SOVIET PHYSICS JETP VOLUME 22, NUMBER 4 APRIL, 1966

CRYSTAL STRUCTURE OF TANTALUM, NIOBIUM, AND VANADIUM AT 110--400°K

Yu. M. SMIRNOV and V. A. FINKEL'

Physico-technical Institute, Academy of Sciences, Ukr. S. S. R.

Submitted to JETP editor May 26, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 49, 1077-1082 (October, 1965)

The structures of tantalum, niobium, and vanadium were investigated in the temperature range 110—400°K by x-ray diffraction analysis; in addition their electrical resistances were measured at 110—300°K. It was shown that in the investigated range of temperatures there were no phase transitions in Ta and Nb; an anomaly observed in the thermal expansion coefficient of vanadium was of the λ-point type and its temperature depended on the metal purity (220-233°K). The thermal expansion and electrical conductivity anomalies were ascribed to a transition in vanadium to the antiferromagnetic state.

THE structure of transition metals of the VA-subgroup of the periodic system (Ta, Nb, and V) has not yet been sufficiently well investigated below room temperature. Nevertheless, the investigation of these metals, vanadium in particular, at low temperatures is of great interest because a transition to the antiferromagnetic state has been predicted theoretically for vanadium (and probably for tantalum and niobium).[1] The only paper dealing with the structure of vanadium at low temperatures [2] reported anomalies in the temperature dependence of the bcc lattice parameter and the x-ray diffraction intensity at 236°K. The anomalous nature of the temperature dependence of a number of physical properties of vanadium has been reported for the 180—240°K range. These properties are the electrical resistance,[2-6] magnetic susceptibility,[3] internal friction,[2] thermoelectric power,[7] mechanical properties,[8] and elastic constants.[9] The present authors are not aware of any investigation of the structure of Ta and Nb at low temperatures.

The purpose of the present study was to investigate the structures of tantalum, niobium, and vanadium at 110—400°K by the x-ray diffraction method. As an auxiliary method, we used the measurement of the electrical resistance of these metals in the temperature range 110—300°K.

INVESTIGATION METHOD

The investigation was carried out on polycrystalline samples in the form of strips or plates, 0.1—0.3 mm thick. The purity of the tantalum was 99.99%, and that of the niobium 99.95%. The samples of vanadium were 99.74% pure (according to a chemical analysis they contained 0.1% O, 0.04% C, 0.005% N, 0.01% H, less than 0.063% metal impurities) and 99.20% (0.61% O, 0.05% C, 0.08% N, 0.03% H, and less than 0.038% metal impurities). The reason for using vanadium samples of different purities was that small admixtures of interstitial impurities markedly altered the properties of the metal, in particular the value of its crystal lattice parameter.[10-13] The crystal structure of Ta, Nb, and V was investigated using a type URS-501 x-ray diffractometer, fitted with a low-temperature attachment.[14] A holder for plate-like samples, surrounded by two hemispherical resistance furnaces, was placed in a copper chamber which was in contact with liquid nitrogen (the upper part of the chamber was the bottom of a Dewar vessel). As a rule, below about 18°C, the test temperature was regulated by varying the level of liquid nitrogen in the Dewar vessel, but at higher temperatures the hemispherical furnaces were switched on.[1)]

The parameters of the bcc lattices of tantalum and niobium were deduced from the diffraction peaks ($K_{\alpha 1}$ and $K_{\alpha 2}$) of the (400) plane using copper radiation. Vanadium was investigated using copper and chromium radiation; the crystal lattice parameters were calculated using the reflections from the (321) planes (Cu K_α radiation) and (211) planes (Cr K_α radiation). In all cases, the diffraction peaks were recorded automatically: in each measurement, a constant range of angles on the 2θ scale was recorded on the chart of the type ÉPP-09 automatic recorder. The backlash

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[1)] The furnaces were supplied with power through a ferroresonant voltage stabilizer.

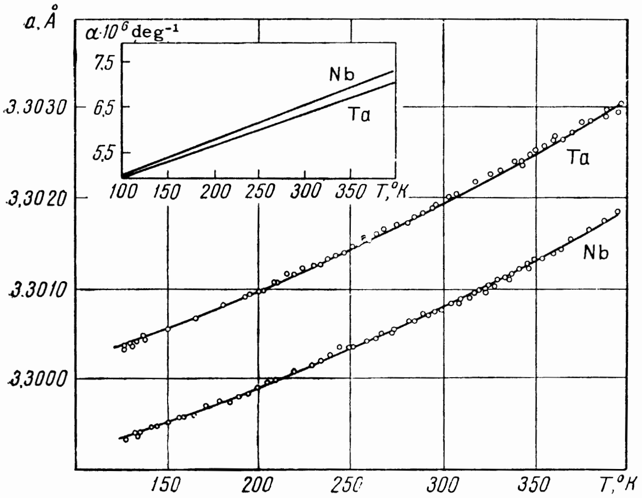

FIG. 1. Temperature dependence of the crystal lattice parameters and linear expansion coefficients of tantalum and niobium.

in the goniometer and automatic recorder was selected first. The diffraction line position was determined by finding the center of gravity with an accuracy of ±0.3′, which ensured an accuracy of not less than ±0.00005 Å in the measurement of the crystal lattice parameters of the investigated metals.

The low-temperature cryostat attachment to the URS-50I diffractometer also made it possible to measure the electrical resistance using the double bridge circuit, based on the PPTN apparatus.[15] The plate samples were placed in massive copper holders and inserted into the isothermal part of the cryostat. The temperature was measured with a differential chromel—alumel thermocouple (cold junction at 0°C); a type PPTN-1 low-resistance potentiometer, was used as the measuring instrument. The accuracy of the temperature measurement was not less than ±0.2 deg. In the measurement of the electrical resistance, we employed two thermocouples (placed near the center of the sample and near the holder); the difference between their readings did not exceed 0.2 deg.

RESULTS OF THE INVESTIGATION AND DISCUSSION

The results of the measurements of the crystal lattice parameters of tantalum and niobium are shown in Fig. 1; the same figure includes the temperature dependence of the linear expansion coefficients. Both metals retained the bcc structure over the whole investigated range of temperatures; no singularities were observed in the temperature dependence of the linear expansion coefficients, which might indicate the presence of phase transitions. The temperature dependence of the crystal lattice parameters of tantalum and niobium in the 110—400°K range was described satisfactorily by the parabolic equations:

$$\text{Ta:}\ a = 3{,}2987(1 + 4.705\cdot10^{-6}\cdot T + 1.895\cdot10^{-9}\cdot T^2), \quad (1)$$

$$\text{Nb:}\ a = 3{,}2970(1 + 3.497\cdot10^{-6}\cdot T + 4.040\cdot10^{-9}\cdot T^2). \quad (2)$$

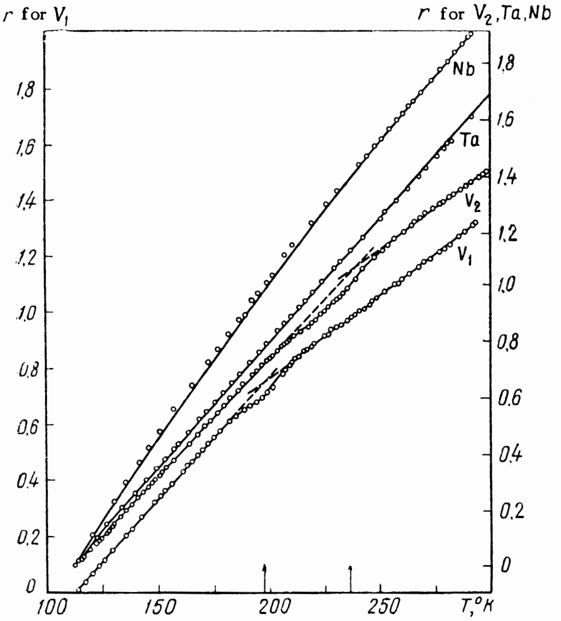

FIG. 2. Temperature dependence of the relative electrical resistance r = [R(T) – R(110°K)]/R(110°K) of tantalum, niobium, and vanadium (V_1 – 99.74% pure, V_2 – 99.20% pure)

The nature of the temperature dependence of the relative electrical resistance of tantalum and niobium also exhibited no anomalies in the 110—300°K range (Fig. 2). No measurements of the electrical resistance of Ta, Nb, and V were carried out at higher temperatures, because at these temperatures the electrical resistance of these metals is affected considerably by the processes of the redistribution of the crystal lattice defects, including interstitial impurities.[5,16] These processes give rise also to a time dependence of the value of the electrical resistance at lower temperatures, and, therefore, in all cases, the measurements were carried out immediately after the annealing of the samples at a high temperature in vacuum.

The temperature dependence of the crystal lattice parameter of vanadium (Fig. 3) was more complex. Although the bcc structure was retained, a nonmonotonic dependence a(T) was observed for samples both of 99.74% purity

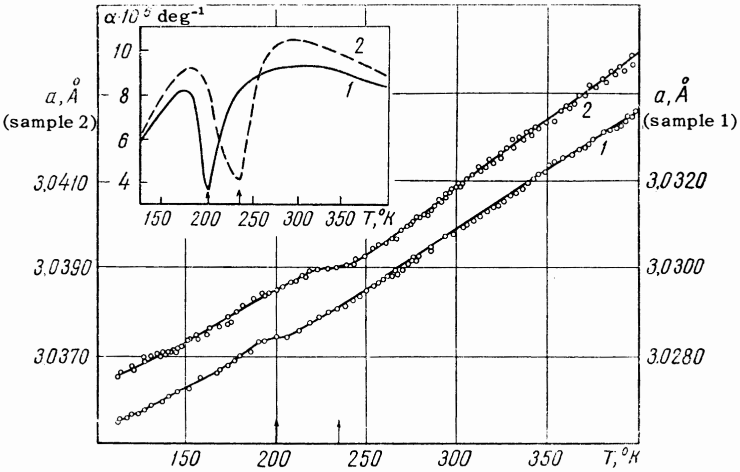

FIG. 3. Temperature dependence of the crystal lattice parameter and the linear expansion coefficient of vanadium of 99.74% purity (curves denoted by 1) and 99.20% purity (curves denoted by 2).

(curve 1) and 99.20% purity (curve 2). Inflections in these curves led to the appearance of anomalies of the λ-point type in the temperature dependence of the linear expansion coefficients (Fig. 3). In the purer sample, the anomaly occurred at ≈ 200°K, in the less pure at ≈ 233°K. The temperature width of the thermal expansion "peak" was less for the purer sample.

An inflection, similar to that in the lattice parameter, was also observed in the temperature dependence of the relative electrical resistance of vanadium (Fig. 2). Some disagreement between the temperatures of the anomalies determined by different methods (the electrical resistance anomalies were observed at 195 and 230°K, respectively) was obviously due to the low accuracy in the plotting of the graphs near T_λ.

Thus, the nature of the temperature dependence of the crystal lattice parameter and of the electrical resistance of vanadium indicates the presence of a phase transition, whose temperature depends on the purity of the metal. Since the crystal structure does not change and there is no discontinuity in the a(T) curves (the crystal lattice parameter is the first derivative of the thermodynamic potentials [17]) but there is a discontinuity in the linear expansion coefficient (i.e., in the second derivative of the thermodynamic potentials), we conclude that the transition in vanadium is of the second type.

There are several published opinions about the nature of this transition. One of these, which suggests a structural transition, i.e., a phase transition of the first kind,[6] is not confirmed by the results obtained. It has also been suggested that, at relatively low temperatures, interstitial impurity ordering takes place in vanadium,[4,5] i.e., a process which obviously could be accompanied by a phase transition of the second kind. The possibility of this type of ordering of impurities in metals has been mentioned earlier for higher temperatures,[18] but no direct confirmation has yet been reported. This hypothesis seems to be supported by the fact that an anomaly is observed not only for c_{11} but also for c_{44}, when the temperature dependence of the elastic constants of vanadium is investigated.[9]

However, it is difficult to see how the ordering of the small amount of the substitutional impurity which was present in the investigated vanadium could produce a noticeable discontinuity in the thermal expansion coefficient, especially as the ordering of interstitial impurities at low temperatures should not occur only in vanadium, but it should occur also in tantalum and niobium, which have tetrahedral and octahedral holes of greater volume. However, this has not been observed. Tetragonal splitting of the x-ray reflections has not been observed either and there is even no asymmetry in the diffraction peaks, which should be observed for an ordered distribution of interstitial impurities. The form of the peaks is approximated satisfactorily by the expression $(1 + \gamma x^2)^{-1}$; the difference between the linear expansion coefficients along the direction $\langle 211 \rangle$ and $\langle 321 \rangle$ has not been observed either.

In view of this, the most acceptable explanation of the nature of the anomaly in vanadium is that proposed at the beginning of this paper, namely, that there is a phase transition of the second kind which is associated with the paramagnetic—antiferromagnetic transition.[1,37] This point of view is supported, apart from the result given here, by the observations of Burger and Taylor [3] who found a small maximum in the temperature dependence of the magnetic susceptibility, which was characteristic of the antiferromagnetic transition. The absence of an anomaly in the $c_{44}(T)$ curve[9] may be due to the magnetic anisotropy of vanadium. The fact that a neutron-diffraction investigation of vanadium powders at 20°K[19] showed no superstructure maxima is insufficient to reject the antiferromagnetic ordering hypothesis: it has been pointed out[20] that, owing to the possible precession of the magnetic moment vector of uncompensated 3d-electrons (precession period $\approx 10^{-14}$ sec), neutron-diffraction analysis using thermal neutrons, having a transit time of $\approx 10^{-13}$ sec/atom, is incapable of detecting antiferromagnetic superstructure reflections.

The observed shift in the transition temperatures toward high temperatures when the interstitial impurity content in vanadium is increased, and the differences between the temperatures of the anomaly reported in the literature, are associated with the considerable influence of the impurities on the temperature of the paramagnetic—antiferromagnetic transition. (A strong shift in the antiferromagnetic transition temperature is observed, for example, in chromium on the addition of small amounts of nitrogen.[21]) The "negative" discontinuity of the linear expansion coefficient observed at the phase transition point does not contradict L. D. Landau's theory of phase transitions,[17] according to which

$$\Delta\alpha = \frac{\Delta C_p}{3VT}\,\frac{dT_\lambda}{dp}. \qquad (3)$$

Since the specific-heat discontinuity is always positive, the sign of the discontinuity in the thermal expansion coefficient is solely due to the nature of the dependence of T_λ on pressure. It should be mentioned that the discontinuity in the linear expansion coefficient is negative also for the paramagnetic-antiferromagnetic transition in chromium[14] (for which $dT_\lambda/dp < 0$ [22]) and obviously in manganese; for cubic ferromagnets (Fe, Ni, Co) $\Delta\alpha > 0$.

The authors thank B. M. Vasyutinskiĭ, G. N. Kartmazov, and I. V. Shpagin for their interest in this work.

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Translated by A. Tybulewicz
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