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Thermal Effects of Phase Transitions of Cerium and Neodymium

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ABSTRACT. Phase transitions of high-purity cerium and neodymium are investigated by using high temperature scanning calorimeter (HT-1500 Seteram) in the temperature range 1500K. The calorimeter was calibrated by standard compounds (benzoic acid, Sn, Pb, Zn, Al, Ag, Cu). The accuracy of enthalpy of transitions (ΔH_{tr}) was about ±2 %. For cerium two types of transformation are detected: at 350-372 K - hexagonal close packing (hcp) - face-centered cubic lattice (fcc) transition, and in 880-960K the face-centered cubic lattice (fcc) transformation into body-centered cubic lattice (bcc). For neodymium the changing of hexagonal close packing (hcp) into body-centered cubic lattice (bcc) is detected at 1093-1113K. This anomalies are in good agreement with the literature data of electrical resistance, thermal conductivity and temperature conductivity. The thermal characteristics of transitions – enthalpy, entropy, temperature domains – are reported, which are as follows: for cerium hcp-fcc transition ΔH_{tr} =2436.3 J/mole; ΔS_{tr}=6.69 J/K.mole; fcc-bcc transition ΔH_{tr} = 4742.7 J/mole; ΔS_{tr}=5.0 J/K.mole; For neodium hcp-bcc transition ΔH_{tr} =3234.2 J/mole; ΔS_{tr}=2.9 J/K.mole. *© 2016 Bull. Georg. Natl. Acad. Sci.*

Key words: cerium, calorimetry, enthalpy of phase transitions, neodymium

Rare earth metals are widely used in modern technic, in particular when creating special magnetic alloys and complex compositions, used as thermoelectric, abrasive, refractory materials, catalysts, chemical current sources, and so on. The study of the physical properties of these substances near points of phase transitions are of great practical importance, because they are characterized by diverse types of structural and magnetic transitions. Of particular interest are the thermophysical parameters of phase transitions at high temperatures [1-5].

This paper presents results of a study of thermal characteristics of phase transformation of cerium and neodymium based on calorimetric measurements. The structure of cerium at high temperatures is changed twice. The first transformation takes place at 350K and corresponds to the transition of double hexagonal close packing (*hcp*) into face-centered cubic lattice (*fcc*). Near 990K the face-centered cubic lattice (*fcc*) transfers into body-centered cubic lattice (*bcc*). At 1093K the change of crystal structure of neodymium is revealed which is caused by transferring the

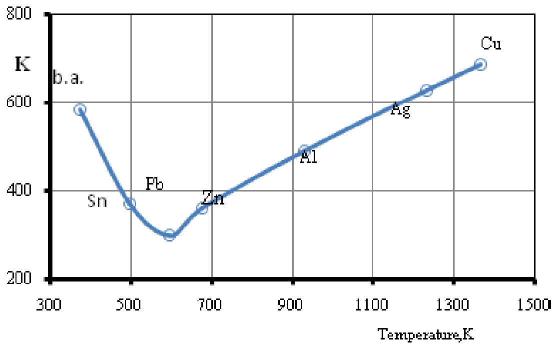

Fig. 1. Calibration curve of calorimeter.

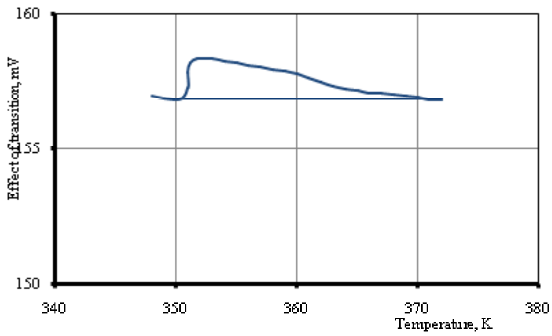

Fig. 2. Calorimetric measurements of thermal property of cerium at*hcp-fcc* transition (ΔH_{tr} of *hcp-fcc* transition at 350 K - 372 K).

hexagonal close packing *(hcp)* into body-centered cubic lattice (bcc). The temperatures of these transitions have been studied earlier on the base of heat-conductivity, temperature-conductivity and electrical resistance measurements [6-8], though the data ambiguity is evident.

Experimental

In order to evaluate the thermal characteristics of phase transitions of cerium and neodymium, such as thermal effects, enthalpy and entropy and temperature ranges, in the present work the calorimetric investigation have been performed using high temperature scanning calorimeter HT-1500 ("Setaram" production), which is very responsive apparatus for measuring a small thermal effects (<20mJ). The conditions of the experiments were as follows: heating rate - 200 K/hour (3K/min); velocity of the detector moving – 2.5 mm/min; galvanometers sensitivity – 500mV. The Pt/Rd-10%Pt thermocouples were used. The experiments were carried out in helium atmosphere. Calorimeter was calibrated by standard compounds: benzoic acid, tin, lead, aluminum, silver and copper (Fig.1).

The thermal effects of phase transitions were calculated as $\Delta H_{tr} = KAM/G$ J/mole, where K is the constant of calorimeter (Fig.1), A – the area under calorimetric effect, M – molar mass of the compound, G – mass of the sample. The number of experiments for each series was 8-10.The standard deviation for mean values was about ±2 %.

Results

On the calorimeter poly-terms (curves) of cerium two anomalous areas have been detected. The temperature of the first thermal effect at 350K, associated with the transition *hcp-fcc,* is in good agreement with [1]. On the other hand the temperature domain of the second phase transition *fcc-bcc* detected by heat conductivity, temperature conductivity and electrical resistance measurements differs from each other and from our calorimetric values significantly. The starting temperature for *fcc-bcc* transition of cerium is much lower (881K) in comparison with the data indicated in [1] – 990K. The enthalpy, entropy and temperature intervals of phase transitions of cerium are:

ΔH_{tr} =2436.3 J/mole; ΔS_{tr}=6.69 J/K.mole; Temperature interval 350-372 K

ΔH_{tr} = 4742.7 J/mole; ΔS_{tr}=5.0 J/K.mole; Temperature interval 850 K - 960K

Following should be mentioned at observation the calorimetric curves of cerium: the transition *fcc-bcc* has specific shape which is formed by three step-by-step peaks (Fig.2). In the heating regime just after the second peak the curve comes to its initial level and is immediately continued by the third one. The similar behavior is detected on the curve of cooling, though the transition temperatures are shifted to the lower temperatures on 30-40K showing the hysteresis effect (differential gap) in thermal properties of cerium. Our experimental result correlates with data of [1] and [2], in which the hysteresis of some physi-

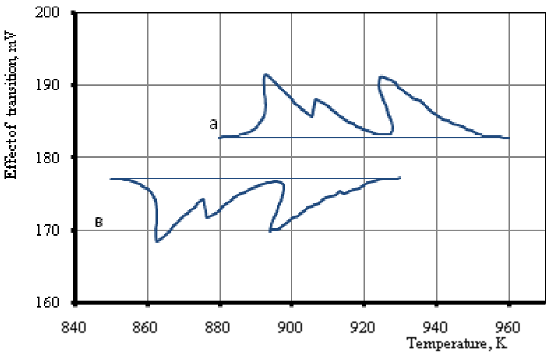

Fig. 3. Calorimetric measurements of thermal properties of cerium at *fcc-bcc* transition (ΔH_{tr} of *fcc-bcc* transition at 850 K - 960K)a - heating, b –cooling.

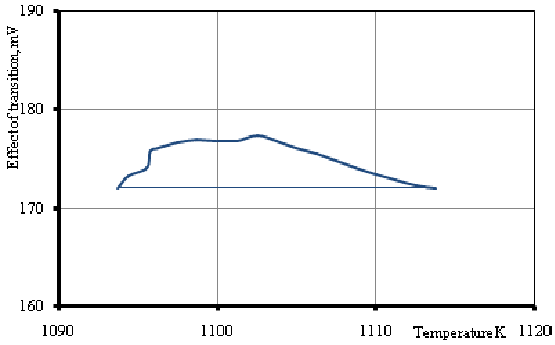

Fig. 4. Calorimetric measurements of thermal property of neodymium at *fcc-bcc* transition (ΔH_{tr} of *hcp -bcc* transition at 1093 K -1113K).

cal parameters of cerium at *fcc-bcc* transition is reported and discussed. At the same time, according to [1], neither electrical resistance nor thermal conductivity of cerium reveals the step curves.It can be supposed that the mentioned above differences between our calorimetric results and the temperature functions of other physical properties reported in [1-2] are due to the different purity of investigated samples and of gas atmosphere, as well as of different rate of heating and cooling in these two sets of experiments. The calorimetric curve for neodymium is presented on Fig.3. The thermal effect at 1093K is connected with phase transition of hexagonal close packing (*hcp*) into body-centered cubic lattice (*bcc*) and perfectly well correlates with the data of [1]. The thermal characteristics are evaluated to be:

ΔH_{tr}=3234.2 J/mole; ΔS_{tr}=2.9 J/K.mole; Temperature interval 1093-1113K.

ფიზიკური ქიმია

ცერიუმის და ნეოდიუმის ფაზური გარდაქმნების თერმული ეფექტები

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**ი. ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტის რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი*

(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ნაშრომში შესწავლილია იშვიათმიწა ლითონების ცერიუმის და ნეოდიუმის ფაზური გარდაქმნები და დადგენილია მათი თერმოფიზიკური მახასიათებლები. ექსპერიმენტული კვლევები ჩატარებულია მაღალპრეციზიულ მაღალტემპერატურულ დიფერენციალური სკანირების კალორიმეტრ HT-1500–ზე, 300–1500K–ის ფარგლებში. გამოვლენილია შემდეგი სახის სტრუქტურულ-ფაზური

გარდაქმნები: ცერიუმისათვის ჰექსაგონალური სტრუქტურიდან წახნაგცენტრირებულ კუბურ სტრუქტურაში გარდაქმნას ადგილი აქვს 350–372K–ზე, ხოლო წახნაგცენტრირებულ კუბური სტრუქტურიდან სხეულცენტრირებულ კუბურ მოდიფიკაციაში გადასვლის ტემპერატურული ინტერვალია 880–960K. ნეოდიუმის შემთხვევაში გამოვლენილია ერთი სახის ფაზური ცვლილება: ჰექსაგონალური მჭიდრო წყობა 1093–1113K–ზე გარდაიქმნება სხეულცენტრირებულ კუბურ სტრუქტურად. კვლევის შედეგად დადგენილია სტრუქტურული ფაზური გარდაქმნების თერმული მახასიათებლები: ენთალპია, ენტროპია და ტემპერატურული ინტერვალი.

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