THE CRYSTAL STRUCTURE OF CHROMIUM AT 113—373° K

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The crystal structure of chromium was studied in the temperature range from 113 to 373°K. It is shown that the body-centered-cubic unit cell is conserved throughout the investigated temperature range. The existence of a second-order phase transition at 317°K (paramagnetism—antiferromagnetism transformation) is confirmed. The first-order phase transition observed at 168°K is apparently related to a change in the magnetic anisotropy at this temperature.

We have shown previously [1,2] that there are no first and second order phase transformations in pure chromium in the temperature interval 40—1700°C. The purpose of the present investigation was a further study of the structure of chromium: we investigated the temperature interval 113—373°K (−160—+100°C), where it was assumed, in accordance with the published data, that there are two phase transformations, at +40 and at −115°C. It has been shown by neutron diffraction means that at +40°C chromium goes over from an antiferromagnetic into a paramagnetic state [3-5], a fact confirmed by the results of measurements of the crystal lattice parameter [6], the coefficient of thermal expansion [3,7,8], the heat capacity [9], and the elastic constants [7,10].

There is no unified point of view concerning the presence, temperature, and nature of the low-temperature transformation in chromium, although it is known that an anomaly of several physical properties is observed in the interval 121—158°K [3,7,10-12]. There exists an opinion that at low temperatures the uncompensated spins of the 3d electrons turn through 90°, i.e., a change takes place in the magnetic anisotropy [4,5,13]. According to a different point of view, the helicoidal antiferromagnetic structure is destroyed in this temperature interval [14]. On the other hand, according to [3], there is no antiferromagnetism at all below 158°K.

INVESTIGATION PROCEDURE

Investigations were carried out with a sample of polycrystalline chromium, constituting a piece of 99.95% pure vacuum condensate [15]. An x-ray-diffraction method was used to investigate the structure over a wide temperature interval. The experiments were carried out with the URS-501 diffractometer, equipped with a low-temperature attachment constructed at the Karpov Physicochemical Institute. The attachment made it possible to take x-ray pictures of flat samples in the temperature interval from −160 to +130°C. The sample holder, surrounded by two hemispherical ovens, was placed in a copper chamber in contact with liquid nitrogen (the upper part of the chamber was the bottom of a Dewar). The temperature was regulated by changing the level of the liquid nitrogen in the Dewar and by varying the conditions under which the hemispherical electric resistance furnaces were heated. The electric furnaces were fed through a type S-0.75 ferroresonant voltage stabilizer. The temperature was measured with a differential chromel-alumel thermocouple (cold junction at 0°C), and the measuring instrument was a PPTN-1 low-resistance potentiometer. The temperature measurement accuracy was not worse than ±0.2°.

The parameter of the body-centered cubic chromium crystal lattice was measured by determining the diffraction peaks ($K_{\alpha 1}$ and $K_{\alpha 2}$) from the (211) plane with chromium radiation. In the investigated temperature interval, the range of variation of the diffraction angles θ was 76°20′—76°38′. To register the diffraction peaks at these angles, some changes were introduced into the construction of URS-50I instrument: the dimensions of the protective cover of the tube were decreased, and a special cut was made in the holder of the entrance slots of the GUR-3 goniometer, making it possible to increase the maximum value of the registered angles θ to 77°50′. The diffraction peaks were recorded

automatically, a constant range of angles (155°30′—158°30′) being recorded on the chart in the 2θ scale for each measurement. The backlash of the goniometer and of the automatic recorder was set beforehand.

The $K_{\alpha 1}$ and $K_{\alpha 2}$ doublets from the (211) plane are fully resolved at the selected counter and automatic-recorder chart speeds, and the form of the $\alpha 1$-component of the doublet is satisfactorily approximated by the expression $1/(1 + \gamma x^2)$.

The position of the maximum of the diffraction line was determined by a method in which the center of gravity of the line was obtained accurate to ±0.3′, which ensured an accuracy not lower than ±0.00005 kX in the measurement of the parameter of the chromium crystal lattice.

RESULTS AND DISCUSSION

Figure 1 shows the measured parameters of the crystal lattice of chromium in the investigated temperature interval. As can be seen, from 113 to ~168°K the parameter of the crystal lattice increases monotonically with increasing temperature; at ~168° the curve a = f(T) experiences a discontinuity (a jumplike change in the atomic volume takes place). With further increase in the temperature, the crystal lattice constant again increases, and in the region of 317°K the plot of the parameter a vs. temperature changes its course abruptly. It must be noted that the jump of the parameter at ~168° is not very pronounced, owing to the smallness of the effect ($\Delta a = 3 \times 10^{-4}$ kX), but the results of a large number of measurements give grounds for assuming that the tendency to a jumplike decrease in the dimension of the crystal lattice does exist.

From the measured parameters of the crystal lattice we plotted [by graphic differentiation of the curve a = f(T)] the temperature dependence of the coefficient of thermal expansion of chromium (Fig. 2). In the 113—168°K interval, the coefficient of linear expansion increases from 1.6×10^{-6} to 5.0×10^{-6} deg^{-1}; at 168° the $\alpha(T)$ curve experiences a discontinuity. At higher temperatures, the coefficient of thermal expansion again increases, and an anomaly of the λ-point type appears at 317°, in accordance with the course of the a(T) curve (Fig. 1): α decreases from 9.0×10^{-6} to 3.0×10^{-6} deg^{-1}.

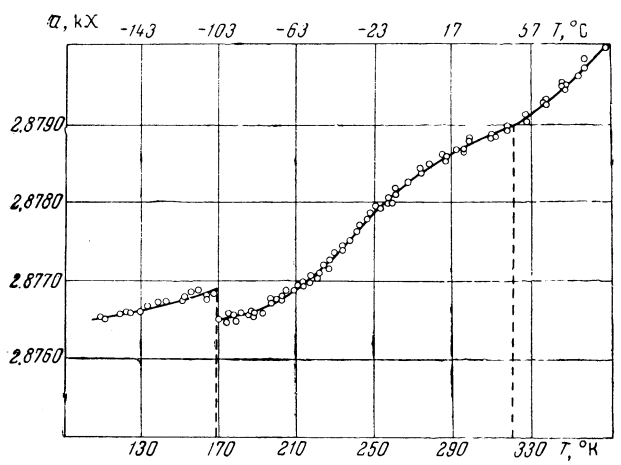

FIG. 1

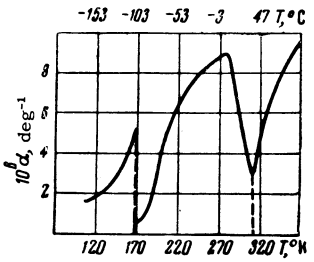

FIG. 2

The anomaly in chromium at 317°K (+44°C) is obviously connected with the transition from the antiferromagnetic into the paramagnetic state (second order phase transition). The slight difference between our value of the transformation temperature and some published data can be attributed to differences in the purity of the metal (the shift of the temperature of the antiferromagnetic transition in chromium as a function of the purity is pointed out in several papers[10,14]). The decrease in the coefficient of thermal expansion of chromium at the λ point does not contradict the Landau theory of phase transformations[16]. Indeed, the jump in the coefficient of thermal expansion at the second-order phase transition point is connected with the jump in the specific heat Δc_p by the simple relation

$$\Delta\alpha = \frac{\Delta c_p}{3VT}\frac{dT_\lambda}{dP}.$$

Inasmuch as Δc_p is always positive[16], the sign of the jump of the linear expansion coefficient is determined only by the sign of dT_λ/dP, in other words, by the character of the pressure dependence of the transformation temperature T_λ.

The character of the change of the chromium crystal lattice parameter at ~168°K (jumplike decrease) indicates that at this temperature there occurs a first-order phase transition. Some "smearing" of the transition temperature can be due to the fact that the volume of the chromium crystal exposed to the x-ray beam does not ex-

perience the transformation simultaneously[1)]. The most probable form of the first order phase transformation at 168°K is a change in magnetic anisotropy[4,5,13].

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[1)] The effect of broadening of the diffraction lines, connected with the coexistence of two phases with different crystal-lattice parameters, cannot be observed owing to the smallness of $\Delta a/a$.

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