Unit Cell Dimension of Face-centered Cubic Chromium Hydride and Space Groups of Two Chromium Hydrides

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Chromium metal normally assumes the body-centered cubic crystalline arrangement. However other crystalline arrangements have been reported for electrodeposited chromium. A hexagonal close-packed structure was first reported in 1926,[2] and an α-manganese type structure was reported in 1931.[3] Several workers have identified the hexagonal structure since 1926, but there has been no corroboration of the α-manganese type structure. Recently one of the present authors presented additional data[4] which show that the hexagonal structure in electrodeposited chromium is actually a chromium hydride, with the hydrogen in interstitial positions in the hexagonal close-packed lattice. In addition, the existence of a face-centered cubic hydride of chromium was reported. It is desired to present here additional recent work which provides a more precise value for the lattice parameter of the face-centered cubic hydride, and to suggest structures for the chromium hydrides.

The initial studies of the F.C.C. hydride of chromium were made with an X-ray spectrometer, with which it was possible to determine the lattice of a given sample in the form of an electroplate, and to follow any structural changes occurring over a period of time. The data gave definite proof of the existence of the new phase. However, to avoid the well-known pitfalls of the spectrometer method as to errors in intensity of the diffraction maxima resulting from grain size or orientation, and to obtain a complete pattern of the new compound, samples were prepared for study by the powder X-ray diffraction method.

The F.C.C. hydride was deposited from an aqueous plating bath originally made up to contain 1021 g./l. of CrO_3, 3.4 g./l. of SO_4 and 20 g./l. of cane sugar. The sugar was added to the bath last as a sirup, and had the effect of reducing to the trivalent state from 7 to 10% of the contained chromium. The bath was refrigerated to 5 ± 4° during plating operations. The current density was approximately 0.8 amp./sq. in. Disks of brass $^1/_2$ in. in diameter and 0.020 in. thick were used as cathodes. The anode was cut from antimonial lead sheet. Plating was continued for periods of from six to twelve hours to provide thick deposits which could be handled easily. After plating, the samples were dropped into dilute nitric acid to dissolve the brass backing disk. Care was necessary in this step, as the heat generated was sufficient to decompose the hydride if the acid was too concentrated. The chromium hydride, which was not attacked by the acid, was then rinsed, dried and crushed into fine particles. It was so brittle that the crushing was easily carried out in a glass beaker, using a glass rod as a pestle. This provided a satisfactory sample for powder X-ray diffraction studies.

The powder photograms were taken with unfiltered chromium radiation ($\lambda K\alpha = 2.29090$ Å.) in a 114.6 mm. camera of the Buerger design. The data obtained from the diffraction pattern of the new "structure compound," corrected for systematic errors by extrapolation, gave 3.8605 ± 0.0005 Å. for the unit cell dimension. A more precise value could not be obtained owing to the fact that the diffraction maxima were broader than those usually obtained from a material as friable as is this compound. This broadening is believed to be the result of either or both of two factors, namely, small particle size and variations in lattice spacing resulting from variations in the number of interstitially placed hydrogen atoms. The intensities of the diffraction maxima are the same as those of a face-centered cubic metal.

Westgren[5] compiled much of the available data on the metal hydrides, which show that the hydrides are interstitial solid solutions of variable hydrogen content within certain definite composition limits. Westgren concluded that the hydrogen atoms occupy the second largest interstices in the metal lattice, since spatial considerations show that the largest interstice would provide too much space for the accepted value of the hydrogen radius. With few exceptions, hydrides of compositions ranging between M_2H and MH tend to adopt the H.C.P. crystal arrangement. Those of formula MH to MH_2 tend to adopt the F.C.C. arrangement. Thus, a complete composition range between the limits M_2H and MH_2 is possible, and the crystalline arrangement is governed by the composition.

In the case of Cr_2H–CrH, the metal atoms fall in a hexagonal close-packed arrangement with the hydrogen occupying the second largest interstitial positions.[4] However, the metal atoms are not in actual contact with each other, but bond through the hydrogen atoms. Two space groups are possible. If the chromium atoms have true holohedral symmetry, the space group is D_{6h}^4-$C6$/mmc. However, if the chromium atoms assume hemihedral symmetry, the space group is C_{6v}^4-$C6$mc. These two space groups are indistinguishable by X-ray diffraction methods, and it is only necessary for our purposes to consider one, *e. g.*, the latter. The chromium atoms assume hexagonal positions as H atoms enter the allowed interstitial point positions specified below, until these are filled, whereupon the addition of another hydrogen atom will cause an unstable structure due to the proximity of two hydrogen atoms. If more hydrogen atoms are present than will be included in the H.C.P. structure, the metal atoms assume a face-centered cubic structure which will accept two hydrogen atoms for each chromium atom. The space group becomes T_d^2-F43m (or O_h^5-Fm3m if all of

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(2) Ollard and Bradley, *Nature*, **117**, 122 (1926).

(3) Sasaki and Sekito, *Trans. Electrochem. Soc.*, **59**, 437 (1931)

(4) Snavely, *Electrochem. Soc.*, Preprint 92-35 (1947).

(5) Westgren, *J. Franklin Inst.*, **212**, 577 (1931).

the equivalent positions are filled). In both of the postulated structures, the apparent radius of the hydrogen atom is 0.39 Å. which is in the lower range of values obtained from calculations for previously reported hydrides. Postulated point positions for CrH and CrH_2 structures[6] are

CrH C_{6v}^4-*C*6mc. Wurtzite Hemihedral
Cr at 2(b) 00Z; $^1/_3, ^2/_3, ^1/_2 + Z$ where Z = 0
H at 2(b) 00Z; $^1/_3, ^2/_3, ^1/_2 + Z$ where Z = $^1/_6$

CrH_2 O_h^5-*F*m3m Fluorite–Holohedral
Cr at 4(a) 000; $0\ ^1/_2\ ^1/_2$; $^1/_2\ 0\ ^1/_2$; $^1/_2\ ^1/_2\ 0$
H at 8(c) $^1/_4\ ^1/_4\ ^1/_4$; $^1/_4\ ^3/_4\ ^3/_4$; $^3/_4\ ^1/_4\ ^3/_4$; $^3/_4\ ^3/_4\ ^1/_4$
$^3/_4\ ^3/_4\ ^3/_4$; $^3/_4\ \overline{^1/_4}\ \overline{^1/_4}$; $\overline{^1/_4}\ ^3/_4\ \overline{^1/_4}$; $\overline{^1/_4}\ \overline{^1/_4}\ ^3/_4$

The important result of the discovery of these hydrides of chromium is that the radius of the chromium atom no longer constitutes an anomaly within the family of metals. Recent discussions of the chromium atom radius[7,8] have treated the hexagonal hydride as a normal H.C.P. allotropic form of the metal. A somewhat complicated postulate regarding behavior of the electrons in the outer rings was advanced to explain the very large apparent radius (1.35 Å.) of the atom in the H.C.P. arrangement. With the introduction of the hydride concept, the chromium atoms may be considered to undergo only the normal radius change of 3% in passing from the F.C.C or H.C.P. hydride phases to the B.C.C. metallic phase (r = 1.25 Å.). The interstitially placed hydrogen atoms expand the metal lattice in both hydride phases and the Goldschmidt correction[9] of 3% provides a radius value of 1.28 Å. which appears to satisfy the X-ray data for these phases.

Summary

1. A determination of the lattice parameter of F.C.C. chromium hydride is reported. The new value is $a = 3.8605 \pm 0.0005$ Å.
2. Structures are postulated for the F.C.C. and H.C.P. chromium hydrides.
3. Argument is presented to refute the concept that chromium is allotropic.

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[6] International Tables for the Determination of Crystal Structures.

[7] Hume-Rothery, "The Structure of Metals and Alloys," 1936.

[8] Pauling, THIS JOURNAL, **69**, 542 (1947).

[9] Goldschmidt, *Z. physik. Chem.*, **133**, 397 (1928).

RECEIVED AUGUST 13, 1948

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies of Vanadium Carbide and Vanadium Nitride

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In previous papers from this laboratory, Anderson[3] has reported low-temperature heat-capacity measurements of vanadium and three of its oxides and Shomate[4] has reported similar data for vanadium di- and trichlorides. The present paper reports heat capacity measurements throughout the temperature range 50.4 to 298.16°K. and entropies at 298.16°K. of vanadium carbide and vanadium nitride. No similar data for either of these substances are in the literature.

Materials.[5]—The starting material for the preparation of vanadium carbide was vanadium containing 8% carbon and only a trace of other impurities. An intimate mixture of this material was made with Norblack sufficient to comply with the formula VC. The mixture was heated in vacuum at 1300 to 1350° for a total of twenty-six hours. After twelve and twenty-two hours heating, the product was analyzed and reground, and minor adjustment was made in the composition. The final product was uniform and showed no signs of incomplete reaction, which also was confirmed by the X-ray diffraction pattern.[6] No free carbon was evident on solution in 1:3 nitric acid. The product was analyzed for vanadium by permanganate titration, after fusion in a mixture of sodium bisulfate and potassium nitrate, and for carbon by absorbing and weighing the carbon dioxide evolved on combustion in pure oxygen in the presence of red lead oxide. The results were 80.90% vanadium and 19.04% carbon, as compared with the theoretical 80.92% and 19.08%, respectively.

Vanadium containing carbon, as mentioned above, also was the source material for the preparation of vanadium nitride. A 5:1, by volume, mixture of purified nitrogen and hydrogen was passed over the finely ground carburized vanadium at 1200° for twenty-eight hours. This gas mixture slowly replaced carbon by nitrogen, the carbon being carried out of the hot zone evidently by free radical formation with hydrogen. At seven-hour intervals, the reaction mixture was cooled, removed from the furnace, and reground. After twenty-eight hours of treatment, the product contained 0.76% carbon and an excess of nitrogen. It then was heated for eight hours at 1100° in a stream of pure hydrogen. The final product was analyzed for vanadium by permanganate titration, after burning to oxide and fusing in sodium bisulfate. The average result was 78.24% vanadium, as compared with the theoretical 78.43%. Combustion analysis for residual carbon gave only 0.05%. The X-ray diffraction pattern showed no evidence of materials other than vanadium nitride.

Heat Capacities.—The heat capacities were measured with apparatus previously described.[7] The results, expressed in defined calories (1 cal. = 4.1833 int. joules) per mole, are listed in Table I and are plotted against temperature in Fig. 1.

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[3] Anderson, THIS JOURNAL, **58**, 564 (1936).

[4] Shomate, *ibid.*, **69**, 220 (1947).

[5] The preparations and analyses of these substances were conducted by A. E. Salo, formerly chemist, Pacific Experiment Station, Bureau of Mines.

[6] X-Ray diffraction examinations of both substances were made by E. V. Potter, formerly physicist, Salt Lake City Station, Bureau of Mines.

[7] Kelley, Naylor and Shomate, Bureau of Mines Technical Paper 686, 1946, 34 pp.