

Zum Schluss wurde die Differenzkurve $C = A - B$ gebildet, welche wieder so gut wie symmetrisch verläuft. Das Minimum, zu 1^m.40, fällt auf 2422473, also 18 Tage vor dem ungestörten Maximum; der Veränderliche erleidet beim Aufstieg eine Verfinsternung, welche ihn von 72 % seines Lichtes beraubt.

Die nicht seltenen vollkommen glatten Aufstiege haben mich veranlasst, auch bei diesem Stern, wie früher bei *R Leonis minoris* (*Proc. Royal Acad. Amsterdam*, 35. 931), *S Coronae borealis* (*Proc. Royal Acad. Amsterdam*, 37. 1) und *V 20 = ST Cygni* (*Proc. Royal Acad. Amsterdam*, 38. 964), für die deutlich gestörten Maxima die einzelnen Differenzkurven zu bilden, und deren Minima zur Deckung zu bringen. Dann entsteht eine völlig symmetrische etwas tiefere Verdunkelungskurve *D*, deren Minimum, zu 1^m.55, auf 2472 fällt, 19 Tage vor dem ungestörten Maximum; der Lichtverlust wird jetzt 76 %. Die Auffassung, dass *R Canum Venaticorum* in gewissen Fällen bei der Aufhellung nicht gestört wird, in anderen Fällen aber um so stärker, kommt mir die wahrscheinlichere vor.

Utrecht, März 1936.

Physics. — *The transition of hexagonal α -Titanium into regular β -Titanium at a high* temperature.* By J. H. DE BOER, W. G. BURGERS and J. D. FAST. (Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken, Eindhoven, Holland.) (Communicated by Prof. G. HOLST.)

(Communicated at the meeting of March 28, 1936).

Metallic titanium is isomorphous with zirconium; at room temperature the crystal structure is hexagonal close-packed. The parameter values¹⁾ for zirconium are $a = 3.22_3 \text{ \AA}$, $c = 5.12_3 \text{ \AA}$; for titanium $a = 2.95_3 \text{ \AA}$, $c = 4.72_9 \text{ \AA}$. The ratio between the a values at room temperature is $\frac{a_{Zr}}{a_{Ti}} = 1.09_1$, that between the values of c : $\frac{c_{Zr}}{c_{Ti}} = 1.08_3$.

At a higher temperature zirconium passes over into another modification²⁾, and the transition point³⁾ is at $862 \pm 5^\circ \text{ C}$. The crystal structure proved to be cubic body-centred ($a = 3.61 \text{ \AA}$ at about 900° C .)⁴⁾ Since in the preparation of zirconium by thermal dissociation of zirconium tetraiodide⁵⁾ the deposition temperature lies far above the transition point,

1) Cf. M. C. NEUBURGER, Gitterkonstanten 1936. Z. Kristallogr. 93, 1 (1936).

2) C. ZWIKER, Physica 6, 361 (1926).

3) R. VOGEL and W. TONN, Z. anorg. allgem. Chem. 202, 292 (1931); J. H. DE BOER, P. CLAUSING and J. D. FAST, Rec. Trav. Chim. Pays-Bas (1936).

4) W. G. BURGERS, Z. anorg. allgem. Chem. 205, 81 (1932); Nature, 129, 281 (1932).

5) J. H. DE BOER and J. D. FAST, Z. anorg. allgem. Chem. 153, 1 (1925); 187, 177 (1930).

crystals of the regular β -zirconium are formed by this method. The rods obtained, which are built up of several well-formed crystals, consist therefore of the hexagonal α -zirconium at room temperature; the external form of the crystals, however, is that of β -zirconium.

Titanium can be prepared by a method analogous to that which is used for the preparation of zirconium, namely by thermal dissociation of titanium tetraiodide⁶⁾. In this case also well-formed crystals may be obtained, and several years ago we found it possible to prepare rods of mixed crystals of zirconium and titanium by simultaneous dissociation of zirconium and titanium tetraiodide⁷⁾. Under the proper conditions these rods appeared to be built up of one single crystal. On the basis of these results it seemed natural to suppose that titanium also passes over into another modification at a higher temperature, and that the β -titanium is isomorphous with β -zirconium and forms an uninterrupted series of mixed crystals with β -zirconium.

On the basis of measurements of the electrical resistance of titanium at higher temperatures SCHULZE⁸⁾ has come to the conclusion that contrary to the above expectation no polymorphous transitions occur in pure titanium. The resistance curve recorded by SCHULZE shows in fact no discontinuities. However, in his curve there is a maximum, after which the resistance decreases slowly with increasing temperature. SCHULZE ascribes this abnormal behaviour to impurities, which are taken up at higher temperatures during heating (in a porcelain tube).

From a very recent investigation with zirconium⁹⁾ we have discovered that, if zirconium is heated in air of low pressure, the discontinuous jump in the resistance at the transition temperature entirely disappears, and is replaced by a continuous change in the resistance, giving a maximum and a minimum, which may lie several hundred degrees apart. The type of the curve is like that originally found by ZWIKKER.

In a special study on the influence of oxygen and nitrogen¹⁰⁾ it appeared that resistance curves were obtained, which were quite analogous to those found by SCHULZE for the titanium rod.

In order to find out whether the presence of a transition from α -titanium to β -titanium could actually be deduced from the electrical resistance, the same measures were taken as in the investigation cited above of the $\alpha \rightarrow \beta$ transition in the case of zirconium: The resistance temperature curve was recorded of a freshly-prepared titanium rod, without the rod having been removed from the preparation tube and thus without exposure of the titanium to the air. During the preparation two separate measuring contacts, which led to the outside, were allowed to be enveloped by the

⁶⁾ A. E. VAN ARKEL and J. H. DE BOER, *Z. anorg. allgem. Chem.* **148**, 345 (1925).

⁷⁾ Cf. J. H. DE BOER and P. CLAUSING, *Physica* **10**, 267 (1930).

⁸⁾ A. SCHULZE, *Z. Metallk.* **23**, 261 (1931).

⁹⁾ J. H. DE BOER, P. CLAUSING and J. D. FAST, *Rec. Trav. Chim. Pays-Bas* (1936).

¹⁰⁾ J. H. DE BOER and J. D. FAST, *Rec. Trav. Chim. Pays-Bas* (1936).

growing rod, and were used to measure the tension in the resistance measurements.

From the values found for current and tension the corresponding values for the resistance and energy supplied were calculated. Since the energy, which has been developed in the portion of the titanium rod between the measuring contacts, is lost exclusively by radiation, we may as a first approximation consider the value of the energy supplied to be proportional to the fourth power of the temperature. In Fig. 1 the measured resistance $\left(\frac{V}{i}\right)$ is plotted against $\sqrt[4]{i \cdot V}$, which quantity, according to the above, is directly proportional to the absolute temperature. We see that titanium actually does pass over into another modification at a very definite temperature, and that the electrical resistance of this other modification, like that of zirconium in the same situation, is lower than that of the α -modification.

In various experiments, while the resistance was being recorded, the temperature was also measured by means of the optical pyrometer. On

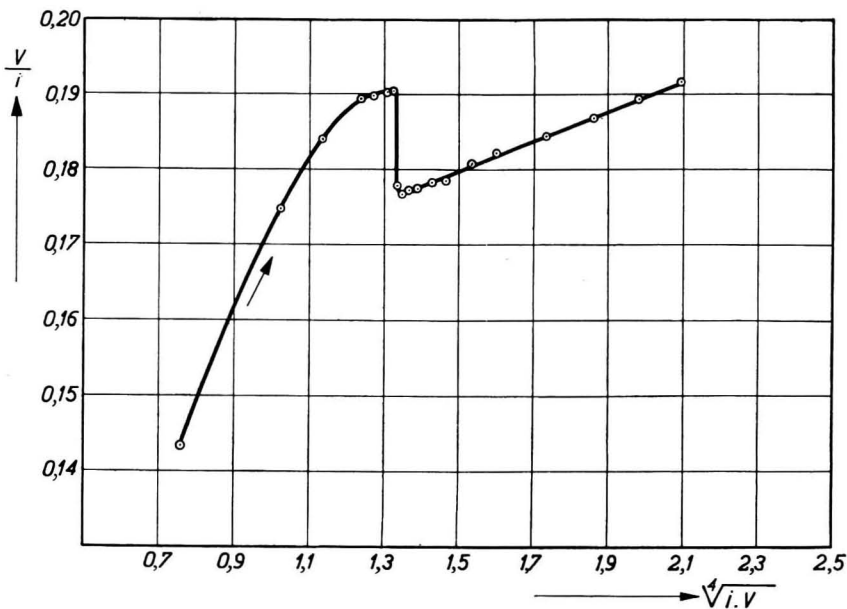


Fig. 1.

the basis of these temperature measurements we may give the value $1115 \pm 20^\circ \text{K}$. (brightness temperature) as the average value of the transition temperature. Dr. J. VOOGD has been kind enough to determine the relation between brightness temperature and true temperature. With his corrections we obtain for the transition temperature $1155 \pm 20^\circ \text{K}$. or $882 \pm 20^\circ \text{C}$. It is striking that the transition temperature of titanium differs only slightly from that of zirconium ($862 \pm 5^\circ \text{C}$).

The crystal structure of β -titanium was determined in a manner similar to that used in the determination of the structure of β -zirconium ¹¹⁾. A titanium wire 300 μ in thickness was stretched between two nickel poles in an evacuated tube of very thin lithium-beryllium-borate glass (LINDEMANN glass). The titanium wire was kept taut at higher temperatures by means of a tungsten spiral. The glass of the tube is transparent for X-rays ($\text{Cu}-K\alpha$ radiation). The tube was introduced into an ordinary DEBYE—SCHERRER camera, and could be rotated about its axis. From the relation between the resistance of the titanium wire and the heating current, that current was determined at which the titanium had just passed from the α - into the β -state, X-ray rotation photographs were taken while the wire was being heated with this current. It appeared that the β -titanium was actually cubic body-centred. The lattice constant a at 900° C. is 3.32 Å, so that the relation between the lattice constants of β -zirconium and β -titanium at 900° C. : $\frac{a_{Zr}}{a_{Ti}} = 1.08_7$ is found to be practically the same as the relation between the constants of the two α -modifications.

In a separate experiment the problem was investigated as to whether the sharp transition point is actually changed to a transition range by the taking up of a small quantity of oxygen in the case of titanium also. In fig. 2 curve *a* is the resistance curve of a freshly-prepared titanium rod, recorded

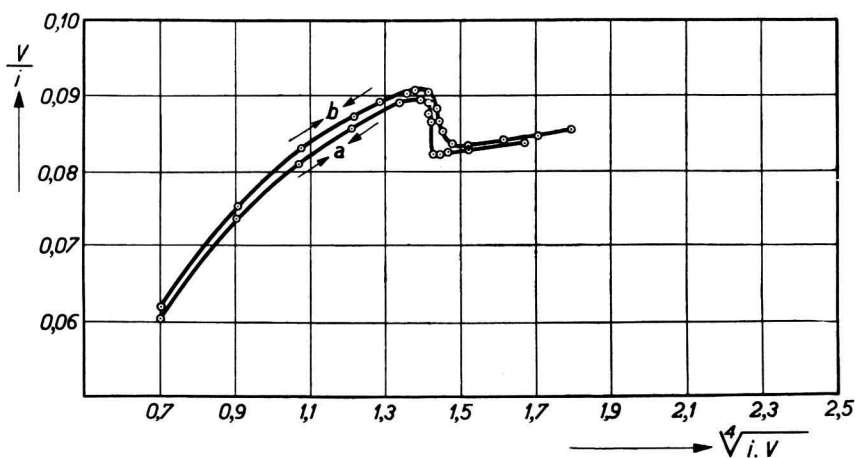


Fig. 2.

with both rising and falling temperature. Curve *b* is the corresponding curve after about two atom-percents of oxygen had been taken up by the rod. This curve too has been recorded for rising and falling temperatures. As with zirconium we see that the resistance rises and that a transition range at higher temperatures takes the place of a single

¹¹⁾ W. G. BURGERS, loc. cit.

transition temperature. Thus also in this case the number of phases remains the same after the taking up of oxygen, so that the number of degrees of freedom increases by one upon addition of one component (the oxygen). After the taking up of oxygen the resistance curves for increasing and decreasing temperature practically coincide, that is, no hysteresis phenomena are observed. If, however, in addition to oxygen, nitrogen is also taken up, then titanium exhibits hysteresis phenomena as does zirconium.

Further details, not only concerning the resistance and temperature measurements, but also concerning the determination of the crystal structure of β -titanium will be published shortly elsewhere.

Eindhoven, 18th March 1936.

Mathematics. — *Einige Integraldarstellungen aus der Theorie der BESSELSchen und WHITTAKERSchen Funktionen.* (Zweite Mitteilung)²¹⁾. Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of March 28, 1936).

§ 3. Spezialfälle des Satzes.

1. Integraldarstellungen für $K_\nu(z)$.

Wegen (1) gilt

$$\Psi_{0,1} \left(\zeta \left| \begin{array}{l} 1-\alpha, \beta \\ b_1, b_2 \end{array} \right. \right) = \frac{\Gamma(\alpha + b_1) \Gamma(\alpha + b_2)}{\Gamma(\alpha + \beta)} \zeta^\alpha \cdot {}_2F_1(\alpha + b_1, \alpha + b_2; \alpha + \beta; -\zeta).$$

Ist $|\arg z| < \frac{1}{2}\pi$, dann folgt also aus (17) und (10)²²⁾

$$K_\nu(z) = \frac{\Gamma(\alpha + \frac{1}{2}\nu) \Gamma(\alpha - \frac{1}{2}\nu)}{2^{2-\alpha+1} z^{2\alpha} \Gamma(\alpha + \beta)} \int_0^\infty v^{\alpha+\beta} J_{\alpha+\beta-1}(v) \times {}_2F_1 \left(\alpha + \frac{1}{2}\nu, \alpha - \frac{1}{2}\nu; \alpha + \beta; -\frac{v^2}{z^2} \right) dv. \quad (48)$$

Hierin sind α und β beliebige Zahlen mit

$$\Re(\alpha - \beta \pm \nu) > -\frac{1}{2}, \quad \Re(\alpha + \beta) > 0, \quad \alpha \pm \frac{1}{2}\nu \neq 0.$$

²¹⁾ Erste Mitteilung: Proc. Royal Acad. Amsterdam, **39**, 394–403 (1936).

²²⁾ Ich setze $u = \frac{1}{2}\nu$ in (10).

Formel (48) gilt wegen (17) und (10), falls ν nicht ganz ist. Durch Grenzübergang findet man aber, dass (48) auch gilt für ganze Werte von ν . Analog bei (55), (56), (57), (60), (65) und (66).