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Low temperature phase transition in samarium

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The crystal structure of α-samarium was investigated in the temperature interval 4.2–300 K. It has been established that the low-temperature transition at $T = 14.5$ K, just at $T = 106$ K, is a second-order phase transition. Both phase transitions are due to successive onset of antiferromagnetic order respectively in layers with hexagonal symmetry of the environment ($T_{N_h} = 106$ K) and in layers with cubic symmetry of the environment ($T_{N_c} = 14.5$ K) in a nine-layer hexagonal compact lattice. At both critical points, the jumps of the linear expansion coefficients are highly anisotropic; $\Delta\alpha_\perp < 0$ and $\Delta\alpha_\parallel > 0$. The singularity of the thermal expansion is most strongly pronounced at $T_{N_c} = 14.5$ K. It is concluded from the calculation of the temperature dependence of the energy of spontaneous deformation of the crystal lattice in the magnetically disordered state that the spontaneous magnetic moment of the cubic sublattice is larger than the moment of the hexagonal sublattice.

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It was shown in an earlier study[1] of the crystal structure of α-Sm in the interval 77–300 K that the paramagnetism–antiferromagnetism transition that occurs at $T = 106$ K is of second order from the thermodynamic point of view. A subsequent neutron-diffraction investigation[2] of single-crystal samarium has established that below 106 K only 2/3 of the atoms of its rhombohedral lattice are antiferromagnetically ordered, and the positions of these atoms correspond to hexagonal close packing (h-layers), while 1/3 of the atoms in positions corresponding to cubic close packing (c-layers) produce a magnetically ordered state below 14 K. The magnetic moments of the atoms of both layers are directed along the c axis and form somewhat different collinear antiferromagnetic structure. Whereas for the hexagonal positions the ferromagnetic layers are normal to the c axis, for the cubic positions they are parallel to the $(10\bar{1}1)$ planes. The results of the measurement of the magnetic susceptibility of samarium single crystals[3] can also be adequately interpreted by representing this crystal as an antiferromagnet with a c axis.

In this paper we continue the structural investigation of α-Sm into a temperature region that includes a second phase transition. The measurement was made in a cryostat where the sample temperature was continuously varied in the interval 4.2–300 K by a stream of cold helium gas. The sample temperature was measured with differential thermocouples; a Cu – Au + 0.01% Fe was used in the interval 4.2–40 K, and a copper–constantan thermocouple above 40 K.

The object of the investigation was, as before, a polycrystalline sample with a large-grain structure, produced by recrystallization annealing.

The single-crystal reflections were recorded on the x-ray diffractometer chart from the (0018) planes ($2\theta \sim 104°$) in CrK_α radiation and from the (220) planes ($2\theta \sim 116.4°$) in CuK_α radiation. This made it possible to measure the parameters of the crystal lattice with accuracy $\Delta a_i/a_i = \pm 1.10^{-5}$. The position of the diffraction peak was fixed in temperature steps of 1–2 K, and in steps decreased to 0.2 K in the phase-transition region.

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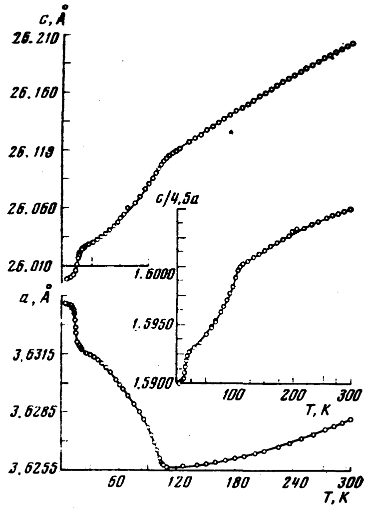

FIG. 1. Temperature dependences of the parameters a and c and of the axis ratio $c/4.5a$ in α-Sm.

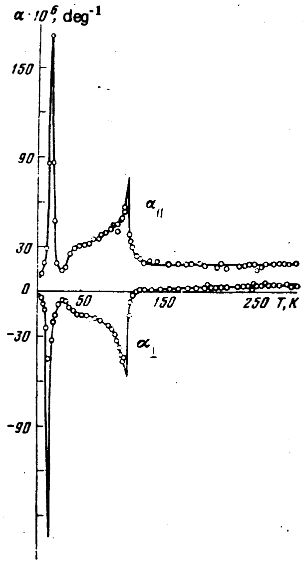

FIG. 2. Temperature dependences of the coefficients of linear expansion of α-Sm ($\alpha_{\parallel}$ and $\alpha_{\perp}$).

Figure 1 shows the results of measurements of the parameters c and a and of their ration $c/4.5a$ in samarium (in the hexagonal setting). The appearance of magnetic ordering in the h layers (at $T_{Nh} < 106$ K) results, when the temperature is decreased, in a continuous decrease of the lattice period along the principal axis, and in an increase of the period in the basal plane. The rate of change slows down somewhat in the interval 30–20 K, and with further decrease of temperature the onset of the antiferromagnetic ordering in the c-layers is accompanied by a substantial increase of the slopes of the $c(T)$ and $a(T)$ curves, which acquire a pronounced inflection point at the temperature $T_{Nc} = 14.5 \pm 0.5$ K. This temperature is quite close to that at which anomalies appear in the physical properties of samarium, viz., the magnetic susceptibility,[3,4] the specific heat,[5] the electric conductivity,[6] the elastic constants,[7] and the thermal expansion.[8]

Graphic differentiation of the $c(T)$ and $a(T)$ curves yielded the temperature dependences of the coefficients of linear expansion: $\alpha_{\parallel} = c^{-1}dc/dT$ and $\alpha_{\perp} = a^{-1}da/dT$. The complete picture of the behavior of the thermal expansion of samarium in the interval 4.2–300 K is shown in Fig. 2. The "jumps" of the coefficient of the thermal expansion is about 2.5 times larger for both the positive and negative on the $\alpha_{\parallel}(T)$ and $\alpha_{\perp}(T)$ curves anomalies at $T_{Nc} = 14.5$ K than at $T_{Nh} = 106$ K.

From the aggregate of the observed attributes, namely the constancy of the crystal symmetry, the jumps of the lattice parameters, the hysteresis of the transition temperature, both in accord with the results of our present structure investigations and in accord with the magnetic-measurement data,[4] and finally from the form of the anomalies on the $\alpha(T)$ curves, it can be concluded that the magnetic transition at $T_{Nc} = 14.5$, just as the first transition at $T_{Nh} = 106$ K, is of second order from the thermodynamic point of view.

The extremal character of the behavior of the temperature dependence of the atomic volume ($V_{at} = 3^{1/2}a^2c/18$) in the magnetically ordered state (Fig. 3) suggested the presence of negative "jumps" of the coefficient of thermal expansion ($\alpha_V = V_{at}^{-1}dV_{at}/dT$) at the anomaly temperatures T_{Nh} and T_{Nc}. This, in accordance with the relation deduced in the theory of second-order phase transitions[9]

$$\Delta\alpha_V = \frac{\Delta c_p}{V_{at}T_N}\frac{dT_N}{dp}$$

to obtain from the known "jumps" of the specific heat Δc_p and T_{Nh} and T_{Nc} (Ref. 5) and from our measured values of V_{at} and $\Delta\alpha_V$) the estimates $dT_{Nh}/dp = -0.6$ deg/kbar and $dT_{Nc}/dp = -0.4$ deg/kbar. The baric dependence of the temperatures of the samarium anomalies have not hitherto been investigated experimentally.

The temperature dependence of the samarium lattice parameters makes it possible to trace the temperature dependence of the energy of the spontaneous deformation of the crystal lattice, due to the action of the exchange forces in antiferromagnetic ordering. In fact, if the spontaneous deformations of the a and c axes are defined in the extrapolation the $a(T)$ and $c(T)$ curves from the paramagnetic region as $\lambda_{\perp} = a_{meas}/a_{ext} - 1$ and $\lambda_{\parallel} = c_{meas}/c_{ext} - 1$, and if the elastic modulus ε is assumed isotropic and its value in the antiferromagnetic phase is taken from the measurement data[7] for polycrystal-

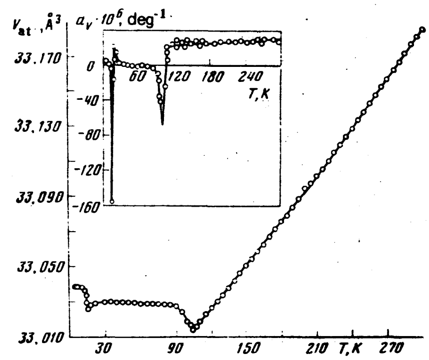

FIG. 3. Temperature dependence of the atomic volume and of the coefficient of the bulk thermal expansion of α-Sm.

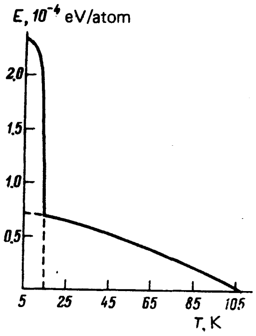

FIG. 4. Temperature dependence of the magnetoelastic energy in α-Sm.

line samarium, then the spontaneous magnetoelastic energy $E = 1/2\varepsilon(2\lambda_\perp^2 + \lambda_\parallel^2$ and its temperature dependence take the form shown in Fig. 4. The calculated energies at $T > 14$ K are referred to one atom of the hexagonal layer and at $T < 14$ K to one atom of the cubic layer. This representation of the exchange energy starts with the assumption that the magnetic moments of the cubic-sublattice atoms do not interact with the moments of the hexagonal sublattice. This is indicated, in particular, by the result of the neutron-diffraction investigations,[2] which points to invariance of the intensities of the reflections from the magnetic structure of the h layer when the samarium samples are cooled below 14 K.

It can be seen from Fig. 4 that in the fully ordered state ($T = 5$ K) the energy for the cubic positions is ~3.4 times larger than for the hexagonal ones, and one can expect therefore their spontaneous magnetic moments to be ~1.85 times larger. A similar conclusion is reached also by McEwen *et al.*[3] who analyzed the magnetic properties of samarium in the ordered state. According to their estimate the magnetic moments of the cubic and hexagonal positions are respectively 0.47 and 0.25 μ_B.

It should be noted in conclusion that the temperature dependence of the $E(T)$ curve gives grounds for assuming that the spontaneous magnetizations of the hexagonal and cubic sublattice of the rhombohedral samarium have strongly differing temperature dependences.

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