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Electron Diffraction Observations of Surface Reaction of Hydrogen Selenide on Zinc Oxide

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The reaction of hydrogen selenide and pigment zinc oxide at room temperature has been investigated, using electron and x-ray diffraction as a means of examining the reaction product. It was found that hydrogen selenide reacts with zinc oxide to form zinc selenide as a coating around the zinc oxide particles. After approximately one-tenth of the zinc oxide is converted to zinc selenide by this surface reaction, the resulting coating of zinc selenide prevents the continuance of the reaction. Since the effective depth of penetration of electrons under the conditions of electron diffraction is much less than the average diameter of the pigment particles used in this investigation, the electron diffraction photograms necessarily arise largely from the particle surfaces. For this reason electron diffraction was successfully used to demonstrate that the reaction proceeded in the manner described. The paper illustrates the applicability of electron diffraction to the general problem of the examination of the surfaces of pigment particles.

DURING the course of the study of the reaction of gaseous hydrogen selenide with zinc oxide powder, interesting observations were made by electron diffraction. These studies are of value from the standpoint of the gas-solid reaction and the physical and chemical structure of the reaction product and also as an example of the applicability of the electron diffraction method to the study of the surfaces of fine particles.

When hydrogen selenide is allowed to react with zinc oxide at room temperature, the white zinc oxide pigment takes on a yellow color. The reaction stops when the zinc oxide has acquired a selenium content of approximately six percent for the particular samples of zinc oxide employed in this investigation. The most likely course of the reaction between hydrogen selenide and zinc oxide would be to form zinc selenide and water ($H_2Se+ZnO \rightarrow ZnSe+H_2O$). If this reaction is carried to completion, the resulting solid phase, zinc selenide, would have a selenium content of 54.8 percent.

Examination of the reaction product by electron and by x-ray diffraction discloses that this reaction does, indeed, take place but the reaction is prevented from going to completion by the formation of a coating of zinc selenide about each zinc oxide particle.

A description of the procedure for carrying out the reaction and a discussion of the electron diffraction results and their interpretation follow.

PROCEDURE FOR EFFECTING THE REACTION

The reaction was effected by passing hydrogen selenide through pure zinc oxide packed in a 30-mm diameter glass tube. The reaction took place at room temperature. Progress of the reaction could be followed easily; a sharp boundary existed between the lemon-yellow reacted material and the white unreacted zinc oxide. The resulting material was dried at 100°C.

The hydrogen selenide was prepared by passing dry hydrogen over selenium at about 500°C.[1] The resulting gas was cooled to room temperature and the condensed selenium was removed by a dust trap. The zinc oxide used was spectroscopically pure and was made by boiling pure zinc and allowing the vapor to oxidize in clean air.

EXAMINATION OF REACTION PRODUCT

X-ray examination was made by the powder method. The powder to be examined was placed in a thin-walled glass capillary tube and its

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[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Co.), Vol. X, p. 758.

diffraction pattern was photographed with filtered molybdenum x-radiation.

Electron examination was made by the reflection and also by the transmission technique using 40-kv electrons in an electron diffraction camera, a description of which has been published.[2] The original qualitative aspects of the problem were investigated by the reflection technique with the pigment pressed onto the surface of a metal block. Recently, Dr. D. G. Brubaker, of this laboratory, has made quantitative lattice measurements by the transmission technique with the pigment mounted in a thin layer on a thin organic membrane.

Determination of the selenium content was made by chemical analysis.

RESULTS

The product of the reaction of hydrogen selenide and zinc oxide was yellow in color. The particular sample to be discussed in detail here was found to contain 6.4 percent selenium. By x-ray examination this pigment appeared to be mostly zinc oxide, the x-ray pattern of zinc selenide being very faint, and that of zinc oxide very strong. This was to be expected since the maximum amount of zinc selenide that could be present was 11.7 percent (equivalent to 6.4 percent Se). Electron examination, on the other hand, indicated that zinc selenide was the major constituent and zinc oxide, the minor constituent. It is concluded from this that the zinc selenide must exist as a coating on the surface of the zinc oxide particles. The zinc oxide particles have an average diameter of 0.25 micron. Since the maximum thickness of zinc oxide that 40-kv electrons can penetrate without losing velocity is approximately 0.05 micron, it follows, therefore, that the electron diffraction pattern arises from the diffraction of electrons passing through the outer layer of the particles only, such that the maximum path of the electrons through the particle is not over 0.05 micron. The electron examination of the zinc oxide-hydrogen selenide reaction product indicates, therefore, that the outer layer of the particle is largely zinc selenide. The results of x-ray and electron examination, coupled with the fact that the reaction reaches an abrupt end when only about one-tenth of the zinc oxide has been converted to zinc selenide, indicate very definitely that the reaction product consists of zinc oxide particles coated with zinc selenide.

Heating the reaction product in air at temperatures up to 250°C causes no change in color, selenium content or appearance of the x-ray and electron diffraction photograms. Heating in air at 300 or 350°C causes the yellow color to change to a light chocolate brown color. At the same time the selenium content decreases and the zinc selenide becomes the minor constituent on the electron photogram, and zinc oxide becomes the major constituent. Only zinc oxide can be detected on the x-ray photogram. One sample, for example, contained 6.4 percent Se originally and after heating one hour at 300°C the selenium content was reduced to 5.9 percent. This is a relatively small loss of selenium considering the decided change in the electron diffraction photogram and the definite change in color. It is believed that much of the zinc selenide has oxidized or otherwise decomposed. The products of oxidation or decomposition are not evident, however, by the x-ray and electron examination. Heating one hour at 350°C in air causes a further reduction of selenium content to 4.4 percent and renders the zinc selenide barely detectable on the electron photogram. Heating one hour at 450°C in air reduces the selenium content to 2.5 percent and the zinc selenide cannot be detected by x-ray or electron examination. After this heating the pigment has lost its color and is white. It seems likely that the zinc selenide oxidizes to zinc oxide and selenium dioxide. The latter sublimes at temperatures above 250°C, thus causing the decrease in selenium content.

The theory that the change accompanying heating results from oxidation is further supported by the fact that heating at 450°C in an evacuated sealed tube or in nitrogen at one atmosphere causes no change in color and no change in structure as revealed by electron and x-ray examination.

Accurate measurements by the electron transmission technique show that the zinc selenide coating and the zinc oxide core have the same crystal structure and lattice dimensions as they

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[2] M. L. Fuller, Metals and Alloys **10**, 85, 122 (1939).

have as individuals, thus indicating that there is no solid solution or chemical combination between the zinc selenide and zinc oxide.

Reproductions of two of the electron diffraction photograms are shown in Fig. 1. Photogram A is of the sample heated one hour at 450°C in a vacuum. In this photogram, the zinc selenide pattern is the more prominent relative to the zinc oxide pattern. This material, like the original unheated material, consists of zinc oxide particles coated with zinc selenide. Photogram B is of the sample heated one hour at 350°C in air. In this material much of the zinc selenide is oxidized and the zinc oxide pattern predominates with the zinc selenide pattern showing faintly.

The observations on the several specimens mentioned in this paper are tabulated in Table I. A number of similar specimens were prepared and studied in this investigation, the ones presented below are regarded as typical.

DISCUSSION OF THE ELECTRON DIFFRACTION METHOD OF STUDYING PARTICLE SURFACES

Thomson and Cochrane in their recent book[3] calculate that the mean free path of 30,000-volt electrons in a solid is approximately 0.04 micron.

TABLE I. *Reaction product of hydrogen selenide and zinc oxide.*

Specimen and Treatment	Color	Per-Cent Se	Indications of Diffraction Examination Electron		X-Ray	
			Phase Major	Minor	Major	Minor
Original—unheated	Yellow	6.4	ZnSe	ZnO	ZnO	ZnSe
Heated 1 hr. 250°C in air	Yellow	6.5	ZnSe	ZnO	ZnO	ZnSe
Heated 1 hr. 300°C in air	Light chocolate brown	5.9	ZnO	ZnSe	ZnO	None
Heated 1 hr. 350°C in air	Light chocolate brown	4.4	ZnO	ZnSe	ZnO	None
Heated 1 hr. 450°C in air	White	2.9	ZnO	None	ZnO	None
Heated 1 hr. 450° C in vacuum	Yellow	6.4	ZnSe	ZnO	ZnO	ZnSe

If one assumes for the experiments in this paper, where 40,000-volt electrons were used, that the mean free path is 0.05 micron, some interesting speculations can be made concerning the study by electron diffraction of the surfaces of pigment particles. If it is assumed that the particles are spheres of a uniform diameter of 0.25 micron, it may be calculated that the surface shell available for electron diffraction is 0.003 micron thick, measured radially. As a matter of fact, however, the zinc oxide particles used here are neither spherical nor uniform in size but have merely an "average diameter" of 0.25 micron. The effect of having some of the particles smaller than 0.25 micron with curved surfaces, or of having edges such as the intersection of two crystal faces, is to increase the depth of penetration of the electron beam, measured radially, and thus make the thickness of surface shell cooperating in electron diffraction greater than the 0.003 micron calculated for the idealized case. For example, the radial thickness of surface shell of a sphere 0.10 micron in diameter that would cooperate in electron diffraction would be 0.007 micron.

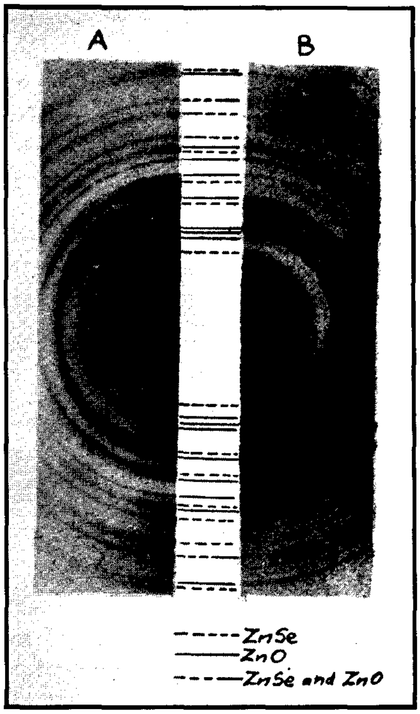

FIG. 1. A—Zinc selenide coated zinc oxide heated one hour at 450°C in vacuum. B—Zinc selenide coated zinc oxide heated one hour at 350°C in air.

If one calculates the thickness of a surface shell of zinc selenide on a sphere of zinc oxide, the diameter of the composite particle being 0.25 micron and the total selenium content 6.4 percent, the thickness of the surface shell is found to be 0.006 micron. It follows, therefore, that if

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[3] G. P. Thomson and W. Cochrane, *Theory and Practice of Electron Diffraction* (Macmillan Company, Ltd., London, 1939), p. 100.

the particles of reaction product are zinc oxide coated with zinc selenide, as the evidence of this paper would indicate, the weak zinc oxide electron pattern arises from certain smaller than average particles and from particles having sharp edges and ends.

The nature of this reaction between hydrogen selenide and zinc oxide suggests that the thickness of the zinc selenide surface layer is probably a definite quantity. In such a case, the extent of the reaction, or the selenium content of the end product, would depend upon the specific surface (surface area per unit mass) of the pigment zinc oxide. If this uniform thickness of zinc selenide is 0.006 micron, for example, a zinc oxide spherical particle of 0.012-micron diameter would be completely converted to zinc selenide. Two cases could arise for which only the zinc selenide diffraction pattern would be obtained: (1) The particles are uniformly large enough so that the passage of the electrons through the particle would necessarily be confined to the zinc selenide coating and (2) the particles are uniformly small enough so that all of the zinc oxide would be converted to zinc selenide. These two cases could, of course, be distinguished from each other by chemical analysis. At intermediate particle sizes, or with non-uniform size distribution, both zinc oxide and zinc selenide would give electron diffraction patterns, the relative intensities of which would depend on the particular conditions of particle size, shape and size distribution. The present example of zinc oxide particles coated with zinc selenide is evidently such an intermediate case. An example of case 1, in which the coated particles are uniformly large enough to yield an electron diffraction pattern from the coating only, is that of zinc dust pigment. Electron diffraction photograms of this pigment were reported in an earlier paper,[2] demonstrating that zinc dust pigment consists of metallic zinc particles coated with zinc oxide.

New Book

The Modern Theory of Solids

By Frederick Seitz. Pp. 698+xv, Figs. 306, 16×23½ cm. McGraw-Hill Book Company, Inc., New York, 1940. Price $7.00.

The new book by Seitz, containing nearly seven hundred pages, belongs to that category of publications which seem too long at the first glance and leave the reader with the wish that they were longer after he has read them carefully.

What do we know about the solid state of matter? The question seems simple enough but whoever has tried to find its answer in the ever growing flood of papers, theoretical and experimental, will realize the size of the task undertaken in this work. Only a competent specialist like Seitz could give a fairly complete answer to our question within the narrow space of a medium-sized volume.

While it is true that the complexity of the theory of solids has greatly increased with the enlargement of its scope, it is also true that quantum mechanics has furnished a key position by allowing a qualitative discussion of the electronic structure ultimately responsible for the various characteristics of crystals. The difference between insulators, semi-conductors, simple and transition metals has been clearly recognized and it is true in this sense that Chapter XIII, dealing with electronic structures, forms the central part of the theory.

As stated in its preface, the book is written for three different types of readers: the student, the practical experimentalist and metallurgist, and the theoretical physicist. The first type will mostly appreciate the easily intelligible text and many idealized graphs, which greatly help the understanding of the various complex aspects. The second type will find the book to contain a valuable compilation of the most characteristic facts, concerning the solid state, both in plotted curves and tables. For the third type, finally, the theoretical physicist, it will serve as a handbook in the sense that it contains a critical survey and reference to the most important papers written on the subject. It is this last type who will mostly regret that the phenomenon of supraconductivity, the last great puzzle of the theory of metals, has not found a more detailed discussion, both in the facts known about it and in the various attempts at explanation and their characteristic difficulties.

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