Summary

The adsorption of nitrous oxide upon pseudomorphs formed by partially dehydrating the crystalline hydroxides of magnesium, calcium and zinc and by partially decarbonating zinc carbonate at 0° has been measured. It is found that although these pseudomorphs exhibit considerable adsorptive activity they are far inferior in this respect to the zeolites, for instance, to chabasite. However, as with the zeolites, the adsorptive activity increases to a maximum at 80–95% dehydration and then diminishes rapidly to almost zero at complete dehydration. This behavior is explained as due to the formation of exceedingly minute crystallites of the metallic oxides and of the metallic hydroxides during the dehydration.

The progress of the dehydration was also followed in the case of brucite by means of X-ray powder photographs and the results were found to be consonant with those obtained in the adsorption measurements.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Interatomic Distances in Cobalt Diselenide

BY BURTON LEWIS AND NORMAN ELLIOTT

The crystal structure of cobalt diselenide has been reported twice in the literature, by de Jong and Willems[1] in 1928, and by Tengner[2] in 1938. The substance has the pyrite structure and is based on a unit cell 5.845 = 0.005 Å.[3] on an edge. The value 0.375 has been assigned to the parameter which fixes the atomic positions of selenium.

It was noted by Pauling and Huggins[4] that the distance between two selenium atoms in cobalt diselenide was 0.24 Å. larger than that found in crystalline selenium, the discrepancy being either unaccounted for by the theory of the additivity of covalent radii or due to an error in the parameter determination. The crystal structure of cobalt diselenide has therefore been reinvestigated using a shorter X-ray wave length than was used by previous experimenters. In this way more reflections have been observed than before. The results are reported in this paper.

The preparation of cobalt diselenide and the analysis of its powder photographs were the same as have been described in a previous paper.[5] The X-ray data are listed in Table I.

The observations (421) > (333) + (115), (423) + (502) = (333) + (115), (601) = (604), (425) + (603) > (116) + (532), (640)α_1 > (444)α_1, (640)α_2 < (444)α_1, and (640) > (600) + (442) limit the parameter to the range of values 0.375–

TABLE I

Copper K_α radiation. λ = 1.539 Å. Camera radius = 5.005 cm.

Sin θ	*hkl*	*I*, obsd.	*I*, calcd.
0.2599	200	195	195
.2913	201	800	845
.3193	112	700	645
.3682	220	155	125
.4327	113	600	580
.4522	222	40	45
.4711	203	250	210
.4886	132	350	360
.5232	400	60	55
.5844	420	20	25
.5994	421	180	175
.6129	332	80	80
.6407	422	40	35
.6795	333 511	160	160
.7042	205 423	160	165
.7175	512	100	105
.7399	440	160	180
.7848	600 442 α_1	30	25
.7860	600 442 α_2		
.7960	601 α_1	40	45
.7973	601 α_2		
.8065	116 532 α_1	150	140
.8076	116 532 α_2		
.8588	533 α_1	90	90
.8598	533 α_2		
.8784	425 603 α_1	130	145
.8794	425 603 α_2		
.8877	136 α_1	100	100
.8891	136 α_2		
.9070	444 α_1	20	20
.9087	444 α_2		
.9462	640 α_1	40	40
.9478	640 α_2		
.9554	207 641 α_1	240	220
.9574	207 641 α_2		
.9647	336 172 552 α_1	300	330

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[1] De Jong and Willems, *Z. anorg. allgem. Chem.*, **170**, 241 (1928).

[2] Tengner, *ibid.*, **239**, 126 (1938).

[3] De Jong and Willems report the edge of the unit cell to be 5.854 Å. This is probably a mistake caused by interchange of the last two numbers.

[4] Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] Norman Elliott, THIS JOURNAL, **59**, 1958 (1937).

0.379. The calculated intensities of these reflections are plotted in Fig. 1 for various values of the parameter, covering de Jong and Willems[1] experimental value, 0.375, and that predicted by Pauling and Huggins,[4] 0.386.

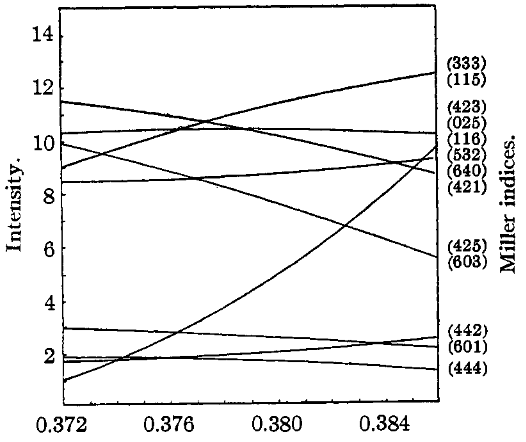

Fig. 1.

The best choice of a parameter value from the present data is $u = 0.377 \pm 0.002$, allowing for a ±20% error in the intensity estimations. Using this value, the intensities of all observed reflections have been calculated. The relative observed and calculated intensities are included in Table I and are shown in Fig. 2.

The new parameter value is nearly the same as that previously reported. However, the slight change leads to a correction in the interatomic distances. These are

$$\text{Co–Se} = 2.43 \pm 0.01 \text{ Å.}$$
$$\text{Se–Se} = 2.49 \pm 0.04 \text{ Å.}$$

The cobalt–selenium distance is 0.03 Å. shorter than the sum of the covalent radii and the selenium–selenium distance is 0.21 Å. larger. De Jong and Willems'[1] investigation of the crystal structure of nickel diselenide shows the distance between two selenium atoms to be 2.61 Å., even greater than in cobalt diselenide.

It has been noted by Pauling and Huggins[4] that cobalt has one and nickel two more electrons than may be accommodated in 3d orbitals when covalent octahedral bonds are formed. The disposition of these electrons in new orbitals involving the selenium atoms is perhaps the cause of an increase in interatomic distances. Preliminary electrical conductivity measurements show that cobalt and nickel diselenides conduct as well as metals while manganese diselenide is a non-conductor. It would be interesting to know the conductivities of the disulfides of cobalt and nickel, for in these compounds the interatomic distances are normal.

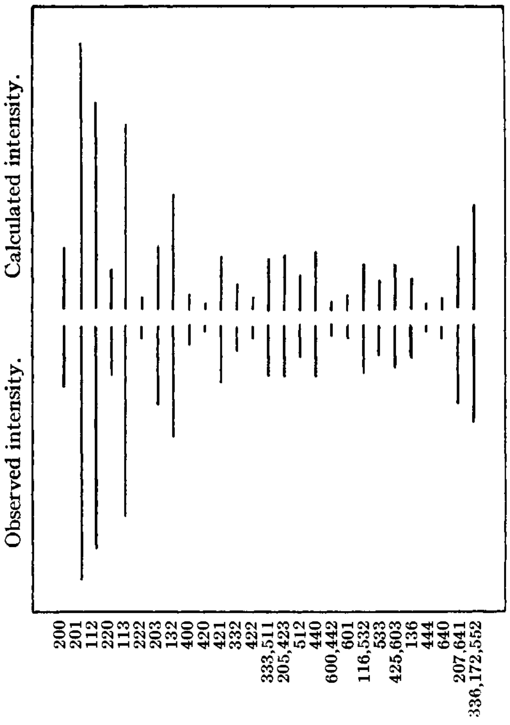

Fig. 2.

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Summary

A redetermination of the parameter in cobalt diselenide leads to the value, 0.377 ± 0.002. The interatomic distances are:

$$\text{Co–Se} = 2.43 \pm 0.01 \text{ Å.}$$
$$\text{Se–Se} = 2.49 \pm 0.04 \text{ Å.}$$

Cobalt diselenide is observed to have metallic properties, and it is suggested that these characteristics and the anomalous selenium radius are related to the presence of "metallic" electrons not used by cobalt in the formation of covalent bonds.

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