

The Phase Transformation of Cobalt as Observed on Single Crystals*

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AS part of a general study of the surface properties of metal single crystals we are carrying out experiments with single crystals of cobalt. The current great interest in phase transformations prompts us to report some preliminary results.

A cobalt crystal¹ was machined in the form of a sphere, $\frac{5}{16}$ in. in diameter, with a small shaft for handling, $\frac{1}{8}$ in. in diameter and $\frac{1}{2}$ in. in length. The strained layer resulting from the machining operation was removed by deep etching, and the sphere was electrolytically polished in 42.5 percent by volume orthophosphoric acid.² The sphere was oxidized in air in separate experiments both below and above 420°C, at which point the low temperature hexagonal close-packed form is converted to the high temperature face-centered cubic form.³ As shown in Fig. 1 at 350–400°C the



FIG. 1. The interference color pattern formed on a single crystal of cobalt with a hexagonal close-packed structure during oxidation in air at 350–400°C. Photograph taken normal to (0001) plane.

oxidation pattern⁴ which formed on the surface was indicative of a hexagonal close-packed structure while at 450–500°C the symmetry of the pattern was indicative of a face-centered cubic structure. Etching of the cobalt crystal at room temperature after the formation of a face-centered cubic pattern at 450–500°C, always resulted in an etch pattern with hexagonal close-packed symmetry. The experiments at 350–400°C and at 450–500°C were repeated several times and the sharpness and perfection of the patterns increased each time the experiments were repeated.

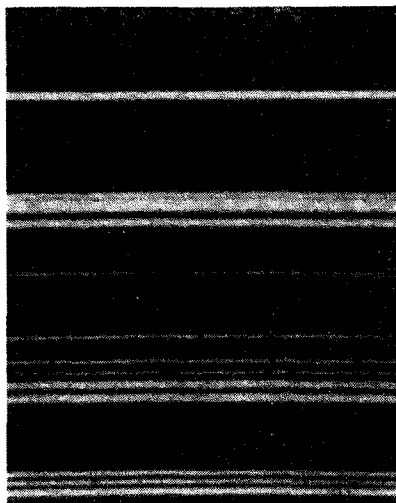


FIG. 2. Photomicrograph of parallel bands formed on a single crystal of cobalt during oxidation. $\times 600$. Curvature of bands is a consequence of the spherical shape of the specimen.

Cobalt crystals were thus passed repeatedly through the transformation point without recrystallization into small grains.

Several interesting observations were made. First, in every experiment the same set of (111) planes in the face-centered cubic structure corresponded to the (0001) planes in the hexagonal form. In other words, although the (0001) planes presumably had a choice of taking the place of any one of 4 sets of (111) planes, they always chose the same set of (111) planes. Second, in all experiments there existed on the surface a system of parallel bands 80–90° from the (0001) pole position such as those shown in the photomicrograph in Fig. 2. The bands ran concentrically around the sphere and had a geometry such that they could be attributed to the intersection of (0001) planes with the surface. The most interesting feature of these bands was that neighboring bands had different activities as indicated by the different interference colors in the bands. In the region in which these bands were concentrated x-ray back reflection photographs showed a multiplicity of each of the Laue spots. This multiplicity may be attributed to a mosaic type of structure with each of the blocks having an orientation only slightly different from its neighbors. The origin of these bands is as yet unknown. They may have been formed by slipping of parts of the crystal along (0001) planes during the machining operation, or more likely they may have been a secondary effect of the shearing process proposed to account for this transformation.⁵ Third, in view of the interpretations of the crystal structure of cobalt⁶ it is of interest to point out that chemically cobalt in bulk behaves as a face-centered cubic metal above approximately 420°C and as a hexagonal close-packed metal below approximately 420°C.

* The results reported herein were obtained during the course of research being carried out for The Texas Company.

¹ Kindly furnished by Dr. Allan Gwathmey of the University of Virginia, who obtained it from Dr. Freed of Columbia University.

² W. C. Elmore, *Phys. Rev.* **53**, 757 (1938).

³ *Metals Handbook* (The American Society for Metals, 1948), eighth edition, p. 1136.

⁴ A spherical single crystal is unique in that all crystal faces are present on the surface. In the case of face-centered cubic metals the (100) face occurs 6 times, the (111) face 8 times, the (110) face 12 times, and the minor faces either 24 or 48 times. The oxidation of cobalt results in the formation of interference color films on the surface. Since the various crystal faces oxidize at different rates, a range of colors is obtained. The repetition of results on each octant of the surface gives rise to a pattern, from which the crystal faces may be identified.

⁵ A. R. Troiano and A. B. Greninger, *Metals Handbook* (The American Society for Metals, 1948), eighth edition, pp. 263–6.

⁶ O. S. Edwards, *J. Inst. Metals* **69**, 177 (1943); O. S. Edwards, *Proc. Roy. Soc. (London)* **A180**, 268 (1942); Edwards, Lipson, and Wilson, *Nature* **148**, 165 (1941).

The Out-of-Plane Deformation Frequency of the NH Group in the Peptide Link

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A CHARACTERISTIC feature of the infrared spectra of proteins is a diffuse absorption band extending from about 800 cm^{-1} to beyond 650 cm^{-1} with an ill-defined maximum near 700 cm^{-1} . A similar band is present in Nylon, in synthetic polypeptides, and in the spectra of *N*-mono-substituted amides. Clearly this band is due to some fundamental frequency of the peptide group.

We have found that partial deuteration of the NH bonds in all of these compounds causes a marked decrease in the intensity of this band. In the case of *N*-methyl formamide almost complete deuteration was accomplished, causing the band to disappear entirely and a new band to appear with its maximum absorption near 530 cm^{-1} . This reduction in frequency by a factor of 1.36 on deuteration is exactly what would be expected for a pure NH deformation vibration free from interaction with other motions.

The dichroism of this band was studied in Nylon which had been oriented by stretching. It was found that the intensity of absorption was greatest with the electric vector of the incident radiation perpendicular to the direction of stretch. Since the NH bonds in stretched Nylon are known to be predominantly perpendicular to

the direction of stretch,¹ this proves that the NH deformation vibration responsible for the 700 cm⁻¹ band must be that in which the motion of the hydrogen atom is perpendicular to the plane of the peptide group.

The behavior of this band in solutions of *N*-mono-substituted amides in carbon disulfide is of considerable interest. As dilution progressively increases, the molar absorption decreases very markedly and, in fact, parallels closely that of the NH stretching frequency near 3300 cm⁻¹. Thus the width and diffuseness of the 700 cm⁻¹ absorption is presumably due to hydrogen bonding. Whereas the wide band near 3300 cm⁻¹, due to the NH stretching frequency, is replaced by a narrow band at 3450 cm⁻¹, when hydrogen bonding is destroyed, we have not yet found the corresponding unbonded frequency in the case of the 700 cm⁻¹ band. It would be expected in the longer wavelength region, and work is in progress to locate it. The resemblance of the 700 cm⁻¹ frequency in the peptide link to the analogous OH deformation frequency in the alcohols is very striking.²

It should be added that the 700 cm⁻¹ out of plane NH deformation frequency has also been identified in the lactams (γ -butyrolactam, δ -valero-lactum, and ϵ -caprolactam), where it exhibits the same behavior on dilution and deuteration as that described above for the *N*-mono-substituted amides.

This work (which will be described in full elsewhere) was supported in part by the Rockefeller Foundation.

¹ C. W. Bunn and E. V. Garner, Proc. Roy. Soc. (London) **A189**, 39 (1947).

² A. V. Stuart and G. B. M. Sutherland, J. Chem. Phys. **20**, 1977 (1952).

Erratum: Preliminary Analysis of the Pure-Rotational Spectrum of Methyl Amine

[J. Chem. Phys. **20**, 1812 (1952)]

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THE following figure should have been included with this letter:

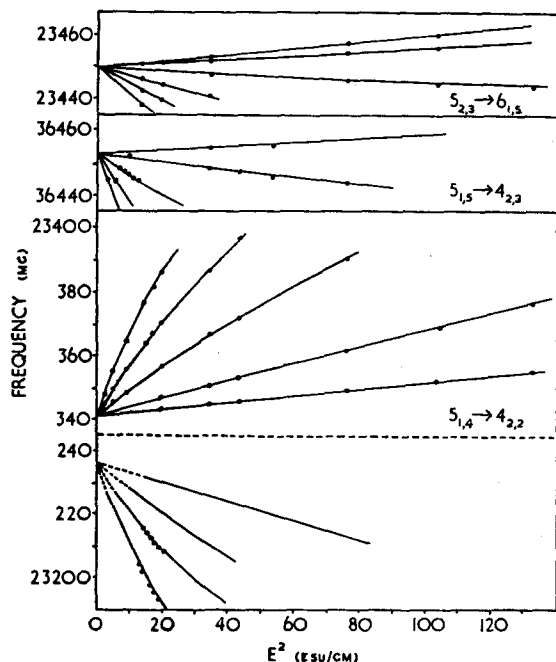


FIG. 1. Stark effects in methyl amine. The curves are predicted Stark shifts; circles are experimental points.

On the Nature of the Hydrogen Bridge

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IN diborane B₂H₆ and related "electron-deficient" compounds, it is now fairly well accepted that two atoms each having an otherwise vacant orbital can be held together by a bridge of two hydrogen atoms, mutually shared, or that two alkyl groups can sometimes bring about a similar bridging. However, the nature of this bonding is not understood.^{1,2} The interesting observation is reported here that such bonds occur only when the hydrogen atoms have partial negative charge.

The basis for determining the nature of the charge on hydrogen is the postulate that atoms adjust to equal electronegativity in a molecule.³ The relative charge on combined hydrogen is taken as the difference between its electronegativity in the compound and its electronegativity in the elementary state

$$\Delta SR_H = SR_m - 3.55,$$

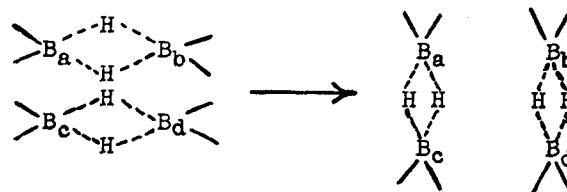
ΔSR_H is the electronegativity change made by hydrogen in combining, SR_m is the electronegativity of the molecule of

TABLE I. Relative partial charge on combined hydrogen (hypothetical compounds in brackets).

Compound	ΔSR_H	Compound	ΔSR_H
MeBF ₂	0.43	Al ₂ Et ₆	-0.03
[BHCl ₂]	0.40	B ₂ H ₂ Me ₄	-0.03
C ₂ H ₄ O ₂ BH	0.25	B ₂ H ₂ Me ₃	-0.05
[BH ₂ F]	0.23	B ₂ H ₂ Cl	-0.06
(MeO) ₂ BH	0.21	B ₂ H ₂ Me ₂	-0.08
(EtO) ₂ BH	0.16	Ga ₂ H ₆	-0.08
Me ₂ BF	0.14	B ₂ H ₂ Br	-0.09
(PrO) ₂ BH	0.14	Al ₂ Me ₆	-0.11
[BH ₂ OH]	0.11	B ₂ H ₂ Me	-0.12
[BH ₂ Cl]	0.10	Al ₂ H ₂ Me ₄	-0.16
[MeOBH ₂]	0.10	B ₂ H ₂ I	-0.16
[(C ₆ H ₅) ₂ BH]	0.08	B ₂ H ₆	-0.19
C ₆ H ₅ BH ₂	0.04	B ₄ H ₁₀	-0.22
GaMe ₃	0.03	B ₄ H ₁₁	-0.24
[B ₂ H ₄ F]	0.01	B ₄ H ₉	-0.28
[BH ₂ Br]	0.01	B ₄ H ₁₀	-0.28
AlPr ₃	0.00	B ₁₀ H ₁₄	-0.31
BMe ₃	-0.01	(AlH ₃) _x	-0.49
[B ₂ H ₄ OH]	-0.03		

hydrogen compound, determined as the geometric mean stability ratio of all the atoms of the molecule before combination,³ and 3.55 is the electronegativity of elementary hydrogen. ΔSR_H values for a number of hydrogen compounds, real and hypothetical, are given in Table I.

Although it is frequently assumed that dissociation to the monomer is a prerequisite to the disproportionation so commonly observed, as in halo- and alkylboranes, it should be recognized that other mechanisms are possible. For example, two dimer molecules might form two new molecules by switching bridges.



If alkyl groups containing negative hydrogen may form bridges also, then similar switching involving alkyl groups as well as, or in place of, hydrogen atoms might occur, accounting for disproportionation in methylboranes, for example. Therefore, although thermal stability of bridge bonds and rates of disproportionation probably have some relationship, it is not necessarily direct. However, it is of interest that in the very similar compounds, the monohaloboranes, fluoroborane is unknown and the rate of