PHASE TRANSITION IN SAMARIUM

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Submitted February 2, 1972

Zh. Eksp. Teor. Fiz. **63**, 213–216 (July, 1972)

The crystal structure of samarium at 77–300°K is studied by the low-temperature x-ray diffraction technique. It is shown that at T ~ 106°K there is a second-order phase transition which is apparently related to the paramagnetism-antiferromagnetism transformation. The discontinuous changes of the linear expansion coefficients at 106°K are pronouncedly anisotropic: $\Delta\alpha_\perp < 0$, $\Delta\alpha_\parallel > 0$. When the temperature drops below 106°K the period a of the nine-layer hexagonal compact lattice is found to increase.

SAMARIUM belongs to the cerium subgroup of rare-earth metals (REM). Unlike other REM, this metal has at room temperature a unique rhombohedral lattice (a_r = 8.966 Å, α = 23°13'[1]), equivalent to nine-layer hexagonal packing (a_h = 3.621 Å, c_h = 26.178 Å, c/a = 7.23). A structure of the α-Sm type is observed in heavy REM subjected to hydrostatic compression[2], and also in certain alloys of heavy and light REM[3]. The low-temperature crystal structure of samarium has not been investigated before. Investigations of various physical properties of polycrystalline samarium, such as the specific heat[4], magnetic susceptibility[5-10], thermal expansion[8], electric conductivity[9,11], and elastic constants[12] have revealed the presence of anomalies both at T ~ 15°K and at T ~ 106°K. The magnetic structure of samarium was not investigated by neutron diffraction[13]; no significant differences were observed in the Mossbauer spectra obtained at 80 and 300°K[14].

There are two points of view regarding the nature of the anomaly of the physical properties of samarium at T ~ 106°K: (i) the temperature 106°K is the Neel point of α-Sm, and further ordering of the magnetic moments takes place at 15°K; (ii) an electronic phase transition takes place at 106°K and can be accompanied by a change in the crystal-lattice symmetry[7,12]. In the latter case, one has in mind a transfer of one valence electron to the 4f level ($4f^5 5d^1 6s^2 \rightarrow 4f^6 6s^2$). In this case, since $V_{at}(Sm^{2+}) \sim 1.5V_{at}(Sm^{3+})$[3], an increase in the atomic volume should be observed. In the REM series, electronic first-order phase transitions were observed in cerium (FCC I → FCC II, 110°K)[15] and in ytterbium (FCC → HCP, 290°K)[16].

The purpose of the present study was to determine the crystal structure of samarium at T = 77–300°K by low-temperature x-ray diffraction. We investigated polycrystalline metal 99.8% pure. The samples were annealed in a vacuum of 2×10^{-7} mm Hg at 700°C for two hours and were cooled slowly to relieve the internal stresses and to obtain a large-grain structure. The x-ray diffraction procedure at 77 – 300°K did not differ significantly from that described earlier[17]. In view of the complexity of the structure of α-Sm, in addition to the diffractometric measurement of the lattice parameters, we obtained x-ray photographs in the investigated temperature interval; these have revealed the absence of any qualitative structure changes. The crystal-lattice parameters were measured using the single-crystal (110) ($2\theta \sim 78.5°$) and (0.0.18) ($2\theta \sim 104°$) reflections in Cr K_α radiation with accuracy $\Delta a = \pm 3 \cdot 10^{-4}$ Å, $\Delta c = \pm 8 \cdot 10^{-4}$ Å. The results of the measurement of the parameters a and c and the ratio c/a of the axes in α-Sm (in the hexagonal setting) are shown in Fig. 1. Clearly pronounced inflections are seen on the plots of a, c, and c/a against T near T = 106°K. At T < 106°K the period a increases, whereas the c(T) curve becomes much steeper than at T > 106°K. This leads to a sharp decrease of the ratio of the axes with decreasing temperature. Graphical differentiation of the a(T) and c(T) curves yielded the following temperature dependences of the linear-expansion coefficients:

$$\alpha_\perp = a^{-1}da/dT, \qquad \alpha_\parallel = c^{-1}dc/dT.$$

At T ~ 106°K, a negative anomaly is observed on the α(T) curve, and a positive one on the α(T) curve (Fig. 2). The absence of a change in symmetry and of discontinuities of the lattice parameters at T ~ 106°K indicates that the anomaly of the properties of samarium is not connected with a structural transformation. The α(T) curves had forms typical of second-order phase transitions (see[16]). An important confirmation of the

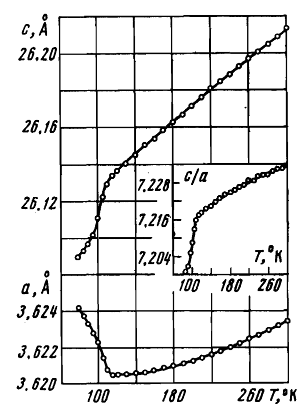

FIG. 1

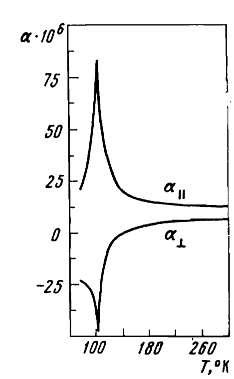

FIG. 2

FIG. 1. Temperature dependence of the parameters a and c and of the axial ratio c/a in α-Sm (in the hexagonal setting).

FIG. 2. Temperature dependence of the coefficients of linear expansion of α-Sm ($\alpha_\perp$ and $\alpha_\parallel$).

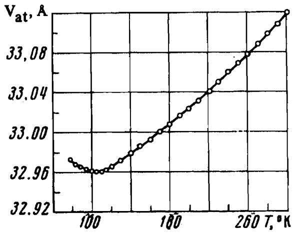

FIG. 3. Temperature dependence of the atomic volume of α-Sm.

fact that the transition at $T \sim 106°K$ in samarium is a second-order phase transition is the absence of hysteresis of the transformation temperature both in the results of the present structure investigations and in the results of magnetic measurements[7].

The character of the temperature dependence of the atomic volume ($V_{at} = a^2c \times 3^{1/2}/18$), i.e., the presence of an inflection on the $V_{at}(T)$ curve at $T = 106°K$ (Fig. 3) correlates qualitatively with the results of dilatometric measurements[8]. With such a $V_{at}(T)$ curve, a negative "jump" of the coefficient of thermal volume expansion should take place at the anomaly temperature ($\Delta\alpha_V = 2\Delta\alpha_\perp + \Delta\alpha_\parallel \sim 31 \cdot 10^{-6}$ deg^{-1}). In accordance with the relation of the Landau theory of second-order phase transitions[18]

$$\Delta\alpha_V = \frac{\Delta C_p\, dT_A}{V_{at} T\, dp}$$

the known value of the jump of the specific heat ΔC_l at the anomaly temperature T_A[4] and the values of V_{at} and $\Delta\alpha_V$ measured by us yield the estimate $dT_A/dp \sim -0.4$ deg/kbar. Direct measurements of the shift of T_A under pressure were not performed.

The most probable cause of the second-order phase transition in samarium at $\sim 106°K$ is the magnetic paramagnetism-antiferromagnetism transformation. Unlike the heavy REM (Gd – Er), which are characterized in the magnetically-ordered state by a negative expansion along the c axis[19,17], which correlates well with their magnetic structures[20], an increase of the parameter a is observed in samarium below T_N. This points to a significant difference between the magnetic structure of α-Sm and the structures of the heavy REM. Apparently in samarium, in analogy with the investigated light REM (Pr and Nd), there can be observed a magnetic structure with sinusoidal modulation of the magnetic moments along the a axis. The assumed presence of an electronic transition in samarium[7,12] contradicts the results, since such a transition should be of first order[15].

The authors thank Academician B. G. Lazarev, V. S. Kogan, V. V. Slezov, and V. M. Tsukernik for a discussion of the present results.

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Translated by J. G. Adashko
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