more negative. This is in line, however, with the findings of Downie & Speakman (1954) for ammonium hydrogen disalicylate hydrate, in which the ammonium ion coordinates water oxygen, carbonyl oxygens of the carboxyl groups, and oxygens of the o-hydroxyl groups, but not hydroxyl oxygens of the carboxyl groups.

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Thermocrystallography of Higher Hydrides of Titanium and Zirconium*

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Low- and high-temperature X-ray diffraction investigations of titanium dihydride ($TiH_{1.99}$) and dideuteride ($TiD_{1.98}$) have indicated apparent 'second-order transformations' in both substances below a critical temperature of 310° K. The tetragonal low-temperature phases are distortions of the cubic fluorite high-temperature phases, and are isomorphous with the tetragonal ZrH_2 structure. A similar study of zirconium dihydride ($ZrH_{1.92}$) has shown that the tetragonality of the lattice of this substance is also temperature-dependent. The critical temperature of the 'second-order transformation' in $ZrH_{1.92}$ is unattainable in the present diffraction apparatus owing to dissociation of the hydride. Possible causes of the transformations are discussed.

Introduction

Many fundamental studies of solid metallic hydrides have been stimulated by the chemical nature of these materials, which seemingly is intermediate between that of interstitial alloys and inorganic compounds. This interest has recently been augmented by practical applications of solid hydrogeneous materials in the field of nuclear engineering.

In particular, investigations of the crystal structures of the hydrides of the Group IV A elements, and the relation of their structures to chemical and physical properties, extend from the early work of Hägg (1931) on titanium and zirconium hydrides to the recent study of the zirconium–hydrogen system by Vaughan

& Bridge (1956) in which high-temperature X-ray diffraction methods were used. Phase diagrams of the titanium–hydrogen and zirconium–hydrogen systems have been presented by Lenning, Craighead & Jaffee (1954) and Vaughan & Bridge (1956), respectively. No diagrams for the hafnium–hydrogen or thorium–hydrogen systems have been published, but, in view of the results of diffraction studies of these hydrides by Sidhu & McGuire (1952) and Rundle, Shull & Wollan (1952), a general similarity with the titanium- and zirconium–hydrogen systems is likely.

The crystal structures of the hydride 'compounds' which exist at compositions between MH and MH_2 (where M is a IV A metal) all appear to be based on a face-centered cubic, or face-centered tetragonal*, array of metal atoms with hydrogen atoms located in

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* A preliminary report of this investigation was presented under the title 'Apparent Second-Order Phase Transformations in Titanium Dihydride and Dideuteride' at the Thirteenth Annual Pittsburgh Diffraction Conference, 3 November 1955.

† Operated by the Union Carbide Nuclear Company for the United States Atomic Energy Commission.

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* Descriptions of these structures in terms of face-centered rather than body-centered tetragonal lattices will be retained throughout this paper for purposes of comparison with the cubic fluorite structure.

the tetrahedral holes producing a fluorite-type structure. Descriptions of the changes in this basic structure with composition differ widely, however. In the case of the zirconium–hydrogen system, Edwards, Levesque & Cubicciotti (1955) have postulated the existence of two discrete hydride phases in the region from 60 to 66 atomic % hydrogen, while Vaughan & Bridge (1956) conclude that only one stable face-centered tetragonal hydride with concentration-dependent axial ratio exists in this region. In the hafnium–hydrogen system, Sidhu & McGuire (1952) have interpreted their results in terms of three hydride phases existing in the regions $HfH_{1.53}$ to $HfH_{1.7}$, $HfH_{1.7}$ to $HfH_{1.8}$ and $HfH_{1.8}$ to HfH_2, although transformations between these forms may be second-order. A single face-centered cubic hydride was reported in the titanium–hydrogen system from 54 to 66 atomic % hydrogen (Hägg, 1931), but Sidhu, Heaton & Zauberis (1956) have recently confirmed a slight room-temperature distortion of the cubic lattice near TiH_2 first noted by Shull & Wilkinson (1955) and the author (Yakel, 1955).

In addition to the stable hydrides listed above, several metastable hydrides have been reported in the zirconium– and the hafnium–hydrogen systems, particularly in the presence of the α solid solutions (Hägg, 1931; Sidhu et al., 1956). The appearance of these phases seems to be dependent on the experimental conditions, however, and attempts to reproduce them have seldom succeeded.

The theoretical and practical importance of the Group IV A element hydrides, together with the several uncertainties apparent in published investigations of these systems, has suggested that still another structural study, with temperature and composition as experimental variables, would prove profitable. The following paper presents the results of an X-ray diffraction investigation of the temperature dependence of the crystal structures of a hydride and deuteride of titanium and a hydride of zirconium which approach the stoichiometric compositions TiH_2, TiD_2, and ZrH_2, respectively.

Preparation of hydrides

High-purity crystal-bar titanium was hydrided according to the following procedure: the metal, contained in a molybdenum boat, was outgassed in vacuum at 350° C. and 1000° C. Hydrogen or deuterium, purified by passage over uranium heated to 700° C., was allowed to enter the reaction chamber at 1000° C., after which the system was slowly cooled to 400° C. and held at this temperature for several hours. A pressure of slightly more than one atmosphere of H_2 or D_2 was maintained in the reaction chamber during cooling. The system was then re-evacuated, brought to 1000° C., and one atmosphere of purified H_2 or D_2 was again admitted. The system was finally cooled slowly to room temperature in this atmosphere. Sections of 5 mil zirconium foil, cold-rolled from arc-

melted crystal-bar zirconium, were hydrided in an analogous manner, except that only one hydriding reaction was completed.

The hydrided metals, although still massive in form, were easily crushed into metallic black powders, which were microscopically opaque. The crushed materials were analyzed for hydrogen or deuterium by complete reaction of samples with oxygen and measurement of the weight of water or heavy water produced. Results for the hydride and deuteride of titanium indicated compositions corresponding to the formulas $TiH_{1.99}$ and $TiD_{1.98}$, while those for the zirconium hydride indicated a formula $ZrH_{1.92}$. Possible errors in the analyses are reflected in uncertainties of ± 0.02 in the hydrogen or deuterium subscripts in these formulas. Hereafter, for sake of brevity, these substances will be referred to as titanium dihydride and dideuteride and zirconium dihydride, although the small deviations from stoichiometric compositions should be remembered.

X-ray diffraction procedure

Examination of the hydrides at low temperatures was accomplished with the aid of a simple cryostat adapted to a standard Norelco High-Angle Goniometer. This apparatus, details of which will appear shortly (Jetter et al., to be published), enables recordings of diffraction patterns of polycrystalline materials to be made at constant temperatures between 60° K. and 450° K.

High-temperature X-ray diffraction experiments were performed with a 19 cm. Unicam S. 150 camera. Samples of titanium dihydride and dideuteride, mixed with small amounts of copper filings for temperature calibration, were placed in sealed evacuated quartz capillaries and examined at temperatures up to 450° K. Cu K radiation* was used here, as in the low-temperature experiments. Examination of the titanium dihydride and dideuteride samples above 450° K. was not attempted since the dissociation of hydrogen or deuterium from these materials should begin to seriously alter the composition of the solid at any higher temperature (Gibb & Kruschwitz, 1951). Identical diffraction patterns at 284° K. before and after the high-temperature experiment showed that no irreversible structural or compositional change had occurred.

A high-temperature diffraction specimen of zirconium dihydride was prepared as above, except that the secondary standard for temperature measurement was omitted†, and the capillary, before sealing, was filled with about one-third atmosphere of hydrogen in an attempt to suppress the dissociation of the hydride at elevated temperatures. There exists some confusion in the literature concerning the temperature dependence of the dissociation of zirconium

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* $\lambda(\text{Cu } K\alpha) = 1.5418$ Å.

† Temperatures were estimated to $\pm 3°$ with a calibrated 36 gage Pt/Pt–10% Rh thermocouple located close to, but not in direct contact with, the specimen.

hydrides near ZrH_2, but a concensus of available data indicates that the dissociation pressure of hydrogen over $ZrH_{1.92}$ should not exceed one atmosphere below 800° K. An initial (room-temperature) external pressure of one-third atmosphere of hydrogen should therefore exceed the dissociation pressure of the hydride examined at least up to that temperature. The success of this procedure also depends, of course, on the practical difficulty of forcing more hydrogen into a hydride of composition $ZrH_{1.92}$ from an atmosphere whose hydrogen pressure exceeds the dissociation pressure of the hydride. In proof of this, checks of the room-temperature (295–297° K.) diffraction patterns of $ZrH_{1.92}$ after each high-temperature experiment up to, and including, 778° K. showed no irreversible changes in the features of these patterns sensitive to hydrogen concentration (vide infra). The checks at room temperature did not prove that small amounts of hydrogen were not lost from the sample at the elevated temperature, then reabsorbed during cooling, but it would be surprising, in view of such variables as cooling rates, etc., if this desorption and reabsorption were quantitatively reversible.

Results

Preliminary scans of the complete diffraction patterns of titanium dihydride and dideuteride at 296, 195, and 79° K. showed, for both substances, a slightly distorted face-centered cubic lattice at room temperature and a greatly distorted lattice at the lower temperatures. The lattice symmetry was apparently tetragonal since the {111} and {222} (cubic) reflections were unsplit, while the {200}, {220}, and {311} (cubic) reflections were each split into two lines. Intensity ratios in these doublets indicated $c < a$. In the interest of economy of time at low temperatures, the detailed study of the thermal variation of lattice parameters was made from $\frac{1}{4}°$/min. scans of an angular range sufficient to record only the {200, 020}–{002} Cu $K\alpha$ doublet of the dihydride or dideuteride and the {111} $K\alpha$ and $K\beta$ reflections of a copper standard mixed into the specimen. Hydride parameters accurate to ±0.001 Å were obtained from well resolved reflections, while the accuracy was reduced somewhat when the reflections overlapped significantly. Scans were made at temperature intervals of approximately 10–20° from 79° K. to 320° K.

It was observed that changes in hydride lattice spacing accompanying a temperature increment ΔT were accomplished almost instantaneously with the temperature change itself. Despite this rapid establishment of equilibrium, measurements at a given temperature were made only after at least one-half hour at that temperature. Experiments in which a given temperature was approached from both higher and lower temperatures showed no essential differences in the final lattice spacings. No dependence of the parameters on ΔT was observed.

The high-temperature (284–449° K.) titanium dihydride and dideuteride patterns were relatively diffuse and the lines too broad for measurements of the highest accuracy. Parameters with a probable error of ±0.001 Å were obtained by extrapolation, however. The lattice symmetries above 310° K. were apparently cubic.

The lattice parameters of titanium dideuteride, calculated from the low- and high-temperature diffraction data, are shown as functions of the absolute temperature in Fig. 1(a). The thermal variations of the axial ratio and unit cell volume are presented in Fig. 1(b) and 1(c), respectively. Smooth curves have been drawn through the experimental points. The apparent
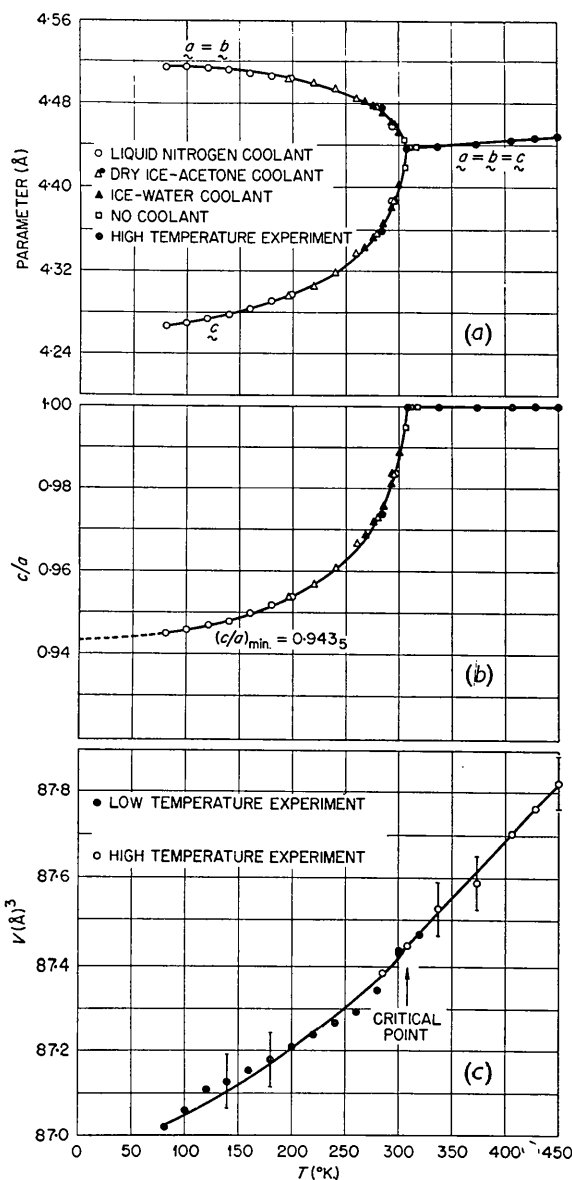

Fig. 1. The variations of (a) lattice parameters, (b) axial ratio, and (c) volume of the unit cell of $TiD_{1.98}$ with absolute temperature.

consistency of variations of experimental volumes from the curve in Fig. 1(c) must be attributed to a systematic error in view of the large probable errors associated with the observed volumes. The corresponding functions for the dihydride are similar in all details, except magnitudes of parameters, to those for the dideuteride and therefore have not been reproduced. The critical temperature below which the distortion of the cubic structure begins is also the same for both hydride and deuteride, namely $310\pm4°$ K. A comparison of the lattice parameters of $TiH_{1.99}$ and $TiD_{1.98}$, given in Table 1, shows the parameters of the dihydride to be consistently larger than those of the dideuteride. This effect has been noted experimentally in other

Table 1. *Lattice parameters of titanium dihydride and dideuteride**

		$TiH_{1.99}$	$TiD_{1.98}$
a (Å)	($T =$ 79° K.)	4·528	4·516
c (Å)	($T =$ 79° K.)	4·279	4·267
c/a	($T =$ 79° K.)	0·945	0·945
a (Å)	($T =$ 315° K.)	4·454	4·440
T_{critical} (°K.)		310±4	310±4

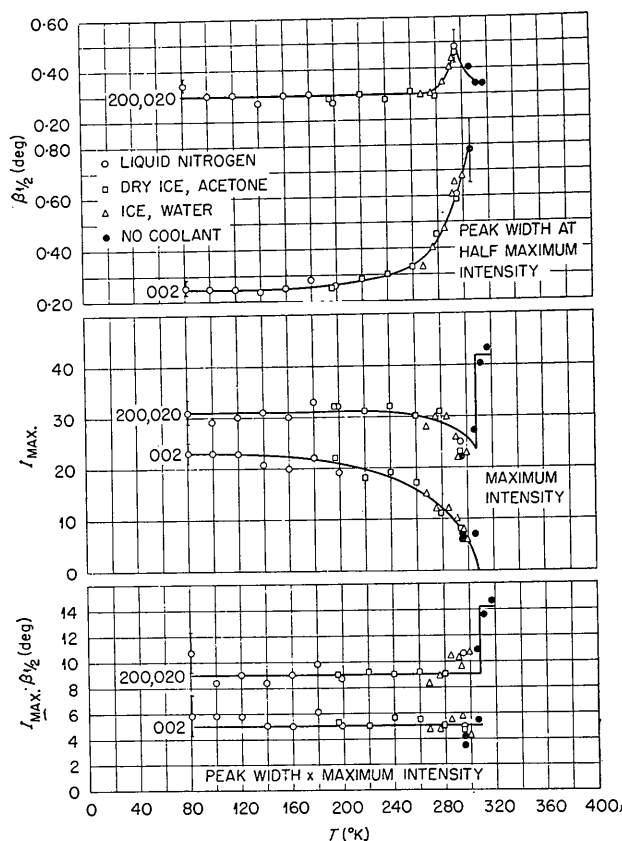* Probable error in all parameters is ±0.001 Å.

Fig. 2. The variations of the peak width at half-maximum intensity, the maximum intensity, and the product of peak width and maximum intensity with absolute temperature for the {200, 020}–{002} reflections of $TiD_{1.98}$ (low-temperature data only).

hydrides and deuterides (Zintl & Harder, 1935; Rundle, 1947; Sidhu, 1954) and has been interpreted theoretically by Nordman & Lipscomb (1951).

In addition to the cubic $\longleftrightarrow$ tetragonal transition evident in the data of Fig. 1, a characteristic broadening of the hydride and deuteride reflections, except those of form {hhh}, occurs just below the critical temperature. This is shown in Fig. 2, where the maximum intensity, peak width at half maximum, and the product of intensity and width of the {200,020} and {002} reflections from $TiD_{1.98}$ are presented as functions of the absolute temperature in the range 79–320° K. The broadening is observed both on warming up toward and on cooling down from the critical temperature, and is readily seen despite partial superposition of diffraction lines. An effect of the same sort has been noted in the cubic $\longleftrightarrow$ tetragonal ferroelectric transformation in $BaTiO_3$ by Miyake & Ueda (1948). Careful analysis of the broadened line shapes near the critical temperature also failed to disclose any evidence of a third diffraction line such as would be present if the cubic phase co-existed with the tetragonal phase in this range.

The low- and high-temperature diffraction data for zirconium dihydride, $ZrH_{1.92}$, are summarized in Fig. 3, in which the tetragonal lattice parameters, axial ratio, and cube root of unit-cell volume are presented as
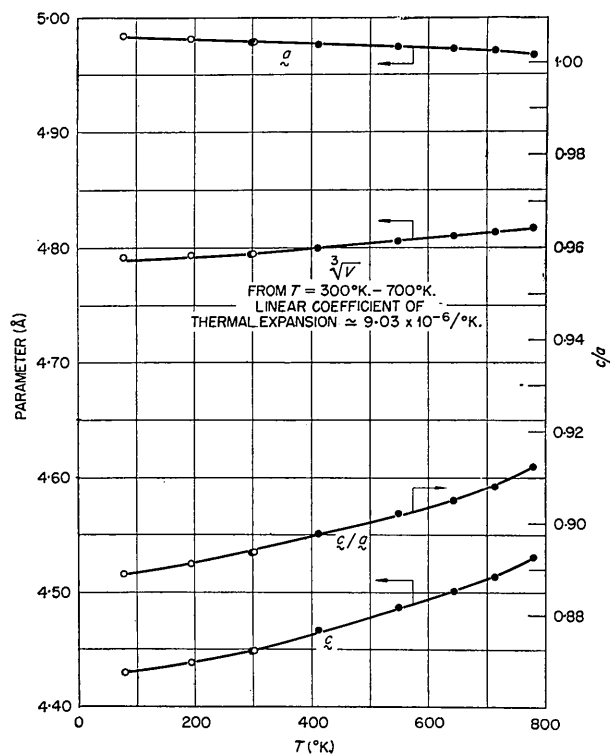

Fig. 3. The variations of lattice parameters, axial ratio, and the cube root of the volume of the unit cell of $ZrH_{1.92}$ as a function of the absolute temperature. Open circles represent low-temperature data; closed circles represent high-temperature data.

functions of the absolute temperature from 80° K. to 778° K. The lattice symmetry is face-centered tetragonal at all temperatures, in agreement with previous investigations. The degree of axial splitting is again seen to be temperature-dependent, with a definite suggestion of a cubic $\longleftrightarrow$ tetragonal transition, similar to that in titanium dihydride and dideuteride, but at a temperature unattainable without high-pressure, as well as high-temperature, diffraction apparatus.

The volume–temperature data supports the contention that no significant compositional changes occurred in the $ZrH_{1.92}$ sample at the higher temperatures of the experiment. The points lie on a smoothly rising curve, nearly linear from 300° K. to 778° K., with a slope which corresponds to a sensible linear expansion coefficient for a metal hydride. If the composition of the solid had changed materially at the highest temperatures included in Fig. 3 (643–778° K.), one would expect this change to be reflected in abnormal changes in volume. From the normal behavior of the volume–temperature function and the repeated room-temperature pattern checks mentioned previously, it may be concluded that the data of Fig. 3 do indeed represent an iso-compositional study of the dependence of the crystal structure of $ZrH_{1.92}$ on temperature.

Discussion of results

Before any discussion of the significance of the structure transitions apparent in the titanium dihydride and dideuteride data and implied in the zirconium dihydride data, a comparison of the results of this investigation with those reported in the literature is of interest.

It has been mentioned that Sidhu et al. (1956) have recently confirmed the small tetragonal distortion of titanium dihydride at room temperature. The average lattice parameter which they give for $TiD_{1.971}$ ($a_0 = 4.440 \pm 0.003$ Å) agrees well with the weighted average of the tetragonal parameters reported in this paper. The structure of the face-centered tetragonal phase cannot be determined uniquely from X-ray data since the hydrogen atoms contribute so little to the diffracted intensity. Neutron-diffraction investigations at room temperature (Sidhu et al., 1956) and at liquid-nitrogen temperatures (Shull & Wilkinson, 1955) have shown, however, that the hydrogen atoms are symmetrically located in the tetrahedral holes of the face-centered metal-atom lattice with no detectable displacements. The structure is then identical with that derived for ZrH_2 and ThH_2 by Rundle et al. (1952). Interatomic distances in titanium dideuteride at 79° K. and 315° K., calculated on the basis of a fluorite-type structure, are presented in Table 2.

The room-temperature lattice parameters for zirconium dihydride, $ZrH_{1.92}$, reported here are in excellent agreement with those given by Rundle et al. (1952). The tetragonality, as measured by the axial ratio, is significantly greater than that reported in a

Table 2. *Interatomic distances in titanium dideuteride,* $TiD_{1.98}$

Atomic positions in cubic or tetragonal lattice

4 Ti in $0,0,0$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$.
8 D in $\frac{1}{4},\frac{1}{4},\frac{1}{4}$; $\frac{1}{4},\frac{3}{4},\frac{3}{4}$; $\frac{3}{4},\frac{1}{4},\frac{3}{4}$; $\frac{3}{4},\frac{3}{4},\frac{1}{4}$;
$\frac{1}{4},\frac{1}{4},\frac{3}{4}$; $\frac{1}{4},\frac{3}{4},\frac{1}{4}$; $\frac{3}{4},\frac{1}{4},\frac{1}{4}$; $\frac{3}{4},\frac{3}{4},\frac{3}{4}$.

$T = 79°$ K.	$T = 315°$ K.
8 Ti–D at 1·920 Å*	8 Ti–D at 1·923 Å
4 Ti–Ti at 3·193 Å	12 Ti–Ti at 3·140 Å
8 Ti–Ti at 3·107 Å	6 D–D at 2·220 Å
2 D–D at 2·134 Å	
4 D–D at 2·258 Å	
Valence of D = 1·14†	Valence of D = 1·13
Valence of Ti = 4·16	Valence of Ti = 4·08

* Probable error in all distances is ± 0.001 Å.
† Valences were calculated from Pauling's metallic radii and radius rule (Pauling, 1947).

65 atomic % hydrogen alloy ($ZrH_{1.86}$) by Vaughan & Bridge (1956), presumably owing to the critical dependence of c/a on hydrogen concentration demonstrated by these authors. It is especially interesting to compare the c/a versus T curve of Fig. 3 with the analogous curve given by Vaughan & Bridge. The rapid increase in c/a observed by Vaughan & Bridge is attributed to compositional changes during heating, and this is probably true at temperatures above two or three hundred degrees centigrade since their experiment was carried out in vacuum. The relatively slow iso-compositional c/a variation reported here is therefore an additional effect independent of the variation with hydrogen concentration.

The ultimate cause of the distortional transformations in the hydrides examined is not clear at present. From Fig. 1, it is evident that several features of the titanium dideuteride and dihydride transitions (continuous variation of **a** and **c**, and the absence of any discernable discontinuity in volume, V, or in dV/dT, at the critical temperature) are consistent with so-called 'second-order transformations' of the type usually associated with ordering processes.*

Ordering of an atomic or magnetic variety is eliminated, however, by the close approach of the compounds to stoichiometric compositions and by the results of neutron-diffraction experiments cited above (Shull & Wilkinson, 1955). A ferro-electric ordering process is also unlikely in view of the symmetrical positions of the atoms in the tetragonal lattice. There remains the possibility of a gradual change in bond character between metal–hydrogen or metal–metal neighbors with decreasing temperature which might lead to the observed lattice distortions. A process of this type has recently been proposed by Goodenough (1955) in order to explain the magnetic and crystallo-

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* A measurement of the specific heats of these materials near the critical temperature has not been made, but a study of the temperature dependence of the magnetic susceptibility of $TiD_{1.98}$ in the range 200–370° K. has shown a broad maximum in the vicinity of 312° K. (Stevens, 1955).

graphic transitions in certain perovskite-type structures, and, while no exact analogies exist, the concept may be extended to the situation in the Group IV A hydrides.

An alternate explanation, based on the band theory of metals rather than a chemical bond theory, may be advanced. The transition from a cubic to a tetragonal lattice would then be considered as arising from an overlapping of Brillouin zone boundaries caused by small variations in electron density with temperature. Experiments at lower hydrogen concentration in both titanium and zirconium may provide some evidence bearing on the correctness of this hypothesis.

A discussion of the mechanism of the transformations must also be deferred pending a more complete microscopic and metallographic study. It is certain that they are diffusionless transitions but those aspects of their kinetics which can be deduced from the X-ray data alone do not suggest any other 'martensitic' characteristics.

The author is indebted to Drs M. K. Wilkinson and C. G. Shull for permission to quote results of their neutron-diffraction experiments. Thanks are also due Mr D. E. LaValle, for the preparation and analysis of the titanium dihydride and dideuteride, and Dr M. L. Picklesimer and Mr P. J. Jones for preparation of the zirconium dihydride sample. The analysis of the zirconium dihydride was performed by Mr J. H. Edgerton.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

On the occurrence of ε-carbide in iron.* By F. W. C. BOSWELL, *Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada*

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It is well known that ε-iron carbide forms during the first stage of tempering hardened steel (Jack, 1951a; Roberts, Averbach & Cohen, 1953; Lement, Averbach & Cohen, 1954). Single-crystal X-ray work (Roberts et al., 1953; Kurdjumov & Lyssak, 1947, 1949) on this material has

shown that the ε-carbide phase exists in metastable equilibrium with martensite containing about 0·25 wt.% carbon and it was concluded (Roberts et al., 1953) that ε-carbide would not form from martensite containing less than this amount of carbon. It thus appeared unlikely that ε-carbide would form directly from supersaturated ferrite. This view was supported by kinetic measurements (Dijkstra, 1949; Wert, 1949) on the precipitation of carbon from quenched iron containing about 0·02 wt.%

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