SOVIET PHYSICS

JETP

A translation of the Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki

Vol. 30, No. 4, pp. 581-790 (Russ. Orig. Vol. 57, No. 4, pp. 1065-1462) April 1970

A PHASE TRANSITION IN VANADIUM

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Submitted January 26, 1969

Zh. Eksp. Teor. Fiz. 57, 1065–1068 (October, 1969)

The crystal structure of single-crystal vanadium is studied by low-temperature x-ray diffraction techniques between 77 and 300°K. A second-order phase transition occurs at 230°K. It entails a decrease of the symmetry of the crystal lattice from body-centered cubic to tetragonal.

IT is known that anomalies of the temperature dependence of a series of physical properties are observed in vanadium in a broad temperature range (180–325°K); in particular, a maximum of the magnetic susceptibility is observed at these temperatures.[1] In studying the crystal structure of polycrystalline vanadium at low temperatures kinks were observed on the curves of the temperature dependence of the lattice parameter of the body-centered cubic lattice at 200°K (for 99.74% pure metal) and at 233°K (for 99.2% pure metal).[2] Such changes in the structure have been explained by the presence of a paramagnetism-antiferromagnetism second-order phase transition. However, no antiferromagnetic ordering was observed in neutron diffraction[3] and nuclear magnetic resonance[4] experiments. The small change in the NMR signal on the ^{51}V nuclei was related to a small distortion of the body-centered cubic structure; the appreciable anisotropy of the thermal expansion of vanadium single crystals[5,6] was also explained by a decrease of the symmetry of the crystal lattice. It was, in addition, proposed that the anomalies of the physical properties of vanadium are exclusively connected with the presence of impurities and should not occur for a pure metal.[7]

The purpose of this work is an accurate low-temperature x-ray study of the nature of the change of the crystal structure of vanadium at the temperature at which the anomaly occurs. Unlike in the previous publication,[2] the investigation was carried out using a single crystal; the use of a single crystal in the investigation enhances the possibility of observing small distortions of the crystal lattice because of the absence of superposition of reflections from variously oriented crystallites. We investigated a single crystal of vanadium in the form of a rod with a [110] growth axis obtained by zone refining[8] and having a residual resistance R(298°K)/R(20.4°K) = 20. Since the temperature of the anomaly T_a depends appreciably on the nature and concentration of impurities,[2,7] we determined it by measuring the electrical resistance in the 77–300°K temperature range.(1) The temperature dependence of the relative electrical resistance R(T)/R(300°K) along the [110] direction is shown in Fig. 1; as is seen, a bend is observed on the curve at $T_a \sim 230$°K.

The x-ray measurements were carried out on a URS-50I setup equipped with a cryostat attachment by a previously described method.[9] For the x-ray measurements the rod was cut by an electroerosion method; the working surface was chemically and electrolytically polished.(2) The temperature dependences of the inter-

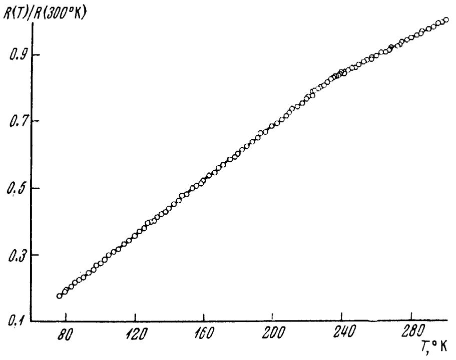

FIG. 1. Temperature dependence of the relative electrical resistance R(T)/R(300°K) of a single crystal of vanadium along the [110] direction.

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(1) The authors consider it their pleasant duty to thank V. S. Pavlov for assistance in the electrical resistance measurements.

(2) After polishing, the crystals were annealed for an hour at 1000°C in a vacuum of ~ 10^{-6} mm Hg.

hkl	λ	θ (290° K), deg	Temperature range, °K					
			80—230			230—300		
			$\Delta a_{\text{cub}}\cdot 10^5$, Å	$\bar{\alpha}_{\text{exp}}\cdot 10^6$, deg^{-1}	$\bar{\alpha}_{\text{calc}}\cdot 10^6$, deg^{-1}	$\Delta a_{\text{cub}}\cdot 10^5$, Å	$\bar{\alpha}_{\text{exp}}\cdot 10^6$, deg^{-1}	$\bar{\alpha}_{\text{calc}} = {}^1/_4\Sigma\bar{\alpha}_{\text{exp}}\cdot 10^6$, deg^{-1}
220	CrK_{β_1}	76.71	305±20	6.7±0.4	6.6	185±10	8,7±0,4	8,85
330	CuK_{β_1}	77.12	300±20	6.6±0.4	6,6	180±10	8,5±0,4	
222	NiK_{α_1}	71.42	400±20	8,8±0,4	8,8	195±10	9,2±0,4	
321	CuK_{α_1}	72.05	320±20	7.0±0.4	7,1	190±10	9,0±0,4	
100	—	—	—	—	6,6 ($\alpha_\perp$)	—	—	
001	—	—	—	—	13,2 ($\alpha_\parallel$)	—	—	

planar distances (d) from various crystallographic planes (hk$l$) were measured in the 77-300°K temperature range using various radiations (λ); the radiation was chosen in such a way that the Bragg reflections of the corresponding planes occurred at large diffraction angles (θ) (see the table); this ensured an accuracy in the measurements of the lattice constants [$a_{\text{cub}} = d_{hkl} \times (h^2 + k^2 + l^2)^{1/2}$] no worse than (5–10) × 10^{-5} Å.

In the table we present the results of measurements of the effective lattice constant (a_{cub}) at temperatures below (80–230°K) and above (230–300°K) T_a, as well as values of the mean linear expansion coefficients

$$\bar{\alpha} = \frac{1}{a(300^\circ\,\text{K})}\,\frac{\Delta a_{\text{cub}}}{\Delta T}$$

in various directions [hk$l$]. It is seen that below 230°K one observes a considerable anisotropy of the thermal expansion of vanadium, which attests to the decrease of the symmetry of the crystal lattice.

The determination of the structure of vanadium for $T < T_a$ is complicated by the fact that the "low-temperature modification" is very close to cubic, whereas the experiment provides information about a very limited number of crystallographic planes. For the structure determination we employed general methods for the testing of hypotheses:[10] from the temperature dependence of the values of two or three interplanar spacings we calculated the parameters of crystal lattices into which a body-centered cubic structure could go over as a result of a second-order phase transition;[11] 3) from the obtained values of the parameters we calculated the interplanar distances (d_{hkl}^{calc}) for the remaining crystal planes which give reflections; the most probable structure type for $T < T_a$ corresponded to a minimum of the sum

$$\sum_{T=80^\circ\,\text{K}}^{T_a} (d_{hkl}^{\text{exp}} - d_{hkl}^{\text{calc}})^2.$$

It turned out that the structure of vanadium at low temperatures is best described by a tetragonal lattice with a c/a ratio of less than unity.

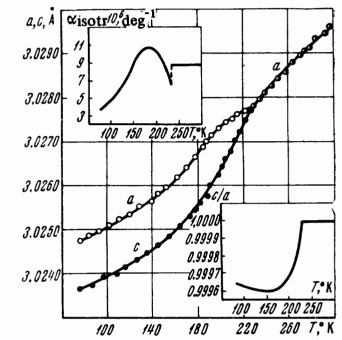

FIG. 2. Temperature dependence of the lattice constants, the axial ratio, and of the thermal expansion coefficient of vanadium.

The temperature dependences of the parameters of the tetragonal crystal lattice, of the axial c/a ratio, and of the linear expansion coefficient [$\alpha_{\text{isotr}} = {}^1/_3(2\alpha_\perp + \alpha_\parallel)$] are presented in Fig. 2. The calculated values of the average linear expansion coefficients in various directions [hk$l$]

$$\alpha_{hkl}^{\text{calc}} = \frac{(h^2 + k^2)\,\alpha_\perp + l^2\alpha_\parallel}{h^2 + k^2 + l^2}$$

are in good agreement with the experimental values (see the table). The $\alpha(T)$ curve has a small "negative" jump; the sign of $\Delta\alpha$ corresponds to the value of $dT_a/dP = -0.85$ deg/kbar known from the literature. Apparently because of the smallness of the thermal expansion coefficient in a second-order phase transition, we did not succeed in observing the jump of the specific heat (ΔC_P) at the temperature of the anomaly[13] whose value estimated from the known Landau equation:[14]

$$\Delta C_P = \frac{3VT_a\,\Delta\alpha}{dT_a/dP},$$

does not exceed 0.3 cal/mole-deg. The axial ratio c/a changes very weakly in the entire range of temperatures. An appreciable increase of c/a takes place only near T_a; at lower temperatures the value of the axial ratio remains practically unchanged—the small increase of c/a on decreasing the temperature is obviously connected with measurement errors.

We have thus shown in this work that a second-order phase transition takes place in vanadium at 230°K; this is accompanied by a decrease of the symmetry of the crystal lattice from cubic to tetragonal. The quantity 1 – c/a plays the role of the ordering parameter in the phase transition. This transition is apparently connected with the fact that at T_a the Fermi surface of vanadium passes sufficiently close to points of obligatory degeneracy (in momentum space) and the appearance of internal strains in the cubic lattice which leads to a decrease of the symmetry and a lifting of the degeneracy turns out to be energetically advantageous.[15] The presence of an anomaly of the electron properties and the considerable effect of pressure[12] and of impuri-

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3) The absence of any discontinuity on the d_{hkl} (T) curves attests to the fact that the transformation in vanadium is a second-order phase transition.

ties[2,7] on the transition temperature in vanadium are also connected with this effect. The effect of impurities on T_a is particularly important because the presence in the metal of impurity centers leads both to a change of the density of states and to a shift of the Fermi energy.[16]

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Translated by Z. Barnea
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