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**A numerical method for indexing uniaxial powder patterns.** By I. R. TANNENBAUM\*, B. J. LEMKE, and D. KRAMER, *Atomics International, A Division of North American Aviation, Inc., Canoga Park, California, U.S.A.*

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The numerical method of Hesse (1948) for the indexing of powder patterns of hexagonal and tetragonal materials has been modified to permit computation on digital computers.

In broad outline the test utilized by this method for tetragonality and for hexagonality rests upon the fact that both of these crystal systems give reflections such that

$$\sin^2 \theta = AM + Cl^2, \quad (1)$$

where  $M = h^2 + k^2$ ,  $A = \lambda^2/4a^2$  for the tetragonal case and  $M = h^2 + k^2 + hk$ ,  $A = \lambda^2/3a^2$  for the hexagonal case.  $C = \lambda^2/4c^2$  in either case. The other symbols have their usual crystallographic meaning.

To solve a pattern the program computes from the observed diffraction angles,  $\theta_i$ , the values for  $\sin^2 \theta_i$  and tabulates these values, the values of  $2 \sin^2 \theta_i$ , and all cross sums of the types  $2 \sin^2 \theta_i$ ,  $\sin^2 \theta_i + \sin^2 \theta_k$ ,  $3 \sin^2 \theta_i$ , and  $2 \sin^2 \theta_i + \sin^2 \theta_k$  (where the  $i$  and  $k$  range from one up to the total number of lines).

Each entry in this table of sums is compared with all other entries to find all equations of the type

$$\sum g_j \sin^2 \theta_j = 0 \pm \epsilon. \quad (2)$$

In equation (2) the summation is taken over four terms, the  $g_j$  have the possible values 0,  $\pm 1$ ,  $\pm 2$ ,  $\pm 3$ , and  $\epsilon$  is the previously assigned limit of error.

Since  $M$ ,  $l$ ,  $A$ , and  $C$  are all positive, equation (2) implies that the sum of the products of the  $g_j$  by the  $M_j$  must equal zero and that the sum of the products of the  $g_j$  by the  $l_j^2$  must equal zero. These are the working equations.

The trial and error solution to these equations is obtained by utilizing a starting combination of permissible  $M$  or  $l$  numbers in the equation containing the smallest number of variables. The numbers obtained from this starting combination are then substituted into the remaining equations in order of increasing numbers of unknowns. Each value obtained is checked against the

list of permitted values for the crystal system under consideration. When a set of numbers is obtained which is internally consistent, the pattern is considered solved.

If a solution is obtained the highest values of  $\theta$  for which  $M_i$  and  $l_i$  were obtained are substituted in equation (1) and  $A$  and  $C$  are obtained by simultaneous solution.

The values of  $M$  and  $l$  are obtained for the  $\theta_i$ 's which did not appear in the working equations by means of the newly determined, approximate, values for  $A$  and  $C$  and equation (3).

$$\sin^2 \theta_i = AM_i + Cl_i^2 \pm \epsilon. \quad (3)$$

The lattice parameters are then computed from the three most reliable high angle lines by the method of Cohen (1935, 1936).

Hesse's method does not apply to cubic crystals so that the tests for tetragonality and hexagonality are preceded by a test to determine if the sample is cubic. Cubic samples are, therefore, excluded from further computation.

This program was checked using data from the American Society for Testing Materials Diffraction Data Cards for indium, zirconium, and nickel. The angles were reported in degrees, using five significant figures although the machine used, IBM-709, automatically carries eight. Running time for the cubic sample tested (8 lines) was 30 seconds; for the tetragonal sample (19 lines), 75 seconds; for the hexagonal sample (25 lines), 2 minutes. If no solution is found, running time is less than three minutes. Running time is almost independent of number of lines. As it now is programmed, the code requires 10,200 locations and, hence, will run on any sixteen thousand word computer. On a sixteen thousand word computer, there is space for 40 angles, of which 15 are utilized to obtain up to 100 working equations. Reduction of the dimensions to 25 angles and 50 equations should permit the use of eight thousand word machines.

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**Lattice-parameter changes in the pseudo-binary system of titanium and zirconium dihydrides.** By A. D. MCQUILLAN and N. PESSALL, *Department of Physical Metallurgy, University of Birmingham, England*

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When titanium and zirconium are saturated with hydrogen they form dihydrides in which the metal atoms are arranged, at room temperature, in a face-centred cubic and face-centred tetragonal structure respectively, and the hydrogen atoms lie in the tetrahedral interstices. Sidhu *et al.* (1956) found, however, that below about 30 °C. the structure of titanium dihydride becomes face-centred tetragonal, and Yakel (1958) later showed that

the extent of tetragonality increased progressively with decreasing temperature. He also observed that the tetragonality of zirconium dihydrides decreased with increasing temperature but still remained tetragonal at 500 °C. The form of his parameter-temperature curves for zirconium dihydride at 500 °C. suggest that the structure may very probably become face-centred cubic in the temperature range 550–600 °C., and the behaviour

of the two hydrides would then be similar, the effects differing only in temperature scale. The problem, therefore, is to establish whether the origin of tetragonality in the two dihydrides is the same, and if so to find it. An obvious first step towards understanding this phenomenon is to examine the crystal structures of mixed dihydrides of titanium and zirconium to see if the degree of tetragonality at room temperature increases progressively on replacing titanium by zirconium.

Alloys of titanium and zirconium were made by melting samples of high purity iodide-prepared metals in an argon-atmosphere arc-furnace. Each alloy was homogenized at 1000 °C. for 3 days in a vacuum furnace prior to saturation with hydrogen by cooling the alloys slowly from 800 °C. in an atmosphere of spectroscopically pure hydrogen. The atomic fraction of hydrogen in each alloy was always greater than 1.98 but slightly less than the stoichiometric value 2. The hydrides were brought to equilibrium by sealing them in evacuated glass capsules and heating first to 275 °C. and then allowing the samples to cool to room temperature at a rate of 10 °C. per day.

X-ray examination of the alloy hydrides at room temperature was made using a Philips Geiger-counter diffractometer with filtered  $\text{Cu } K\alpha$  radiation and a scanning speed of  $\frac{1}{2}^\circ/\text{min}$ . Diffraction lines at high angles, except those cubic reflections of the form  $\{hhh\}$ , were very broad and diffuse, so that the final lattice-parameter values were obtained only from the mean values given by the peaks of the  $\{200\}$ ,  $\{220\}$  and  $\{311\}$  cubic reflections which were each split into two lines. No attempt was made to resolve the  $\alpha_1, \alpha_2$  doublets, the lattice parameters being deduced by using the weighted mean of the wavelengths of the  $\alpha_1$  and  $\alpha_2$  components for the centroid of the spectral distribution, as suggested by Pike (1958).

At the temperature of the measurements ( $26 \pm 3$  °C.) both titanium dihydride ( $\text{TiH}_{1.98}$ ) and zirconium dihydride ( $\text{ZrH}_{1.98}$ ) were found to have a tetragonal structure. The parameters for zirconium dihydride ( $a = 4.992 \pm 0.005$ ,  $c = 4.455 \pm 0.005$  Å) agree well with those reported by Yakel (1958) and by Rundle *et al.* (1952). The parameters obtained for titanium dihydride ( $a = 4.465 \pm 0.005$ ,  $c = 4.453 \pm 0.005$  Å) are slightly higher than the values given by these workers.

The experimentally determined values of the lattice parameters of the mixed dihydrides are shown in Fig. 1. An extensive range of solid solution of titanium dihydride in zirconium dihydride exists but the titanium dihydride shows only limited solubility for zirconium dihydride. In zirconium-rich dihydrides, the parameters are linear functions of composition, and the  $a/c$  ratio decreases progressively with increasing titanium content. Extrapolation of the  $a$  parameter to zero zirconium content gives a value in close agreement with the value of  $a$  for titanium dihydride. For the  $c$  parameter agreement is less perfect but the difference is not great. It would seem, therefore, that these results support the hypothesis that the cause of tetragonality in the dihydrides of titanium and zirconium is the same.

The reason for the onset of tetragonality at low temperatures in these dihydrides is still obscure. Libowitz (1958) has suggested that it might be due to the onset of antiferromagnetism, and indeed Trzebiatowski & Stalinski (1953) found that the magnetic susceptibility of titanium dihydride showed an anomaly at 26 °C. of

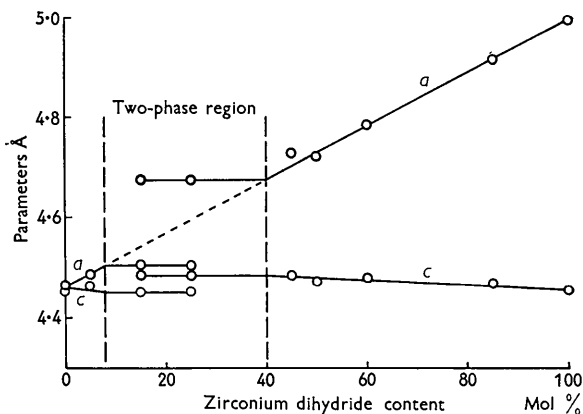


Fig. 1. The lattice parameters of mixed dihydrides of titanium and zirconium at room temperature as a function of composition.

a form which strongly resembled the type of behaviour to be expected of an antiferromagnetic material on passing through the Néel point. Subsequently Stalinski & Bieganski (1960) found a  $\lambda$ -point in the specific heat curve of the same material at the same temperature, but the magnitude of the anomaly was too small for a true Néel point. A neutron-diffraction study by Shull & Wilkinson, according to a private communication in a paper by Yakel (1958), indicated that antiferromagnetic effects were undetectable in titanium dihydride. It would seem, therefore, that the disappearance of tetragonality in titanium dihydride is not a magnetic effect. Furthermore it would be difficult to imagine zirconium dihydride remaining antiferromagnetic up to temperatures in the range 550 to 600 °C. It seems more probable, according to two recent papers on proton magnetic resonance in titanium dihydride (Stalinski *et al.* (1961)), and heat capacity work on zirconium dihydride (Flotow & Osborne (1961)), that the disappearance of tetragonality in both hydrides is closely associated with the onset of mobility of hydrogen in the lattice. It is not altogether impossible, therefore, that the change may be connected with the temperature dependence of the nature of the electronic bonding mechanism by which hydrogen is held in the hydride structure. A systematic investigation of the physical properties of mixed hydrides now in progress, may well help to solve this problem.

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