Anomalies of the specific heat of samarium at high temperatures

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Some peculiarities in the specific heat $C_p(T)$ of samarium are observed at 560–700 °K and near 835 °K, and correspond to the well-known anomalies of its thermal expansion. The anomaly of C_p near 835 °K, characterized by a hysteresis of ∾15 deg, is ascribed to the previously-determined structural transition from the rhombohedral to the hexagonal close-packed lattice. It is assumed that the broad anomaly of C_p at lower temperatures, which terminates in a δ singularity at ∾694 °K with a hystersis of ∾3 deg is due to an electronic phase transition.

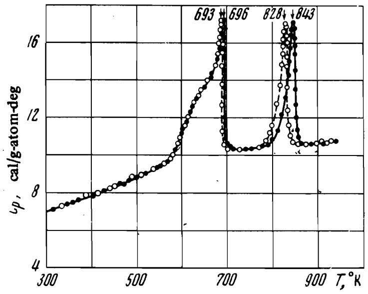
Samarium occupies a special position in the series of rare-earth metals (REM) primarily because of its unique crystal structure. The rhombohedral structure of α-Sm (space group R3m with 3 atoms per unit cell) is equivalent to a nine-layer close packing of the atomic layer in the sequence ABABCBCAC...[1]. Two-thirds of the lattice sites of α-Sm have hexagonal symmetry for the nearest neighbors, as in the usual hexagonal close packed (hcp) structure with a period of two layers ABAB..., and one-third has the cubic symmetry characteristic of cubic close packing (fcc) ABCABC... In all cases when a structure of the α-Sm type is produced, namely in pure metallic samarium, in alloys of light REM with heavy ones[2], and in a number of REM subjected to hydrostatic compression[3], the structure is characterized by an axis ratio $c/a \approx 1.605$, which is close to the ideal 1.633.

The question of the origin of many crystal structures (including the α-Sm structure) cannot be answered at present on the basis of general principles and data on the electron configurations of the individual atoms. The determination of the conditions under which a definite crystal structure appears, and the reasons why the structure is modified, are therefore potential sources of information on electron interaction in solids.

The appearance of the unusual structure of α-Sm and of a number of other crystal structures of REM, which differ in essence only in the sequence of the packing of identical atomic layers and in the deviation of the axis ratio c/a from ideal, seems to be connected with energy-band structure singularities in which the differences between the free energies of the phases are small[4]. There are published discussions of the connection of the characteristic structures of REM with the stability of the electron configurations formed by localized 4f-shell electrons[5], with the extent of participation of the f states in the symmetry of the electronic states at the Fermi level[6], with the contribution made to the binding energy by the indirect exchange via the conduction electrons[7], and with the singularities of the multiply-connected Fermi surface of the REM, which stabilize the modulated distribution of the close-packing defects[8].

Samarium has, besides a rhombohedral phase which is stable at room temperatures, also a body-centered cubic (bcc) modification at temperatures above ~1190°K[9], and a doubly hexagonal packing (dhcp) with a c-axis period that spans over four atomic layers ABACABAC... at temperatures 600–1200°K and pressures 40–20 kbar. In[11] it was reported that a fourth hcp polymorphic modification of samarium exists in vacuum-sputtered thin films. This assertion, however, was refuted by the authors of[12], who stated that the experimental conditions under which the films were obtained in[11] led to oxidation of samarium and to formation of the monoclinic B-Sm_2O_3 phase, the electron-diffraction pattern of which is similar to that presented as proof of the existence of the new phase of samarium. Mardon and Koch[13], using x-ray diffractometry, dilatometry, and measurement of the resistivity of pure polycrystalline samples (99.9%), have demonstrated that the rhombohedral structure of samarium is preserved only up to 713–873°K. In this temperature interval (depending on the dimension and shape of the samples and on the employed research method) the α-Sm phase is transformed into an hcp structure.

The phase-equilibrium temperature, in the opinion of Mardon and Koch[13] is strongly influenced by contamination of the samples during the tests. In sufficiently bulky resistometric and dilatometric samples, the contamination of which by oxygen does not exceed 0.01–0.05 at.% after 5–6 temperature cycles 300–923°K, the α-Sm ⇄ hcp structure transition occurs at 871–861 and 823–793°K, respectively. In the same samples at lower temperatures (523–623°K) there were observed anomalies of the resistivity and of the linear expansion ΔL/L, and were ascribed to a change in the energy band structure of α-Sm. X-ray diffraction investigations have revealed an anomalous behavior of the lattice parameter of rhombohedral samarium in the temperature interval 523–623°K. Near ~580°K there is a noticeable increase in the rate of change of the α-Sm crystal-lattice parameter a with temperature, whereas the temperature dependence of the hexagonal axis c remains monotonic. The anomalous character of the thermal expansion of α-Sm becomes most noticeably manifest in the variation of the axis ratio c/a with temperature ($c/a = 1.6044$ at ~300°K). The ratio c/a first increases with temperature, but remains practically constant (~1.6087) once 580°K is exceeded, up to the α-Sm → hcp structure transition ($c/a \approx 1.595$). The structure transition is accompanied by a 0.8–1.0% jump in the atomic volume. In x-ray diffraction samples (fine powder or thin ribbon), this transition is observed at ~713°K, where the temperature hysteresis has a width 20–50 deg. To explain the lower temperature of the α-Sm ⇄ hcp transition in thin x-ray diffraction samples (~713°K) in comparison with the transition temperature (823–871°K) in the bulky resistometric and dilatometric samples, Mardon and Koch[13] were forced to assume a larger contamination of the



Specific heat curve $C_p(T)$ of samarium, obtained by heating at a rate 0.15 deg/min (black circles) and cooling at the same rate (white circles).

thin samples by oxygen during the test time (up to ~0.13 at.%). The contamination of samarium by extraneous impurities and its oxidations hinder greatly the investigation of this metal at high temperatures.

Perakis and Kern[14] have detected a jumplike change in the magnetic susceptibility $\chi(T)$ of a sufficiently pure sample of metallic samarium (99.7%) at ~940°K, and a noticeable change in the slope of the $\chi(T)$ curve at ~630°K. However, after a prolonged soaking of this sample at 1380–1440°K, these anomalies of $\chi(T)$, as well as the anomalies due to the known phase transitions at 106°K (Neel point), ~1190°K (temperature of the transition to the bcc phase), and 1345°K (melting point[15]) become smeared out and subsequently vanish. The sample remains crystalline even at 1540°K, and its magnetic behavior differs little from the behavior of the sesquioxide Sm_2O_3. The irreversible changes of $\chi(T)$ of samarium with increasing temperature and duration of annealing[14] were due apparently to contamination of the metal by impurities.

The existence of phase transitions in metallic samarium near 575 and 800°K is indicated by the anomalies of its electric and magnetic properties (thermoelectric power, resistivity[16], and magnetic susceptibility $\chi(T)$[17]), which were pointed out by Vedernikov[16].

The specific heat of polycrystalline samarium of purity ~99.7% at temperatures 300–1400°K was determined by the "mixing method" in a Bunsen icecalorimeter[15]. The specific-heat curve of samarium, $C_p(T)$, obtained by differentiating the heat-content ($H_T - H_{273°K}$) curve plotted in intervals of ~100 deg, revealed only the anomalies due to the structure transition (≈1190°K) and the melting of the metal (~1345°K). The purpose of the present study was a detailed investigation of the temperature dependence of the specific heat of samarium in the interval 300–950°K, to verify the assumption that phase transitions occur in this temperature region, and to determine their thermodynamic characteristics.

The measurements were performed in a differential microcalorimeter by direct registration of the exchange between the sample and the bulky shell under conditions of monotonic heating and cooling. The measurement procedure and the calculation of the specific heat were analogous to those used in[18]. When the procedure was checked on single-crystal and powder samples of α-Al_2O_3, the deviation of the measured values from the tabulated ones[19] did not exceed ±3%. The investigation object was a sample weighing 4.8 g and containing 99.9% samarium (as certified by the manufacturing plant) and a resistance ratio $R_{293°}/R_{4.2°} \approx 30$. Prior to the high-temperature investigations, this example exhibited, in good agreement with the data of[20], a distinct λ anomaly of the specific heat at the Neel point (~105.8°K), with a discontinuity width ΔC_p not exceeding ±1 deg. To eliminate the possible oxidation of the samarium and its evaporation at high temperatures, the sample was wrapped with tantalum foil and placed in a carefully outgassed quartz ampule, which was evacuated at room temperature to a pressure $\sim 10^{-7}$ mm Hg and was filled with helium. The specific heat of the foil and of the ampule were determined in a separate experiment and taken into account in the calculation.

The result of the measurement of C_p of samarium are shown in the figure (the dark circles were obtained while heating at a rate of ~0.15 deg/min, and the light circles while cooling at the same rate). The measurement results in the first and succeeding heating and cooling cycles coincided within the limits of the assumed error. The points in the figure designate the mean values of C_p obtained in five temperature cycles. The criterion of the reliability of the results with the absence of irreversible changes in the residual resistance, in the character of the anomaly of C_p at the Neel point (106°K), and in the weight of the sample (with accuracy ±0.0001 g) after the heating and cooling cycles. The first peak of C_p, located approximately at 694°K, has a broad base (from 560 to ~700°K) and consists apparently of the λ singularity of the specific heat, on which a symmetrical δ singularity, characterized by a thermal hysteresis of ~3 deg, is superimposed. The second peak of C_p is almost symmetrical relative to its vertex, which is located at ~834°K in the case of heating and at 828°K in the case of cooling. The estimate of the entropy increment due to the singularity of C_p at 694°K yields a value 0.56 ± 0.03 cal/g-atom-deg. For the anomaly at 830°K, the corresponding average increment is 0.13 ± 0.01 cal/g-atom-deg (the integral change of the enthalpy is $\Delta H = 108 \pm 9$ cal/g-atom).

The results of the measurements of the specific heat of a bulky sufficiently pure sample of samarium (the dimensions and the mass of the calorimetric sample were close to those for the dilatometric sample[13]) confirm the assumed existence in this metal of two previously unknown phase transitions above room temperature.

The anomaly of the specific heat near 835°K, with a hysteresis of ~15 deg, is typical of a smeared-out first-order phase transition. The results of an x-ray diffraction investigation[13] allow us to assume that this anomaly is connected with the α-Sm ⇄ hcp structure transition. It is interesting to note that the jump in the axis ratios c/a of the α-Sm and hcp lattices at the transition point, calculated on the basis of the results of[13], is

$$\frac{(c/a)_{\text{rhomb}}-1.633}{(c/a)_{\text{hex}}-1.633}\approx 0.63,$$

where 1.633 is the ratio of the axis of the ideal closest packing, agree well with the jump (~0.67) predicted by Hodges[8] on the basis of the pair-interaction model in the pseudopotential theory. The results obtained in the present study offer evidence that the change of the enthalpy in the α-SM ⇄ hcp structure transition ($\Delta H \approx 108$ cal/g-atom) is much lower than the latent heat of the transition from the hcp to the "looser" bcc structure at 1190°K ($\Delta H = 744 \pm 40$ cal/g-atom)[15]. This is not surprising, inasmuch as one third of the sites in the α-Sm lattice has a symmetry relative to the nearest neighbors different from the symmetry in the hcp lattice. Rocher[7] estimated the energy difference ΔE of the fcc and hcp ($c/a \sim 1.57$) crystalline modification of REM, assuming that this difference is due mainly to exchange interaction of the conduction electrons with the spins of the 4f shell. For trivalent gadolinium, in particular, the value obtained was $\Delta E \sim 0.3$ eV. Taking into account the difference between the de Gennes factors $(g_J - 1)^2 J(J + 1)$ of gadolinium and samarium (g_J is the Lande factor and J is the total angular momentum quantum number) and the relative fraction of the cubic packing in the α-Sm structure, the heat of the α-Sm $\rightleftharpoons$ hcp transition can be roughly estimated at ~65 cal/g-atom, which agrees in order of magnitude with the experimental value (~109 cal/g-atom).

The thermodynamic phase transition in samarium near 700°K is more complicated. In a wide temperature range (560–690°K) there are observed fully reversible (hysteresis-free) changes of the excess specific heat, and also the δ singularity of C_p at ~694°K with a hysteresis of ~3 deg, evidencing a jump-like change of the internal parameter with which the phase transition is connected. It is difficult to draw at present definite conclusions concerning the nature of this transition. To attribute the anomalies of the physical properties of samarium at 570–700°K to magnetic ordering[16] would contradict a recent neutron-diffraction investigation of this metal[21], according to which an atomic magnetic order in this metal is established at ~106°K (the ordering of the magnetic moments in the hexagonal positions of the lattice) and at ~13.8°K (the ordering of the moments in cubic positions). The anomalies of the thermal deformation of the α-Sm lattice[13], observed in the temperature region where the specific heat has an anomalous behavior (560–690°K), are customarily attributed to electronic phase transitions[22]. An important role in the determination of the causes of these transitions in samarium can be played by the following circumstances:

1. In the free Sm atom, the states of the 4f, 5d, 6s electrons have nearly equal energy[23]. This allows us to assume that in metallic samarium there exist near the Fermi surface virtual electronic states (4f), which are localized but are broadened as the result of resonance with the collectivized 6s and 5d electrons[24], so that under definite conditions a mutual transition of the electrons of the 4f, 5d, and 6s shells can occur, similar to that observed in cerium[25] and ytterbium[26]. The crowding out of the 4f electrons from the conduction band, with partial change of the valence of Sm from 3+ to 2+, occurs apparently in the bcc structure at high temperature[27] and in the liquid state[28]. The possibility of a thermodynamic phase transition in samarium as a result of a redistribution of the electrons among the energy levels was admitted in[22,29–31]. According to[31], this transformation should be of first order. A situation in which the crystal structure of the metal remains unchanged is possible in this case[32].

2. The splitting of the deepest multiplet levels of the Sm^{3+} ions is small. The energy difference $\Delta E/k \approx 1500°K$[33] between the first-excited ($J = 7/2$) and ground level ($J = 5/2$) is comparable with the energy of the thermal motion even at room temperature. Consequently, the main contribution to the magnetic susceptibility of the free Sm^{3+} ions is made by thermal excitation of the nearest levels of the multiplet and by the virtual transitions induced between them by the magnetic field (Van Vleck transitions)[34]. The proximity of the multiplet-structure levels results in an anomalous contribution of the exchange polarization of the conduction electrons to the magnetic properties of the metallic samarium[35]. Owing to the negative polarization of the conductions electrons, the effective moment of the Sm^{3+} in the metal is lower by an approximate factor of six than that determined from spectroscopic considerations[21,35]. It follows from formula (2.39) of the theoretical paper[35] that the contribution of the exchange polarization to the paramagnetic properties of metallic samarium can be appreciable up to ~400°K. The change of the local polarization of the carriers by the magnetic ions can be one of the causes of the observed anomalies of the physical properties of samarium.

The excess specific heat due to thermal excitation of the multiplet structure of Sm^{3+}, which is given by

$$C_{\text{excess}} = \frac{R(\Delta E/kT)^2 (g_0/g_1)\exp(\Delta E/kT)}{[(g_0/g_1)\exp(\Delta E/kT)+1]^2}$$

where R is the gas constant and g_0 and g_1 are the degeneracy multiplicity of the energy levels ($g = 2J + 1$), has at ~600°K a maximum of height ~1.1 cal/g-atom-deg. which is much lower than the maximum at ~700°K observed in experiment ($C_{\text{excess}} > 7$ cal/g-atom-deg). One cannot exclude, however, the possibility that the participation of the excited levels in the formation of the energy band structure leads to changes in the conditions of stabilization of the long-period crystal structure of α-Sm and is the cause of the observed phase transition.

For a final answer to the question of the nature of the phase transition in samarium at high temperatures, additional data are needed, and in particular reliable information on the structure changes and also data on the effect of high hydrostatic pressures on the transitions.

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162