# Anomalies of the heat capacity of neodymium and praseodymium at high temperatures

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The heat capacity of ~99.6% pure polycrystalline Nd and Pr samples was measured in the interval 300–850 K. λ-anomalies of the heat capacity, corresponding to the known anomalies of the thermal expansion, were observed at 700 K (Pr) and 773 K (Nd).

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A number of rare-earth metals (REM) of the cerium subgroup exhibit in the paramagnetic region ($T > 300$ K) anomalies in the temperature dependences of the lattice parameters, of the magnetic susceptibility, and of the kinetic properties.[1–5] In Sm[6] and Eu[7] these anomalies correspond to distinctive λ singularities of the heat capacity at ~695 and ~765 K, which are typical of second-order phase transitions. The plots of the high-temperature heat capacity of Pr and Nd, obtained by Spedding and co-workers,[8,9] have no singularities whatever between room temperature and the temperature of the polymorphic double hcp ⇄ bcc transition (1065 K in Pr and 1135 K in Nd).

To verify the hypothesis[3] that phase transitions take place in Nd and Pr at 600–750 K, we have investigated in detail the temperature dependence of the heat capacities of these metals from room temperature to 850 K. The measurement procedure did not differ from that used earlier for Sm and Eu.[6,7] We investigated polycrystalline samples ~99.6% pure with resistance ratios $R_{293}/R_{4.2\,K} \approx 30$. The measurement results are shown in Fig. 1 (a—for Pr and b—for Nd).[1)] Immediately above room temperature, the $C_P$ curves agree within the limits of the measurement error (±3%) with those previously published.[8,9] A discrepancy with the data of[9] is observed for Pr in the interval 550–740 K, where the heat capacity has a λ singularity with a discontinuity $\Delta C_P$ ~0.5 cal/g-atom-deg near 700 K. An analogous singularity appears for Nd in a narrower temperature interval (720–800 K), and the heat-capacity jump near 773 K reaches ~12.5 cal/g-atom-deg. The singularities of $C_P(T)$ of both metals have no noticeable temperature hysteresis ($\Delta T < 1$ deg).

Rare-earth metals are strong absorbers of gas impurities, particularly hydrogen.[9] It is therefore important to verify that the observed anomalies are not due to the presence of hydrogen. It is known that hydrogen can be effectively removed from REM by high-temperature annealing in a dynamic vacuum.[10] We have annealed the Nd and Pr samples at 1000 °C (4 hr) in a vacuum of $1 \times 10^{6}$ Torr, but observed no substantial change in the character of the observed anomalies of the heat capacity. The reproducibility of the $C_P(T)$ curves after numerous heating and cooling cycles in the interval 300–850 K, as well as the absence of irreversible changes in the residual resistivity, indicate that the observed phenomenon is not due to a redistribution of the impurities or to formation of metastable phases. The latter circumstance is of particular importance in the case of Pr and Nd, since rapid cooling from the liquid state to room temperature can secure partially the fcc phase of these metals,[11] which is usually stable only at high pressures.[12]

The results confirm the hypothesis that Pr and Nd are subject at high temperatures to hitherto-unknown phase transitions close to second order. The transitions correspond to the following integral changes of the entropy ($\Delta S$) and enthalpy ($\Delta H$): $\Delta S = (9.8 \pm 0.6) \times 10^{-2}$ cal/g-atom deg and $\Delta H = 75 \pm 4$ cal/g-atom for Nd, and $\Delta S = (4.3 \pm 0.3) \times 10^{-2}$ cal/g-atom-deg and $\Delta H = 29 \pm 2$ cal/g-atom for Pr.

Unfortunately, in view of some difference between the temperatures of the $C_P(T)$ anomalies and the thermal-expansion curves,[3] it is impossible to establish a reliable correlation between the results of the thermal and structural investigations. It can be noted, however, that the larger anomalies of the lattice parameters of Nd in comparison with Pr[3] correspond also to a larger jump of the heat capacity.

From a comparison of the anomalous behavior of the physical properties of Pr, Nd, Sm, and Eu in the vicinity of the high-temperature phase transitions[1–7] it becomes evident that the observed effects have a common nature, and that their distinguishing feature is the constancy of the crystal-lattice symmetry (decisive role of the electron system in the transition mechanism). Despite the differences between the crystal structures of the investigated REM (rhombohedral—Sm, double hcp—Pr and Nd, bcc—Eu), in the ion charge (Eu is

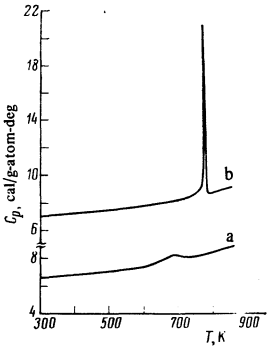


FIG. 1. Dependence of the specific heat of Pr (curve a) or Nd (curve b) on the temperature.

divalent in the metallic state), and in the assumed share of the $f$ states in the formation of the electron energy spectrum,[13,14] the temperatures $T_c$ of the observed $\lambda$ anomalies of the heat capacity are surprisingly close—700, 773, 695, and 765 K for Pr, Nd, Sm, and Eu, respectively. The characteristic energy ($kT_c = 0.06$–$0.07$ eV) responsible for the phase transitions turns to be of the same order as the energy parameter $A_{sf}$ of the exchange interaction of the "rigid" spins of the $f$ shells with the conduction electrons.[15,16] In the paramagnetic region, the indicated interaction manifests itself in experiment as a change of the magnetic moment of the REM ion as a result of the spin polarization of the conduction electrons.[16] If the electronic transitions in Pr, Nd, Sm, and Eu are indeed due to the interaction between localized and collectivized electron states, then it becomes necessary to explain the presence of singularities in the thermodynamic potential of these metals at temperatures when there is certainly now long-range order.[2)]

The theory[17] predicts a splitting of the conduction band by the $s$–$f$-exchange interaction even if the localized spins are randomly distributed, provided that the interaction parameter $A_{sf}$ is comparable in order of magnitude with the Fermi energy. This condition is satisfied above all for collectivized electrons, which correspond to sufficiently narrow energy bands and high values of the effective mass and of the state density. It can be assumed that the conditions of strong $s$–$f$-exchange interaction are realized in the investigated REM (possibly near singular points of the energy spectrum), and the observed phase transitions are connected with the mechanism whereby the corresponding energy gaps are destroyed at high temperatures.[17]

The exchange interaction of localized and collectivized electronic states as two autonomous subsystems with a conserved number of electrons is not the only possible explanation of the observed phase transitions. Arguments have been advanced[14] in favor of the existence of localized $f$ levels immersed in the conduction band near the Fermi energy of REM. In this situation, the metals can exhibit instability with respect to the "supermixing" that leads to a pairing of the states of the band and atomic (localized) electrons.[18] Unfortunately, at present there are no reliable data with which to estimate accurately the critical temperature $T_c$ of the corresponding phase transition. At reasonable values of the parameters of the model[18] one cannot exclude temperatures $T_c \sim 1000$ K. A final explanation of the nature of the transition calls for further investigations of light REM using sufficiently pure and perfect samples.

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[1)]The $C_P(T)$ curves were calculated from thermograms registered with an automatic potentiometer in the course of monotonic heating and cooling at a rate ~0.15 deg/hr.

[2)]The magnetic order is established in REM at temperatures $\Theta \sim A_{sf}^2/E_F \ll T_c$ ($E_F$ is the Fermi energy).[15]

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