Thermal expansion and crystal structure of Pr, Nd, and Sm in the 87–1073 °K range

Yu. N. Smirnov and I. A. Prokhorov

(Submitted April 26, 1974)
Zh. Eksp. Teor. Fiz. 67, 1017–1022 (September 1974)

The temperature dependences of the lattice periods and electrical resistivity of Pr, Nd, and Sm were determined. These dependences had anomalies at 605–680 °K for Pr, at 648–750 °K for Nd, and at 380–500 °K for Sm. The discontinuities of the atomic volume and electrical resistivity of Sm near 980 °K were attributed to a first-order phase transition from the rhombohedral to the hexagonal close-packed structure: $Sm_{rh} \rightleftarrows Sm_{hcp}$.

Considerable progress has been made in understanding the principal physical properties of the light rare-earth metals at low temperatures and several magnetic phase transitions have been observed and identified.[1-5] The data on the crystal structure and other physical properties are ambiguous in respect of the existence of polymorphic and other transitions.

The thermal expansion curves of Pr and Nd[6,7] have no singularities between room and the hcp $\rightleftarrows$bcc transition temperature. Samarium exhibits a phase transition of the first kind from the rhombohedral to the hexagonal close-packed structure, $Sm_{rh} \rightleftarrows Sm_{hcp}$, and the transition temperature (~900°K) decreases with rising oxygen impurity concentration up to 710°K (0.13 at.% oxygen).[8] Near 570°K, the temperature dependence of the lattice period a of the nine-layer hcp lattice has a kink. The temperature dependence of the specific heat of Sm has two peaks: one in the range 560–700°K and the other near 825°K.[9] It is suggested in[8,9] that the low-temperature anomaly is due to an electronic phase transition.

The temperature dependence of the magnetic susceptibility[10] has three discontinuities, at 940, 1200, and 1300°K, which correspond to first-order phase transitions $Sm_{rh} \rightleftarrows Sm_{hcp}$, $Sm_{hcp} \rightleftarrows Sm_{bcc}$, and the melting point. It is reported in[10] that Sm can also have the orthorhombic lattice. On the other hand, it is suggested in[11] that the anomalies in the temperature dependences of the magnetic susceptibility, resistivity, and thermoelectric power of Sm observed in the 800–850°K range are due to a magnetic phase transition.

The purpose of the investigation described below was to determine the causes of these doubts about the structure of Pr, Nd, and Sm above room temperature and of the considerable scatter of the reported values of the $Sm_{rh} \rightleftarrows Sm_{hcp}$ transition temperature (700–940°K).

EXPERIMENTAL METHOD

We investigated coarse-grained platelets of at least 99.8 wt.% purity. The measurements were carried out using a DRON-1 diffractometer, fitted with high-temperature (GPVT-1500) and low-temperature (KRN-190) attachments. Above room temperature, diffractograms were recorded in $\sim 5 \times 10^{-6}$ Torr vacuum as well as in an argon atmosphere at a pressure of ~760 Torr. The maximum temperature during measurements was restricted by the rapid rise in the oxidation rate of Pr, Nd, and Sm plates. We used Cu K_α radiation to record the (10, 14) and (316) reflections of Pr and Nd and (21, 23) and (10, 32) reflections of Sm. The dependences a(T) and c(T) were calculated from the smoothed-out temperature dependences of the interplanar distances. The error in the determination of the Bragg angle was $\Delta\theta = 0.5'$ and the relative errors in the determination of the lattice periods were

$$\Delta a/a = 0.6 \cdot 10^{-4}, \quad \Delta c/c = 0.6 \cdot 10^{-4}$$

in the case of Pr and Nd, and

$$\Delta a/a = 1.7 \cdot 10^{-4}, \quad \Delta c/c = 0.5 \cdot 10^{-4}.$$

in the case of Sm. The diffractograms of the investigated metals were recorded above room temperature to provide a more reliable interpretation.

The electrical resistivity of Pr, Nd, and Sm was determined by the compensation method in the 293–1000°K range at a pressure of $\sim 2 \times 10^{-5}$ Torr. In this case, we used bulk polycrystalline samples whose dimensions were 0.15 × 0.5 × 4 cm. Potential and current leads were made of a nickel wire of 0.1 cm diameter and they were pressed along the edges of the samples. Rapid oxidation was prevented by wrapping the samples in titanium foil. An R-306 potentiometer was used as the measuring instrument. The error in the determination of the temperature dependence of the relative resistivity did not exceed ± 0.2%. The temperature was measured with a Chromel-Alumel thermocouple. The temperature was maintained to within ±2 deg K and measured to within ±0.5 deg K.

RESULTS

The temperature dependences of the lattice periods and reduced axial ratios of Pr, Nd, and Sm are plotted in Figs. 1–3.

Praseodymium. The lattice period a varies weakly with temperature up to ≈ 470°K and above this temperature it rises rapidly, exhibiting a singularity at 605°K. An anomaly in the temperature dependence of the period c is weaker and it is observed at 625°K. The temperature dependence of the atomic volume is similar to the a(T) curve, whereas the reduced axial ratio has a singularity at 605°K.

Neodymium. The thermal expansion curves are similar to those of Pr except that the temperature of the anomalies exhibited by the dependences of a, V, and c/2a on T is 648°K, whereas the anomaly of the dependence c(T) is at 610°K.

Samarium. The singularity exhibited by a sample annealed in an argon atmosphere at 800°K is located at 380°K, whereas a sample cut from an ingot has a singularity at 480°K. The nature of the singularities is similar to those exhibited by Pr and Nd. The singularity at 106°K corresponds to the antiferromagnetic ordering of the magnetic moments of the atoms in a hexagonal environment.[2]

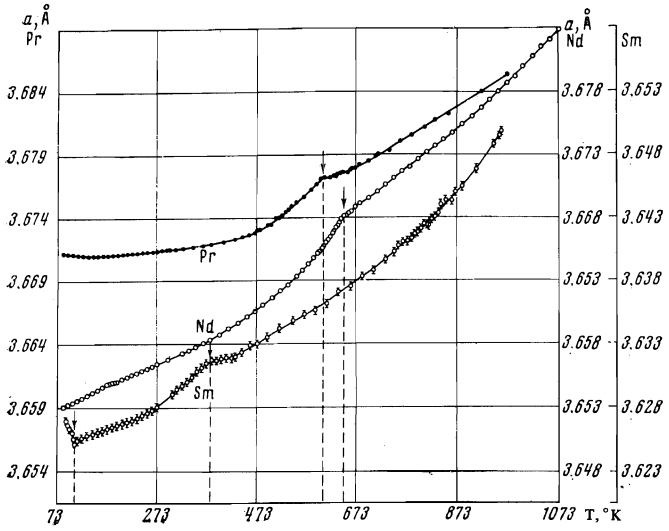

FIG. 1. Temperature dependences of the lattice period a of Pr, Nd, and Sm.

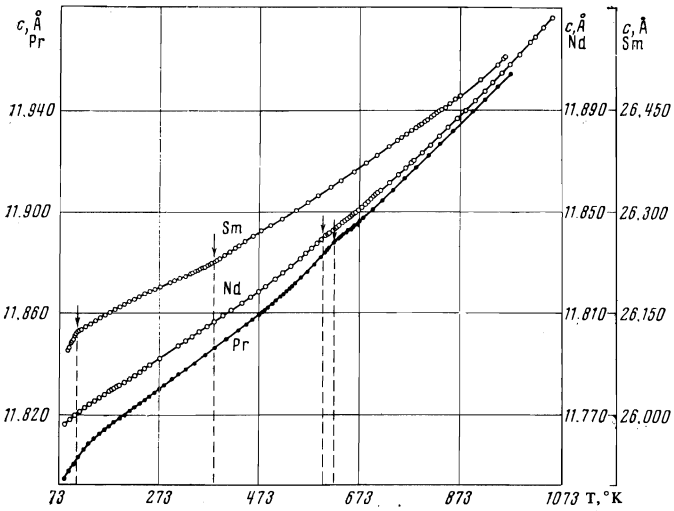

FIG. 2. Temperature dependences of the lattice period c of Pr, Nd, and Sm.

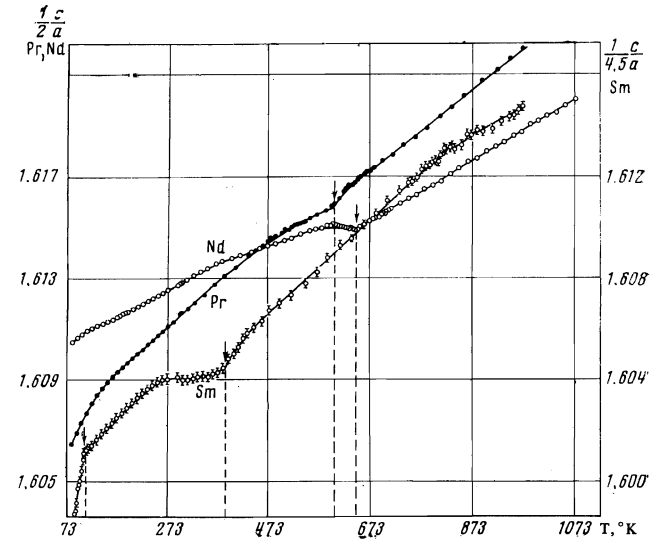

FIG. 3. Temperature dependences of the reduced axial ratio of Pr, Nd, and Sm.

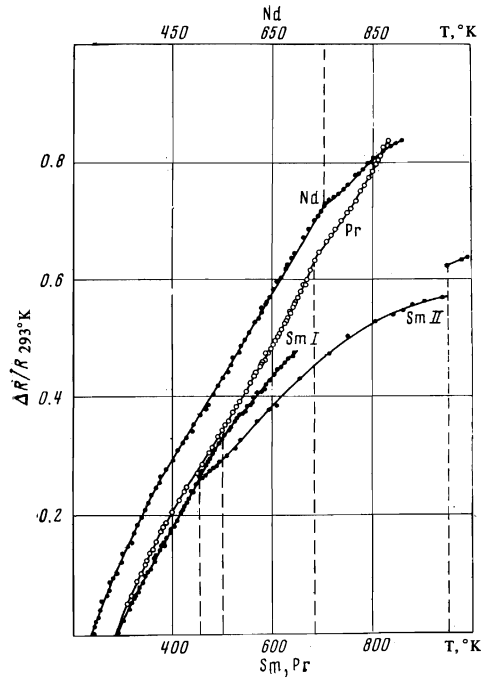

FIG. 4. Temperature dependences of the ratio $\Delta R/R_{293°K}$ of Pr, Nd, and Sm. Here, Sm I is a coarse-grained sample cut from an ingot; Sm II is the same sample after a slow heating to 660°K.

The diffractograms obtained below 800°K in an inert atmosphere reveal only the lines of the nine-layer hexagonal lattice of Sm and of the two-layer hexagonal lattices of Pr and Nd. Above 800°K the lines of the metals are accompanied by the lines of the oxides SmO, Pr_2O_3, and Nd_2O_3. At 980°K, the lines of the nine-layer hexagonal lattice of α-Sm disappear and are replaced by three lines which can be identified as the strongest lines of the hcp lattice with periods a = 3.644 ± 0.005 Å and c = 5.876 ± 0.005 Å. The discontinuity of the atomic volume at the transition point is comparable with the precision of the measurement of V(T) but its value is an order of magnitude less than that given in[8].

Two modifications of the oxide Sm_2O_3 and one modification of the oxides Pr_2O_3 and Nd_2O_3 appear on the surface of the samples in vacuum above ~650°K. At temperatures exceeding 850°K, Sm_2O_3 decomposes into SmO.

The temperature dependences of the quantities $\Delta R/R_{293°K}$ (where $\Delta R = R_T - R_{293°K}$) of the unannealed samples have kinks at 680, 750, and 500°K in the case of Pr, Nd, and Sm, respectively (Fig. 4). Measurements of the electrical resistivity of the same sample of Sm indicate an anomaly at 455°K. A sudden change in $\Delta R/R_{293°K}$ occurs at 960°K. The temperatures of the anomalies deduced from $\Delta R/R_{293°K} = f(T)$ are ~100 deg K higher than those deduced from the thermal expansion curve.

DISCUSSION OF RESULTS

The nature of the anomalies of the thermal expansion and electrical resistivity curves of Pr (605–680°K), Nd (650–750°K), and Sm (380–500°K) shows clearly that they are all due to the same cause, which is a phase transition of the first kind. These anomalies can be due to the following effects:

a) a magnetic phase transition, but this is in conflict with the observations that no magnetic ordering occurs at temperatures T > 106°K;[1-5]

b) ordering of interstitial impurities, but this is in conflict with the low solubility of the gaseous impurities and, particularly, of oxygen;[12]

c) attainment (during measurements) of the equilibrium or nonequilibrium solubility limit for interstitial impurities but this disagrees with the measurements of the specific heat of Sm,[9] which effectively exclude the solubility of gaseous impurities and reveal an anomaly in the dependences cp(T) at 696°K;

d) a change in the electronic structure.

A redistribution of electrons between the energy bands of some of the light rare-earth metals may induce a phase transition of the first kind (Ce and Yb). The relative positions of the 4f, 5d, and 6s bands of the rare-earth metals[13] suggest that only Sm, Yb, and Ce can exhibit electronic phase transitions of the first kind.

It is suggested in[14] and proved in[2] that the polarization of the conduction electrons affects the properties of Sm. The excitation of spin-density waves of the conduction electrons with an arbitrary polarization vector is one of the mechanisms which can give rise to singularities in the temperature dependences of the thermodynamic potentials.[15]

X-ray structure investigations give information only on layers 10^{-3} cm deep. The formation of oxides in the surface layers may have resulted in the attainment of the solubility limit of oxygen in Pr, Nd, and Sm (~0.1 at.%[12]). The electrical conductivity is the bulk characteristic of the metal, and the difference between the temperature anomalies found by the x-ray diffraction and resistivity methods corresponds to different concentrations of oxygen on the surface and in the bulk of a sample. The temperature of the anomaly exhibited by Sm, which is 500°K, falls strongly after annealing and during subsequent measurements. Interstitial impurities, particularly oxygen, depress this temperature; it may also be sensitive to structure defects and stresses.

In conflict with the results reported in[8], the $Sm_{rh} \rightleftarrows Sm_{hcp}$ phase transition temperature does not decrease with increasing oxygen concentration in the lattice. The transition from one close-packed lattice to another is of the martensitic type, resulting from the nucleation and growth of stacking faults.[16] The transition temperature is governed by the imperfections in a sample (dimensions and shape of grains, microstresses, and macrostresses). Our study shows no evidence of orthorhombic samarium.[10]

The authors are grateful to V. A. Finkel', R. M. Moon, and A. Leman-Shveĭkovskaya for valuable discussions, B. Lebech for kindly supplying preprints of her papers, and to V. M. Moiseev for helping in the measurements of the electrical resistivity.

[1]R. M. Moon, J. W. Cable, and W. C. Koehler, J. Appl. Phys. **35**, 1041 (1964).
[2]W. C. Koehler and R. M. Moon, Phys. Rev. Lett. **29**, 1468 (1972); J. W. Cable, R. M. Moon, W. C. Koehler, and E. O. Wollan, Phys. Rev. Lett. 12, 553 (1964).
[3]B. Lebech and B. D. Rainford, J. Phys. (Paris) **32**, Suppl. C1, 370 (1971).
[4]T. Johansson, B. Lebech, M. Nielsen, H. B. Møller, and A. R. Mackintosh, Phys. Rev. Lett. **25**, 524 (1970).
[5]A. Millhouse, Helv. Phys. Acta **45**, 5 (1972).
[6]F. Barson, S. Legvold, and F. H. Spedding, Phys. Rev. **105**, 418 (1957).
[7]F. H. Spedding, J. J. Hanak, and A. H. Daane, J. Less-Comm. Met. **3**, 110 (1961).
[8]P. G. Mardon and C. C. Koch, Scripta Met. **4**, 477 (1970).
[9]V. M. Polovov, Zh. Eksp. Teor. Fiz. **65**, 1557 (1973) [Sov. Phys.-JETP **38**, 775 (1974)].
[10]N. Perakis and F. Kern, C. R. Acad. Sci. (Paris) B **275**, 677 (1972).
[11]M. V. Vedernikov, ZhETF Pis'ma Red. **15**, 326 (1972) [JETP Lett. 15, 230 (1972)].
[12]F. H. Spedding and A. H. Daane (eds.), The Rare-Earths (Proc. Symposium, Chicago, 1959), Wiley, New York, 1961 (Russ. Transl., Metallurgiya, M., 1965).
[13]J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. **B6**, 1913 (1972).
[14]A. M. Stewart, Phys. Rev. **B6**, 1985 (1972).
[15]A. W. Overhauser, Phys. Rev. Lett. **3**, 414 (1959); **4**, 462 (1960); **13**, 190 (1964); Phys. Rev. 128, 1437 (1962).
[16]C. R. Houska, B. L. Averbach, and M. Cohen, Acta Metall. **8**, 81 (1960).

Translated by A. Tybulewicz
114