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ELECTRON DIFFRACTION INVESTIGATION
OF
PHOTOCONDUCTIVE CRYSTALLINE LEAD SULFIDE SURFACES

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ELECTRON DIFFRACTION INVESTIGATION

OF

PHOTOCONDUCTIVE CRYSTALLINE LEAD SULFIDE SURFACES

INTRODUCTION

The techniques of examining thin films of lead sulfide by electron diffraction and microscopy were described in the previous report¹. Particle size and orientation produced in the films condensed on glass at temperatures up to 350°C were also described, together with the results of an examination of certain chemically deposited films obtained from the Eastman Kodak Company. It was found that the particle size in films of 0.15-micron thickness could be controlled between 0.01 and 0.1 micron. It appeared from the observations of the more sensitive Eastman films that particle sizes of 0.1 micron or more are desirable for good photoconductive sensitivity in the oxidized films.

In the period from 5 March to 5 June 1953 covered by the present report, the introduction of preferred orientation, amounting to the formation of single crystals of lead sulfide over appreciable areas of the film, has been systematically investigated with the aid of substrates consisting of single crystals of sodium chloride. It is anticipated that films showing a predominance of a particular crystallographic plane in the surface may have a photoconductive sensitivity differing from that of the film of randomly oriented particles, and thereby provide data significant to the theoretical interpretation of the photoconductive effect.

The other line of investigation started in this period is the partial oxidation of the films, both on glass and on sodium chloride, by heating for various times in various pressures of dry air. The intent of this study is the chemical identification of the oxidized phases. The films on sodium chloride are susceptible to a more complete study than those on glass, since the former can be removed from their substrate fairly readily

and can be examined by transmitted electrons as well as by reflected electrons. This permits a comparison of the properties of the interior of the film with the surface properties. For example, the depth of penetration into the film of oxidized phases produced by particular oxidizing treatments should be determined in this way and correlated with the varying photoconductivity.

EXPERIMENTAL RESULTS

Lead Sulfide Films Condensed on Sodium Chloride Surfaces

The sodium chloride substrates were prepared by cleaving large single crystals on the cube faces, i.e., (100) planes. Natural crystals showed a marked tendency toward the occurrence of steps on the cleavage surfaces, and synthetic crystals obtained from the Harshaw Chemical Company were used mainly, because they often gave better cleavage planes. The large crystals were cleaved into blocks of about 3 x 10 x 25 mm.

One of the large faces on each block was smoothed by rubbing lightly on a cloth dampened with water, drying, and polishing on 4/0 emery paper. The polishing debris and some of the worked surface were removed by treatment in a fast stream of tap water for two or three seconds followed by drying in absolute alcohol and a stream of air. The block of NaCl was then mounted in the evaporator previously described, with the prepared face directed toward the source of PbS vapor.

Several of the prepared NaCl faces were examined by electron microscopy and diffraction. The micrograph of a surface replica in Fig. 1a shows occasional rectangular etch pits up to 0.2 micron in size on an otherwise extremely smooth and uniform surface. The diffraction patterns (Fig. 1b) show no misoriented material, and the occurrence of Kikuchi lines indicates the lack of serious strain in the surface layers.

Lead sulfide was evaporated onto the NaCl heated to a definite temperature by the same procedure as that used in condensing PbS films on glass. A reflection diffraction pattern was usually taken from the surface of the PbS film immediately on removal of the specimen from the evaporator. A collodion film was then formed on the surface and after drying was marked in two parts with a razor blade. The collodion and PbS were removed from the surface by dissolving the NaCl in water. One portion of the composite film was washed by floating on distilled water and then mounted on a wire-gauze specimen screen for examination by transmission in both the microscope and the diffraction unit. The patterns obtained in this way are due to the PbS and are unaffected by the collodion, whose electron scattering power is much less.

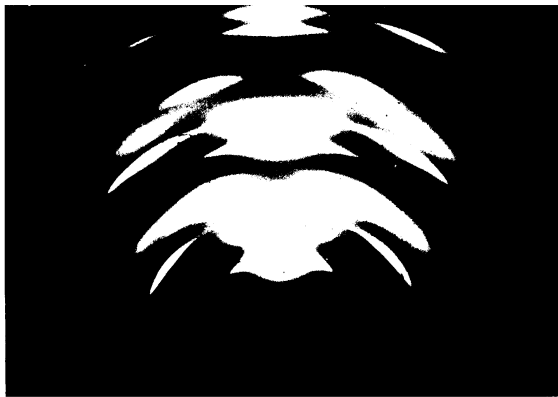


Fig. 1 Polished and Etched NaCl (100) Face
(Micrograph and Diffraction Pattern)

The other portion of the composite film was treated with nitric acid while floating on the NaCl solution to dissolve away the PbS. The remaining collodion film provides a replica of the original PbS surface; and after washing in distilled water the replica was mounted on a specimen screen, treated with a drop of the standard suspension of polystyrene latex, and shadow-cast with palladium in the usual preparation for electron microscopy.

The two portions of the film removed from the NaCl thus provide a replica of the PbS surface as well as a specimen of the PbS film for direct electron microscopy. Experiments on PbS films removed without the collodion support were not very useful, since the unsupported films were nearly always badly distorted and folded, if not destroyed by the necessary handling.

The structures of PbS films approximately 0.15 micron thick condensed on (100) faces of NaCl at 25 and 300°C are illustrated in Fig. 2. At 25°C the PbS is imperfectly oriented to the NaCl, as shown by reflection and transmission diffraction patterns (Figs. 2a and b). On increasing the substrate temperature the condensing PbS crystallizes more nearly with the orientation of the NaCl, until at 300°C the PbS film gives a pattern showing a single crystal with the (100) directions precisely oriented with those of the NaCl (Figs. 2c and d). The transmission pattern of Fig. 2d is particularly striking in showing no indication of more than one crystal of PbS over an area corresponding to the beam diameter of about 0.5 mm. The crystallographic cell size agrees to within less than 0.2 percent of the value 5.9233\AA , reported by Wyckoff². The cell sizes measured from



a. 25°C - Reflection



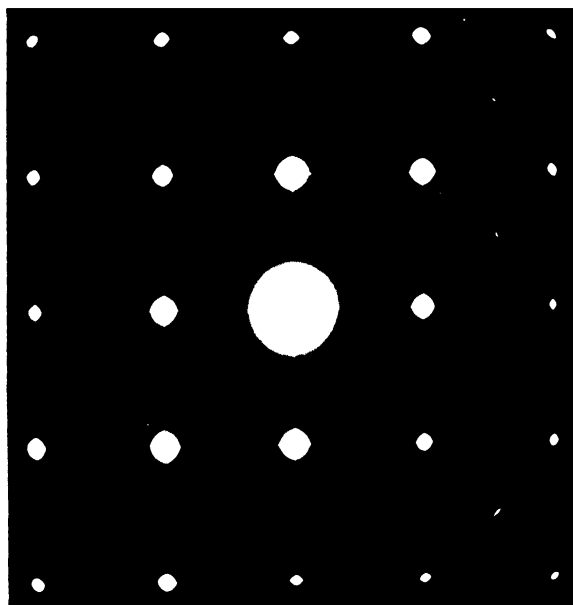
b. 25°C - Transmission



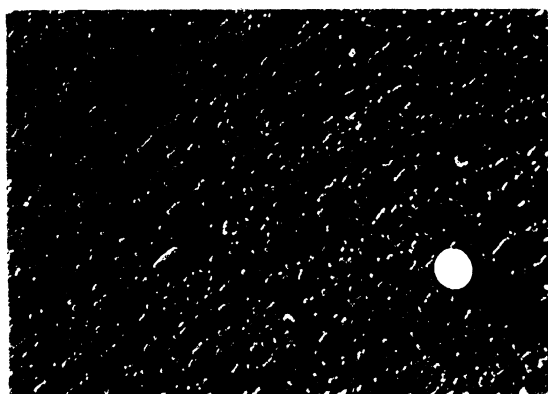
c. 300°C - Reflection along
(110) Direction

Fig. 2 PbS Films Condensed on NaCl at 25 and
300°C (Diffraction Patterns)

(continued on following page)



d. 300°C - Transmission



e. 300°C - Surface Replica
X20,000



f. 300°C Direct Micrograph
X16,000

Fig. 2 (continued). PbS Films Condensed on NaCl at
25 and 300°C (Micrographs and Diffraction Patterns)

reflection patterns vary as much as 3 percent because of the distortion of the pattern of diffracted electrons by stray charge accumulated on the non-conducting surface.

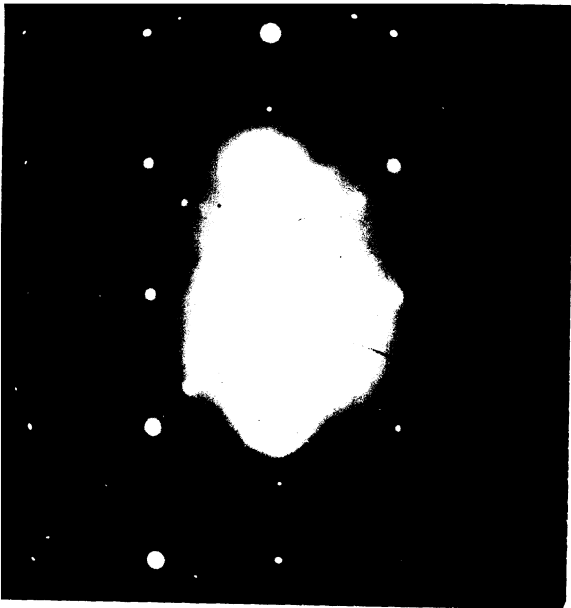
Micrographs of the 300°C film and its surface replica, Figs. 2e and f, show regions about 4 microns long. The principal feature of the replica is the surface cracks and indentations running mainly in two perpendicular directions with a very smooth surface in between. The indentations may be the result of re-evaporation of PbS or loss of sulfur before the film was cooled; their two directions mark the alignment of the cube edges of the PbS crystal. The appearance of the replica is in sharp contrast to those from films evaporated onto glass at the same temperature, which have separate crystallites about 0.1 micron in diameter. In the direct micrograph cracks appear with separations of about 1 micron. These separations may be entirely due to handling distortions, which are responsible for the multiple layers of PbS appearing in the denser corners of Fig. 2f. The diffraction pattern of Fig. 2d proves that regions as large as 500 microns in diameter can have the same crystal orientation even though cracks may appear in the film after mounting.

Not all areas of the mounted films show perfect single-crystal patterns; some of the more interesting variations are shown in Fig. 3. Two single-crystal patterns appear in Fig. 3a; both have (100) planes parallel to the substrate but one crystal is rotated about 45° from the other. In Fig. 3b one crystal is accompanied by a small amount of randomly oriented material. Figure 3c shows two crystals, one of which has the (111) plane parallel to the substrate while the other has the usual (100) orientation. The other patterns each show two crystals in films thick enough to give much double or secondary scattering. It is not certain whether any of the two crystal regions occur in the original film. It is noteworthy that all reflections can be accounted for by PbS crystals and that the complex appearance of the patterns is not due to the presence of any other phase or material.

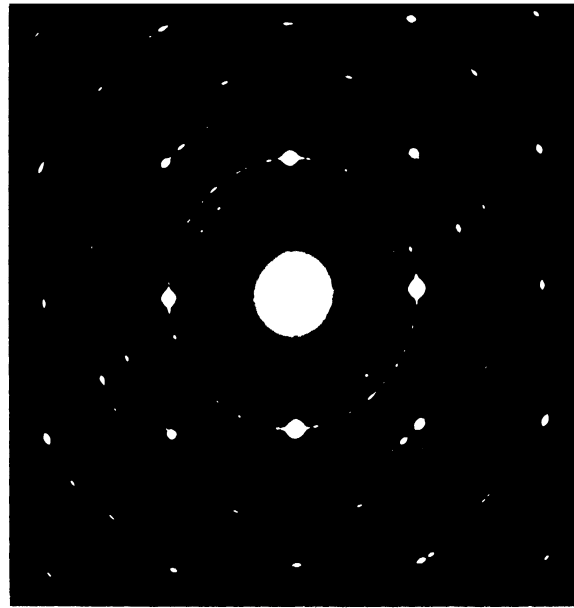
Oxidized PbS Films on Glass and Sodium Chloride

The experiments on oxidation during the present period consisted of admitting dry air at pressures varying from 0.1 mm to 1 atm for times ranging from 1 to 35 minutes into the evaporation chamber where the PbS film, previously condensed in a vacuum ($<10^{-4}$ mm) onto glass or NaCl, was maintained at 300°C. The effect on the film was examined by diffraction and micrography, but no tests for photoconductivity were made.

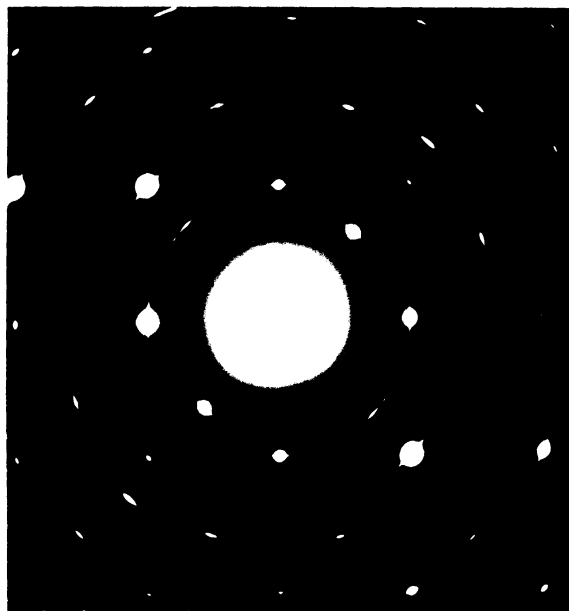
The films on glass previously described¹ show extensive attack in the micrograph (Fig. 4a) on treatment with air at 1 atm for 20 minutes, although much of the characteristic crystalline appearance is retained



a. Two Orientations



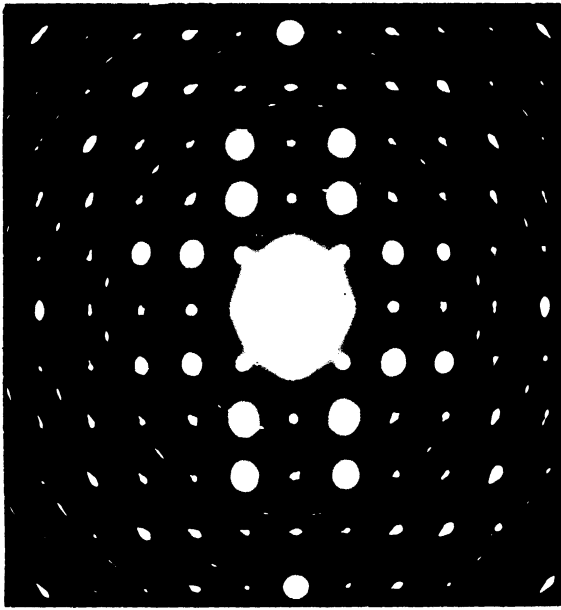
b. One Predominant Orientation
plus Some Random Arrangement



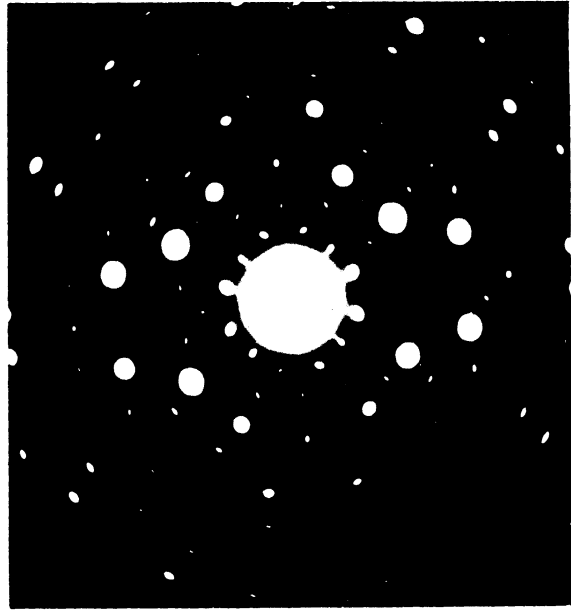
c. Two Predominant Orientations
plus Some Random Arrangement

Fig. 3 PbS Films Condensed on NaCl at 300°C
(Transmission Diffraction Patterns)

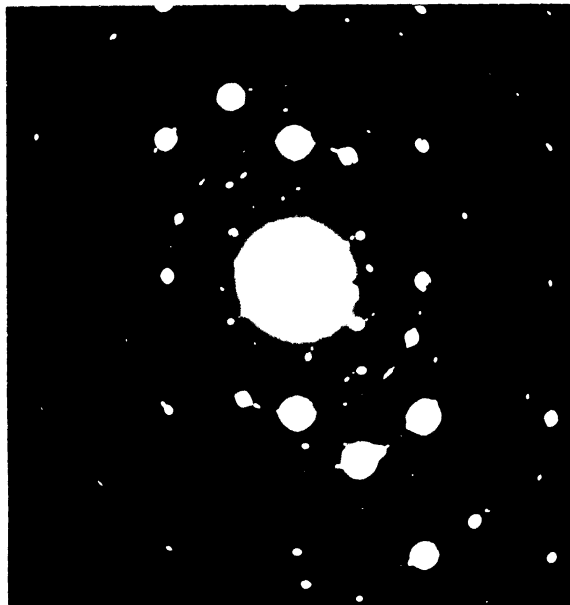
(continued on following page)



d. Two Orientations Giving Rise to Secondary Diffraction Spots

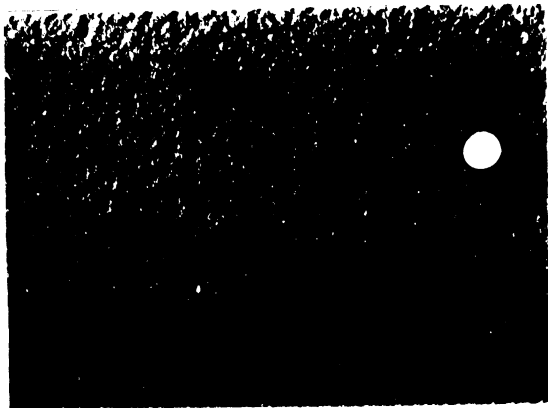


e. Two Orientations Giving Rise to Secondary Diffraction Spots



f. Two Predominant Orientations of Unequal Weight Giving Rise to Secondary Spots; Also Some Random Arrangement

Fig. 3 (continued). PbS Films Condensed on NaCl at 300°C (Transmission Diffraction Patterns)



a. X20,000



b.

Air - 1 atm, 20 minutes



c. Air - 0.2 mm, 10 minutes
X20,000

Fig. 4 PbS Films Oxidized on Glass at 300°C
(Micrographs and Diffraction Patterns)

under treatment at 0.2 mm for 10 minutes (Fig. 4c). The diffraction pattern (reflection only, since the film cannot be removed from the glass) is that of a new phase, but the distortion due to charging of the surface has so far prevented any reliable measurement of Bragg d values for comparison with known diffraction patterns. Most of the oxidation experiments were done on PbS on NaCl because of two advantages: (1) the monocrystalline character of the PbS and of the NaCl substrate often provide reflections by which the pattern can be standardized, and (2) the films separated from the substrate can be mounted for the transmission technique, which is not subject to serious charging effects.

All reflection diffraction patterns from specimens heated in air have strong features due to new phases, i.e., not NaCl or PbS. Several examples are given in Fig. 5. The spot patterns in Figs. 5a, c, d, f, and h represent one or more new phases with crystallites randomly oriented around a particular zone axis which usually is normal to the substrate. In Fig. 5b there are faint arcs due to a new phase superimposed on a spot pattern corresponding to the characteristic structure of PbS and NaCl, but with spacings intermediate between those for these two compounds. In this case the uncertain effect of specimen charging prevents a positive identification of the substrate pattern, although PbS seems most probable. The micrographs in Figs. 5e and g show how the surface has been disturbed by the oxidation in air in contrast to the unoxidized surface shown in Fig. 2e.

Transmission diffraction patterns were taken of a number of oxidized films after separation from the NaCl substrate in the manner described above. Two distinctions from the reflection patterns are expected: (1) the effect of specimen charging is negligible, and (2) the transmission pattern arises from the material in the body of the film and will show any differences in composition between the surface and the body of the film on comparison with reflection patterns. It is found that except in a few isolated areas all the oxidized specimens gave transmission patterns of only PbS. This means that the oxidation by air affects a surface layer much thinner than 0.15 micron, the average thickness of the PbS film.

The exceptional areas showing other patterns may be regions of the film which are thinner than the average, so that the oxidized layer represents an appreciable part of the total thickness. These exceptional transmission patterns showing diffraction features in addition to those of PbS are illustrated in Fig. 6; the largest number of new features is found in Fig. 6c. The Bragg d values, calculated with the aid of the PbS reflections as an internal standard, are listed in Table I together with d values reported by Wilman³ for PbS prepared on the surface of lead acetate solution and subsequently oxidized in air. Both of these sets agree reasonably well with the values calculated for lanarkite, $\text{PbO} \cdot \text{PbSO}_4$, a monoclinic crystal with $a = 13.73\text{\AA}$, $b = 5.68\text{\AA}$, $c = 7.07\text{\AA}$, and $\beta = 116^\circ 13'$. The data from the present experiments are somewhat incomplete because of the limited number



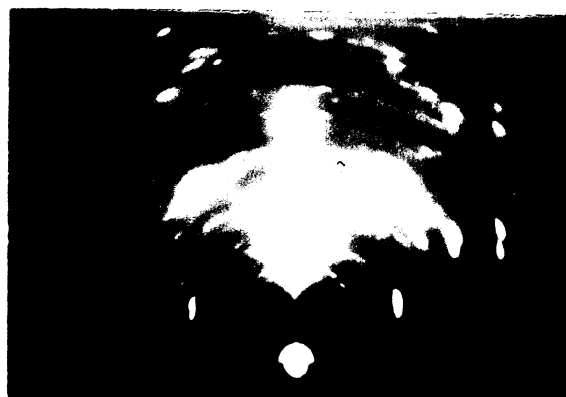
a. Air - 0.1 mm, 1 minute



b. Air - 0.1 mm, 10 minutes



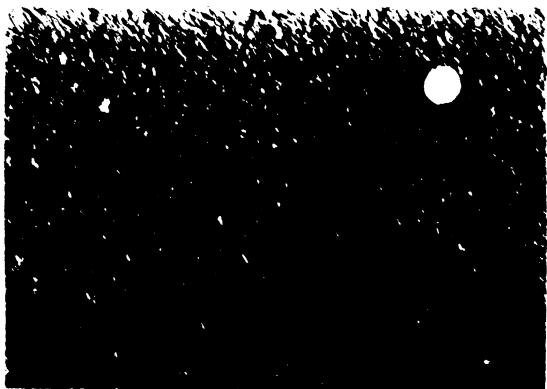
c. Air - 0.2 mm, 15 minutes



d. Air - 1 atm, 15 minutes

Fig. 5 PbS Films Oxidized on NaCl at 300°C
(Diffraction Patterns)

(continued on following page)

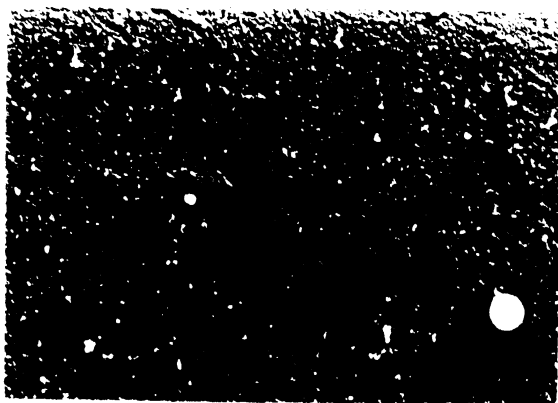


e. X20,000

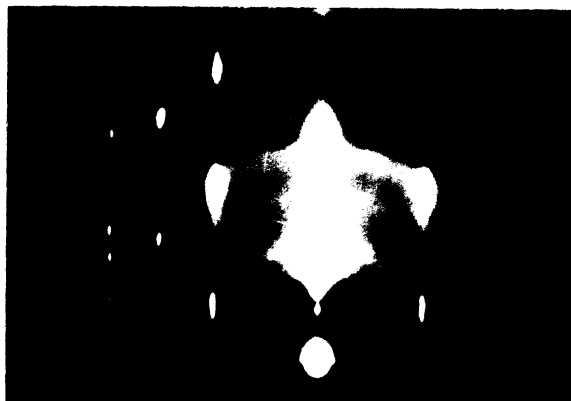


f.

Air - 1 atm, 20 minutes



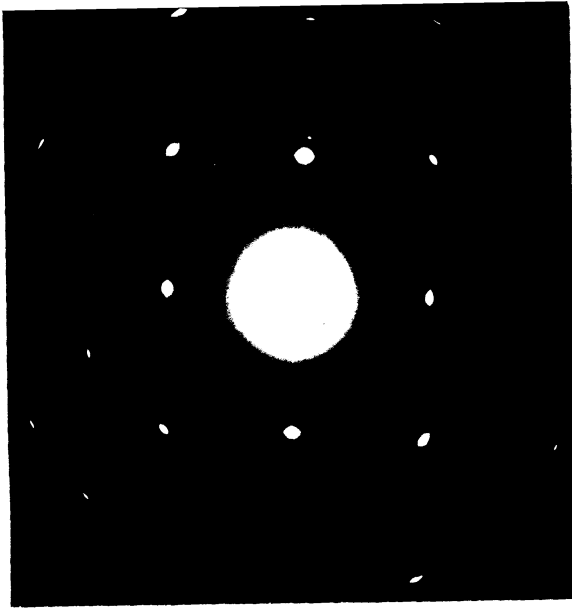
g. X20,000



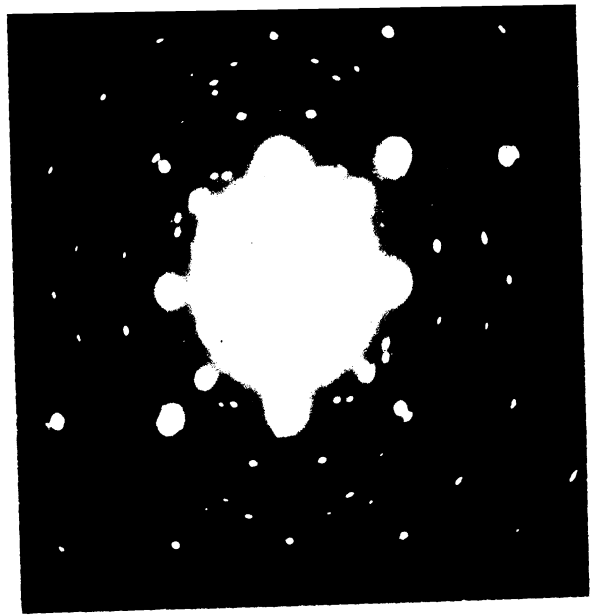
h.

Air - 1 atm, 25 minutes

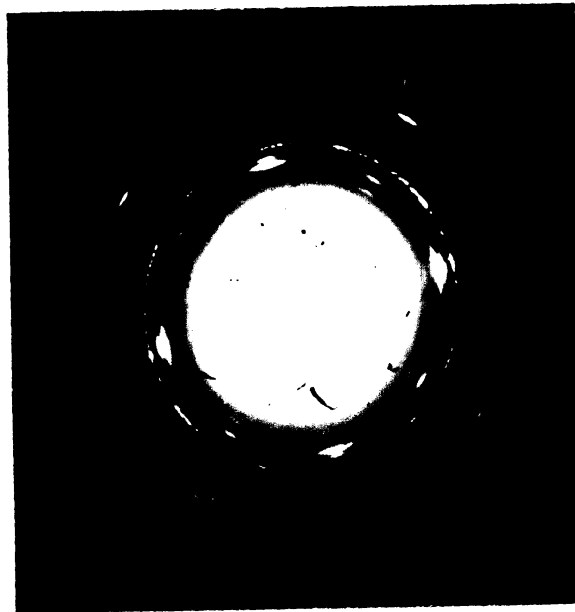
Fig. 5 (continued). PbS Films Oxidized
on NaCl at 300°C (Micrographs and
Diffraction Patterns)



a. Air - 0.1 mm, for
10 minutes



b. Air - 1 atm, for
20 minutes



c. Air - 1 atm, for
35 minutes

Fig. 6 PbS Films Oxidized on NaCl at 300°C
(Transmission Diffraction Patterns)

TABLE I

Diffraction Pattern (Transmission) of Oxidized PbS on NaCl
Compared with Wilman's Lanarkite Preparation

| Oxidized PbS | | Wilman's Preparation | | | |
|--------------|----------|----------------------|---------|---------|---------|
| d, Å | I(est.)* | d, Å | I(est.) | | |
| 9.93 | w | | | | |
| 6.54 | w | 6.41 | w | (1.83) | 1.83 s |
| 5.90 | w | 5.88 | w | 1.71 m | 1.69 m |
| | | 5.23 | w | 1.67 w | 1.67 w |
| 4.45 | | 4.45 | w | 1.63 w | 1.65 mw |
| 4.20 | | | | | |
| 3.85 | w | | | | 1.59 m |
| 3.76 | | 3.70 | mw | 1.56 m | 1.56 mw |
| | | 3.49 | w | 1.51 | 1.51 w |
| | | 3.33 | m | (1.49) | 1.48 w |
| 3.26 | s | 3.26 | s | 1.46 | 1.45 w |
| | | 3.08 | mw | 1.43 | 1.43 w |
| | | 2.95 | s | 1.39 | 1.39 w |
| 2.86 | s | 2.85 | s | | 1.36 w |
| 2.78 | | | | 1.34 m | 1.33 vw |
| 2.66 | s | 2.66 | m | (1.31) | 1.31 vw |
| 2.61 | s | 2.57 | m | 1.29 | 1.28 vw |
| (2.49) | | 2.46 | w | 1.27 | |
| | | 2.42 | w | 1.25 | 1.26 mw |
| | | 2.33 | w | 1.23 | 1.21 vw |
| 2.23 | m | 2.26 | m | | 1.19 w |
| 2.20 | | 2.21 | w | 1.16 | 1.17 vw |
| 2.15 | m | | | 1.13 | 1.13 w |
| 2.11 | | 2.12 | m | | 1.12 vw |
| 2.01 | s | 2.05 | ms | (1.09) | 1.10 vw |
| 1.96 | | 1.96 | s | (1.08) | |
| (1.92) | | | | 1.04 | |
| (1.86) | | 1.85 | w | 1.01 | |
| | | | | 0.983 | |
| | | | | 0.935 | |
| | | | | (0.924) | |
| | | | | (0.885) | |

* Intensities (estimated)

s - strong; ms - medium strong; m - medium; mw - medium weak; w - weak.

() - d values in parentheses indicate reflections occurring less frequently.

of lanarkite crystallites contributing to the patterns. For this reason three lanarkite reflections (3.33, 2.95, and 1.95Å) which should appear with strong or medium intensity are absent. It is also noted that another oxidized phase is indicated by the appearance of extra reflections, especially that at 9.93Å. There is a possibility that the oxidized phases in these patterns may have been affected by the contact with water during preparation of the transmission specimens.

SUMMARY AND FUTURE WORK

Current observations have been made on the effect of using NaCl single-crystal substrates for condensed PbS films and on the oxidation by air of PbS films on glass and on NaCl.

PbS films condensed on glass show randomly oriented crystals of from 0.01- to 0.1-micron diameters according to the conditions of the evaporation. PbS films condensed on NaCl at 300°C very often occur as single crystals with their (100) faces matching those of the substrate, and some of these PbS single crystals are larger than 500 microns in diameter.

Oxidation in air produces new phases, one of which has been identified as lanarkite, $\text{PbO}\cdot\text{PbSO}_4$, from transmission; but additional oxidized phases occur (especially in the reflection patterns) although they have not yet been identified. The oxidized layer is of the order of 0.01 micron or less in average thickness as indicated by the appearance of only oxidized phases in reflection patterns and of only PbS in most of the transmission patterns. The oxidized layer is much thinner than 0.15 micron, the average thickness of the PbS film.

The oxidized phases on the monocrystalline PbS films show particular orientations, which will later be specified after the identification of the phase compositions and after a study of the symmetry of their reflection diffraction patterns.

The foregoing results will be useful in correlating these properties with the observed variations in the photoconductive sensitivity of such films.

Work will continue on the identification of the oxidized phases, tests for photoconductivity of the oxidized films will be started, and some work on chemically prepared films will also be started.

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3. Wilman, H., Proc. Phys. Soc., 60, Part 2, 117 (1948).

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