹ X-ray measurements in diamond anvils have shown² that neodymium undergoes a dhcp↔fcc transition at a pressure of 5.0 GPa at room temperature; praseodymium undergoes the same transition at 4.0 GPa; and lanthanum undergoes this transition at 2.3 GPa. A study by differential thermal analysis of several rare earth metals under pressure at high temperatures, up to the melting point,³ has shown that in Pr and Nd the slope of the line of the phase transition bounding the region in which the high-temperature bcc phase of the metals exists changes at pressures of 0.8 and 2.1 GPa, respectively. It has been suggested that near this break there may be a triple point of the dhcp, bcc, and fcc phases and that the dhcp-fcc phase-equilibrium line has a negative slope. In the high-temperature region, however, the dhcp-fcc transition was not detected by differential thermal analysis. A generalized phase diagram has been proposed for the lanthanides by Johansson and Rosengren.⁴ According to the principles underlying the construction of that diagram, the dhcp-fcc conversion should be observed in Nd at atmospheric pressure at high temperatures. No data are available on the transition from the dhcp phase to the fcc phase at atmospheric pressure. Nakaue⁵ has reported x-ray studies of compressed Nd over a broad temperature range. It has been found that the line of the dhcp-fcc phase transition has a

negative slope of about -117 K/GPa in the temperature interval 600–900 K on the P - T diagram. Above 900 K, it is apparently difficult to unambiguously identify the structure of Nd. At room temperature, the dhcp→fcc transition has not been observed at pressures up to 9 GPa. Extrapolation of the phase-boundary line found at high temperatures (600–900 K) to room temperature yields a transition pressure of about 7.0 GPa.

The discrepancies among the data reported by different investigators and among their assumptions regarding the positions of the boundaries in Nd (Refs. 2–5) demonstrate the need for a more careful study of the P - T diagram of this metal. In the present paper we report data obtained under hydrostatic conditions on the position on the P - T diagram of the lines of the direct transition (dhcp→fcc) and of the inverse transition (fcc→dhcp) in Nd. The results reveal that the phase transition behaves singularly at high temperatures.

EXPERIMENTAL PROCEDURE

An experimental procedure developed previously⁶ was used to measure the kinetic coefficients of bulk samples subjected to hydrostatic pressures up to 9 GPa and to temperatures up to 800 K. Samples with linear dimensions $6 \times 1 \times 0.5$ cm are cut by an electric-spark method from bars of 99.9%-pure polycrystalline Nd. The ratio of the electrical resistances of the samples at 293 and 4.2 K is 11. The temperature is measured to within 1 K during the experiments by copper-constantan thermocouples. The pressure in the cell holding the sample is measured with a manganese resistance gauge held in the lower part of a capsule in the hydrostatic medium at a constant temperature, near room temperature. This gauge is calibrated on the basis of the pressures of two known transitions in bismuth at $p = 2.54$ and 7.7 GPa. The error in the pressure measurements is less

than 10 MPa. The experiments are carried out in a pressure chamber with a usable volume of 0.8 cm³.

EXPERIMENTAL RESULTS AND DISCUSSION

The transition from the double-hcp phase of Nd to the high-pressure phase at room temperature is accompanied by significant anomalies in the thermal-emf and the electrical resistance. Figure 1 shows a plot of the absolute differential Seebeck coefficient (thermal-emf coefficient) of Nd versus the hydrostatic pressure obtained near room temperature as the pressure was raised and lowered. At the phase transition in the pressure interval between 7.0 and 8.5 GPa the Seebeck coefficient changes abruptly in magnitude and also changes in sign; the magnitude of the jump is $\sim 2.5 \mu\text{V/K}$. The observed transformation shows a significant hysteresis amounting to $\sim 1.5 \text{ GPa}$ with respect to the initial pressures of the direct and inverse transitions. The jump in the electrical resistance of Nd near room temperature (the $T = 300 \text{ K}$ isotherm in Fig. 2) is $\sim 10\%$ for this transition. Comparison of these curves of the Seebeck coefficient and the electrical resistance yields evidence that at the beginning of the direct phase transition (in the pressure interval 7.0–7.5 GPa) the resistance of the sample not only fails to decrease but in fact increases slightly. It may be that the mechanism for the phase transition at room temperature involves the formation of structural defects which have a competing effect on the behavior of the resistance when the sample contains a mixture of two phases.

High-temperature studies of the dhcp \leftrightarrow fcc transition in Nd were carried out by measuring the resistance of samples under isothermal and isobaric conditions (Figs. 2 and 3). It can be seen from these figures that over the entire high-pressure range the phase transition is accompanied by significant jumps in the resistance. Figure 4 shows generalized data on the high-temperature region; the pressures and temperatures at which the transitions begin and the transition intervals are shown here. The average slope of the line of the inverse transition, fcc \rightarrow dhcp, in the temperature interval 500–700 K is about -175 K/GPa , or roughly twice (in absolute value) the slope of the direct transition, dhcp \rightarrow fcc. Near 2.0 GPa and 750 K, the hysteresis of the dhcp \leftrightarrow fcc transition vanishes. We believe that this feature of the hysteresis is evidence that the first-order transition between the

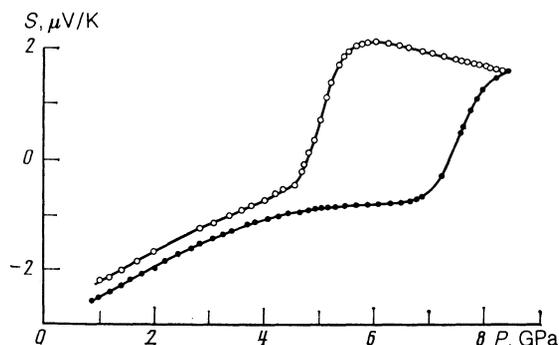


FIG. 1. Absolute differential Seebeck coefficient of Nd versus the hydrostatic pressure. ●—As the pressure is raised; ○—lowered ($T = 300 \text{ K}$).

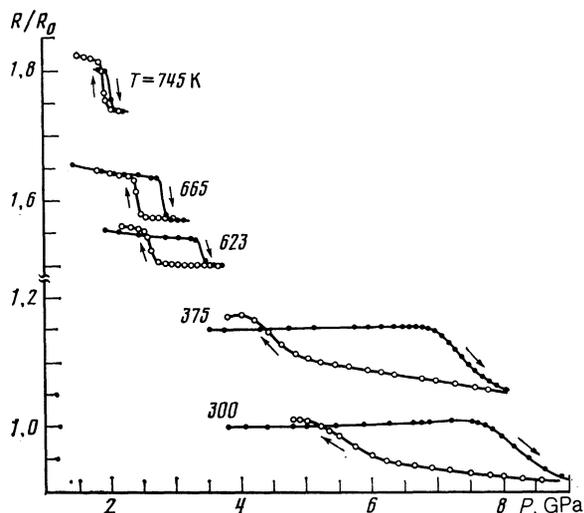


FIG. 2. Isotherms of the relative electrical resistance of Nd under hydrostatic conditions. ●—As the pressure is raised; ○—lowered.

close-packed structures at high temperatures may be converted into a nearly second-order transition in terms of the changes in the thermodynamic characteristics of the transitions.

The inset in Fig. 4 shows the suggested equilibrium P - T diagram of Nd. The phase boundary of the bcc structure of Nd was taken from Ref. 3. It may be that a transition accom-

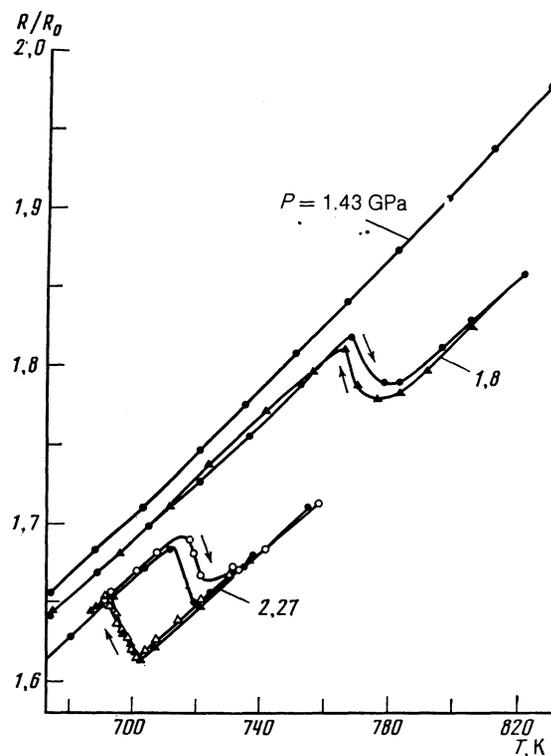


FIG. 3. Isobars of the relative electrical resistance of Nd. Filled points—As the temperature is raised (●) and lowered (▲) during the first cycle; open points—as the temperature is raised (○) and lowered (△) during the second cycle.

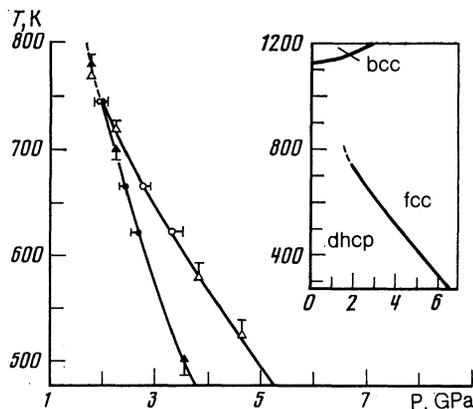


FIG. 4. P - T diagram of phase transitions in Nd under hydrostatic conditions. \circ , Δ (or \bullet , \blacktriangle)—Initial points of the direct and inverse transitions, respectively, as the pressure or temperature is raised and lowered. The error bars show the width of the transitions. The inset shows part of the suggested equilibrium P - T diagram of Nd.

panied by vanishing hysteresis terminates at the point where the slope of the line of the phase transition to the bcc phase changes. There are other pieces of evidence supporting these suggestions.

Figure 3 shows the behavior of the resistance of Nd in the course of a double thermal cycling of the transition $\text{dhcp} \leftrightarrow \text{fcc}$ at a pressure of 2.27 GPa. The results found in this cycling demonstrate that the transition which occurs at high temperatures (~ 700 K) is of a martensitic nature. A transition with a time delay occurs in a temperature interval 10 K wide; the hysteresis of this transition is ~ 14 K. It can be seen from Fig. 5 that for the given martensitic transition the change in structure may occur by means of four relative displacements of individual close-packed planes or blocks of these planes over a distance $a/\sqrt{6}$ with a period of 12 atomic layers. An important point for the case of a displacement mechanism for the change in the structure of the lattices of the phases is the possibility of a change in structure without a change in the final interatomic distances, i.e., without a change in volume.

Figure 3 shows the temperature dependence of the resistance at 1.4 GPa. This curve demonstrates that there are no anomalies in the behavior of the resistance up to 840 K and that it would not be legitimate to carry out a linear extra-

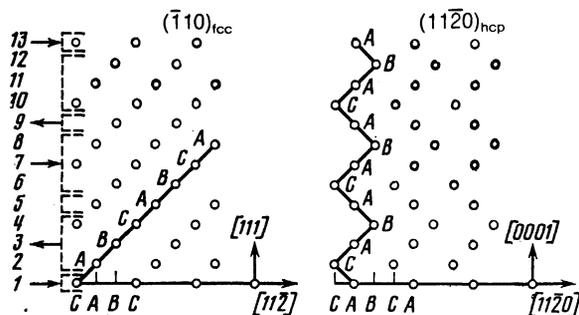


FIG. 5. Arrangement of atoms and change in the structure of the close-packed atomic planes of the fcc and dhcp structures [projected onto the (110) plane in the fcc case and the (1120) plane in the hcp case].

polation of the line of the dhcp - bcc transition at pressures below 1.43 GPa on the P - T diagram. The transition line at high temperatures is probably vertical or nearly so. In this case, the difference between the entropies of the two neighboring phases should be very small or zero. This circumstance could apparently explain why the dhcp - fcc transition in Nd is not observed by differential thermal analysis in experiments under pressure at high temperatures.³

The results of the studies which have been carried out demonstrate that there is an analogy in the structural phase transitions which occur in rare earth metals and that there may exist transitions between close-packed structures in metals with vanishingly small hysteresis, change in volume, and change in entropy of the phases.

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