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TECHNIQUES**BEST COPY AVAILABLE**

The following improvements in techniques have been developed during the month.

Auxiliary pinholes have been added to the collimating systems of the vacuum cameras which reduce to a minimum scattering from the pinholes. The regular system was intended for use with thick fiber samples which gave so much scattering themselves that special care with the pinholes was unwarranted.

A manometer for measuring pressure in the camera, vacuum valves and other associated equipment have been added to one vacuum camera so that it can now be kept filled with oxygen at any desired pressure below about twenty-five centimeters. In this way one can eliminate the scattering from the nitrogen component of the atmosphere when photographing oxygenated samples. Moreover, suitable pressures for partially oxygenated samples can be maintained. These steps are necessary because the samples are not confined in tubes. Tubes and other confining or supporting devices contribute to the general background of scattered rays.

Up until recently this last ideal had not been attained. Samples were supported upon thin glass fibers about .03 mm. in diameter. These were coated with vaseline and dipped in the sample. The glass and vaseline no doubt gave a weak diffuse pattern. Various methods for preparing self-supporting samples which have been described in the literature have proved unsatisfactory. They frequently require admixture of a binder. At present we appear to be having success with samples extruded from fine stainless steel tubes of the kind used in making hypodermic needles. The tube is filled with powder by

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jabbing it repeatedly into a thin layer of sample on a glass plate, forcing the tube squarely against the glass each time. The sample is then forced out with a steel or chromel wire which closely fits the bore of the tube and which has been ground flat on the end with fine abrasive. The tubes and wires are about one centimeter long and are permanently attached to a regular sample holder by which they are handled. The sample is extruded just out of the end of the tube and sticks to the end of the wire. The whole arrangement then fits into the camera. Tubes from a number twenty-three needle make samples .35 mm. in diameter. This is a bit large for our smallest camera and we are ordering smaller sizes for trial. There are some difficulties. If the sample is packed too tightly the tube becomes jammed and must be cleaned out with a fine wire. If not packed tightly enough the sample may disintegrate when the camera is evacuated. Each sample must be tested before putting film in the camera and making the exposure.

The shop will soon have made shields for the oscillation cameras which will permit maintaining in the cameras pure atmospheres of oxygen or nitrogen at atmospheric pressure. Vacuum or reduced pressure is not required as air scattering is not important for single crystal pictures if the samples are of reasonable size.

#### POWDER PHOTOGRAPHS

In the report for June it was stated that the Rumford oxygenated sample supplied us probably contained a few percent of impurity which showed in the powder picture as two lines not showing on a picture of the corresponding U. of C. sample. These lines were said to correspond to graphite lines.

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Unfortunately there was an error in the spacing calculation for these two pictures due to use of an improper constant factor. When correctly calculated it appears the impurity cannot be graphite or any other substance listed in the Hanawalt Tables. In a letter Dr. Calvin has stated that the Rumford sample contains about two percent of talc. But the lines observed do not correspond to any lines of the talc pattern which has been described in the literature. In fact it is unlikely that two percent of either talc or graphite would show in a picture of a cobalt compound. The source of these lines seems now to be some new substance which forms when the salcomine is cycled. Quite incidentally one sample of the U. of C. active compound, which originally showed no trace of these two lines, was cycled twice in the camera by alternately standing a day or two in air and a day or two in vacuum. Pictures were made at various times. After one cycle the lines appeared very faintly and after two cycles they could easily be seen. Figure 1 attached is a print of this picture and the two lines in question are indicated. It is now proposed to cycle a larger sample a number of times and to take x-ray samples occasionally at oxygen-free stages of the process and make vacuum pictures.

In the above series of photographs the samples contained varying unknown quantities of oxygen. Yet the intense line which has  $d = 7.42\text{\AA}$  for the oxygenated samples and  $d = 7.68\text{\AA}$  for the oxygen-free samples was not blurred but was doubled, the intensities of the two components (which were of the spacings given) depending upon the amount of oxygen present. At small spacings lines due to both compounds appeared side by side unblurred. Although

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in these experiments conditions were such as to preclude the possibility of equilibrium the results indicate strongly that there is no gradual shifting from one structure to another on adding oxygen, but that there are two definite structures (which may be very similar) and that considerable volumes of crystal have one structure or the other with fairly sharp boundaries between volumes. Oxygen is added or lost at the boundaries and the oxygen-free volumes decrease or increase. If there was a gradual change of lattice parameters through intermediate values the lines would be blurred. This must be repeated under equilibrium conditions with the pressure controlled camera.

SINGLE CRYSTALS FROM BENZENE

Much of the month was spent investigating these crystals grown at Berkeley. It was stated by Dr. Wilmarth that on the basis of powder pictures and oxidation studies these crystals seem to be identical with salcomine. Powder pictures made here seemed to confirm these conclusions and the examination was started with considerable interest.

Under the microscope the needles appear dichroic. With the electric vector perpendicular to the needle axis they are red and with the vector parallel to the axis they are black for thick specimens and a very dark shade of some color for thinner ones. It is difficult to say if they are brown or violet. Extinction is very close to parallel but seems to be slightly off. But this is difficult to be sure about because of the strong absorption.

Specimens ranging from .03 mm. to .20 mm. in thickness were easily mounted on goniometer pins. On the optical goniometer signals were very poor, partly because of the poor resolving power of the very narrow faces in one

direction, but partly at least because of imperfect crystallization. Signals on opposite sides which should be  $180^\circ$  apart sometimes missed this by as much as  $4^\circ$ . Some individuals show as many as eight faces.

A set of  $24^\circ$  oscillation pictures was made about the needle axis. Figure 2 is a print of one of these. The needle axis repeat distance is about  $6.6 \text{ \AA}$ . It should be noticed that some of the spots are sharp, as expected from fine needles, but that others are quite diffuse.

A second needle was used in preparing a zero layer Weissenberg picture. A print is shown in Figure 3. Unfiltered Cu rays only were available for this camera but since only a narrow band of fluorescent Co radiation falling along the equator is spread out over the whole picture it is not excessive. This picture is not very good as such pictures usually run. But repetitions with various other needles including a very fine one are similar or worse and indicate the trouble is inherent to the crystal. The spots are drawn out in the direction of the motion of the film over a range up to  $3^\circ$ . This indicates the crystal consists of crystallites with their needle axes all parallel but their side axes only approximately so. Since there are very intense spots in each reflection most of the crystal is well lined up. By using these intense points it was easy to index the photograph. Since the oscillation pictures show no plane of symmetry at the equator and the zero layer Weissenberg shows no symmetry, the crystal is triclinic. As there are no end faces on the crystal the cell angles must be determined somewhat laboriously from x-ray measurements. This has not yet been done for reasons brought out below. However, calling the needle axis  $c_0$  we have  $d_{100} = 12.6 \text{ \AA}$ ,  $d_{010} = 11.9 \text{ \AA}$ ,  $c_0 = 6.6 \text{ \AA}$ .  $\gamma^*$ , the reciprocal lattice angle, is about  $68^\circ$ . From preliminary pictures about other axes it appears that  $\alpha$  and  $\beta$  will

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differ from  $90^\circ$  by only a few degrees so that  $\psi$  will not be far from  $112^\circ$ .

Further inspection shows that the spots are also drawn out along lines of constant  $h$  and varying  $k$ . Some strong neighboring spots are thus seen to be connected by curved lines. The  $Ok0$  spots are fuzzy as are many others. This probably indicates some imperfection of crystallization in the direction chosen as  $b_0$ . These pictures were made in air and the crystals were probably picking up oxygen. If it added on in an irregular way in the  $b_0$  direction it might account for the effect. There is one other fairly continuous line of varying intensity such as would be produced on a Weissenberg by a partially oriented powder. It runs parallel to the direction of film motion at spacing  $d = 3.78 \text{ \AA}$ . The most likely source of this was revealed upon making a few oscillation pictures of this crystal.

One of these is shown in Figure 4. Here it is noticed at once that there are spots falling between the regular layer lines as found on Fig. 2. These faint extra layer lines are incommensurate with the main system and indicate an entirely different crystal grown in perfect alignment with the principle one. The second and fourth layer lines of the new crystal are almost superimposed on the first and second of the main crystal. The new needle axis repeat is  $14.4 \text{ \AA}$ , a little more than double the other value of  $6.6 \text{ \AA}$ . The new spots are the same size and shape as the others. They seem to be due to crystallites aligned perfectly so far as the needle axis is concerned but very poorly in other directions. They thus give oriented powder lines on the Weissenberg which can be seen only for the most intense example. Exceedingly faint spots of the new system can be found on Fig. 2, which is from the first crystal.

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A rotation photograph was made of a third needle using slits instead of a pinhole system in order to improve the intensity. This is Figure 5. The intermediate layer lines are comparable in intensity with those from what was originally considered the single crystal. The second strongest spot on the zero layer is due to the new pattern. Finally a picture was made of this crystal with the rotation motor turned off. With a normal crystal and absolutely monochromatic radiation no diffraction pattern would result except possibly for a few spots if the crystal has accidentally been set properly for a few families of planes to reflect. With ordinary filtered rays there would also be a weak Laue pattern coming from the weak "white" radiation passed by the filter. In Figure 6 we see the result of this experiment. There are literally hundreds of spots visible on the negative but unlike Laue spots all fall on layer lines. This substantiates the view that a crystal needle consists of many small crystallites all accurately aligned with respect to one crystal axis but rather poorly aligned with respect to the other two axes. These remarks apply to both kinds of crystallites although the Weissenberg results indicate better orientation for the "original" crystallites of axial repeat  $6.6\text{\AA}$ .

It so happens that the intensities of the second pattern from different crystals increase in order of the age of the crystal at time of photographing. Since all were first exposed to air at approximately the same time one might like to think that the second set of crystallites has been growing from the old one, either spontaneously or as a result of the addition of oxygen. Three examples are not enough to establish the truth of such a guess. Two of these crystals have been saved and will be examined soon again to see if the relative intensity of the two patterns is changing.

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The information obtained above should be sufficient to permit partial indexing of the powder photographs. Upon attempting this it became obvious that the original pattern does not correspond to the powder photograph. There are several strong reflections of approximately but not really the same spacing as the intense  $13.08\text{\AA}$  line of the powder photograph. There is no strong spot or combination of spots to explain either the intense  $7.68\text{\AA}$  line of the oxygen-free powder or the intense  $7.42\text{\AA}$  line of the oxygenated powder. Information about the second pattern is meager because of its reduced intensity on most pictures. It appears improbable however that it can account for these lines. At present it seems that neither pattern corresponds to salcomine and that the crystals revert to salcomine during powdering. This rather surprising conclusion will be checked further as more pictures are obtained. The question arises however as to whether much more effort should be expended upon these crystals from benzene if they are not salcomine itself.

PICTURES BY DR. I. FANKUCHEN

In a recent letter Dr. Stevenson has transmitted x-ray diffraction pictures of salcomine and of single crystals sublimed from salcomine made by Dr. I. Fankuchen of the Anderson Institute for Biological Research at Red Wing, Minnesota, along with a brief report by Dr. Fankuchen.

These pictures have not been very carefully handled and their usefulness is somewhat impaired by dirt and scratching. The single crystal pictures are somewhat weakly exposed because of difficulty with the x-ray transformer. They have been made with Cu rays which produce bad general fog from fluorescent Co radiation. In general one can measure about twice as many rings on our pictures made with Co radiation. However, they are a valuable contribution.

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Dr. Fankuchen's cameras, designed for protein work, go to much larger spacings than those regularly used here. His salcomine pictures show large spacing rings, one of  $d = 45.0\text{\AA}$ . We have such a camera but had not yet thought of using it on salcomine. His salcomine sample is oxygenated and shows the impurity lines described above. It seems not unlikely that these large spacings are part of the impurity pattern since they and the known impurity lines are absent from his pictures of the powdered sublimed material. If this proves to be the case this large spacing may indicate some polymerization during cycling.

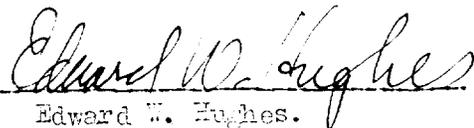
In his letter Mr. Stevenson expresses some doubt as to whether the sublimed single crystals are salcomine. Comparison of the powder picture with our pictures indicate quite clearly that the powdered sublimed material is, as one would expect, the oxygen-free salcomine. It is possible that the difference between the oxygenated and the oxygen-free patterns plus the difference caused by the absence of impurity in the sublimed material may have caused doubt as to the identity of the samples.

In view of the experience recorded above with the single crystals from benzene we may wonder if the sublimed single crystals are also salcomine. From the cell constants given by Dr. Fankuchen they apparently are different from the crystals from benzene. If he is right when he says that the powder picture can be indexed from the cell constants then the crystals must be salcomine. We have been planning to try sublimation since discovering how bad the crystals from benzene are and Dr. Fankuchen's results are very encouraging.

Pasadena, California  
August 8, 1942

cc: 2 to Calvin  
1 to Pauling  
1 to Hughes

Signed



Edward W. Hughes.

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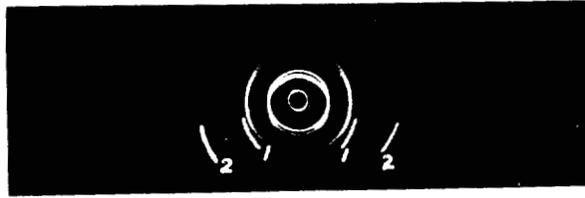


Figure 1.

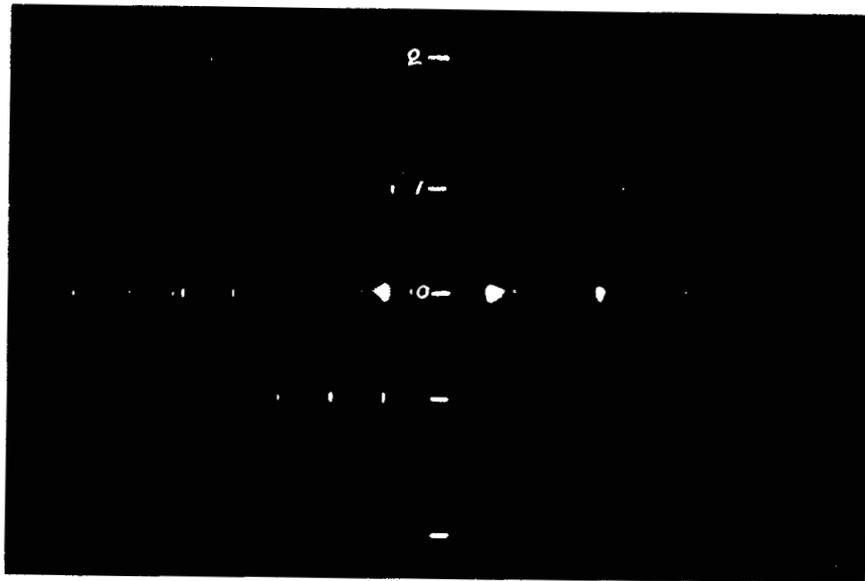


Figure 2.

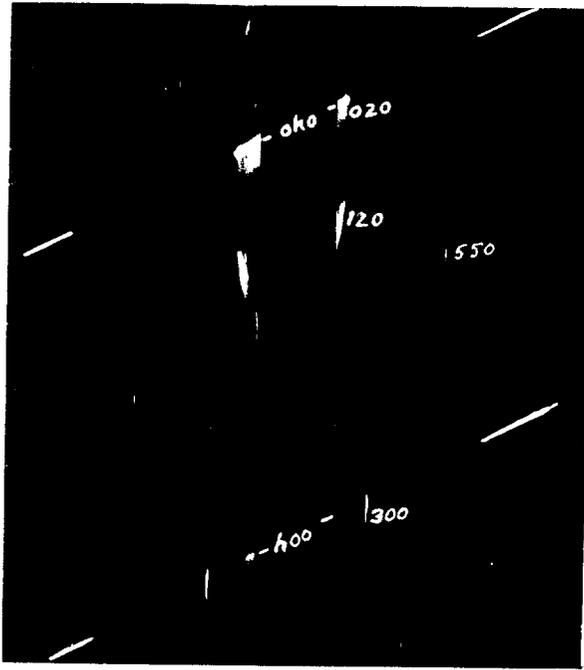


Figure 5.

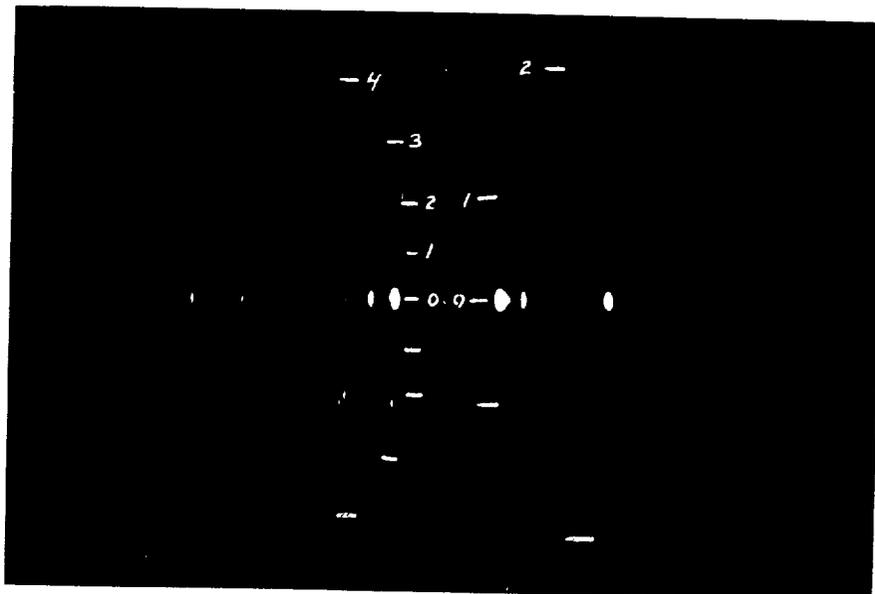


Figure 6.

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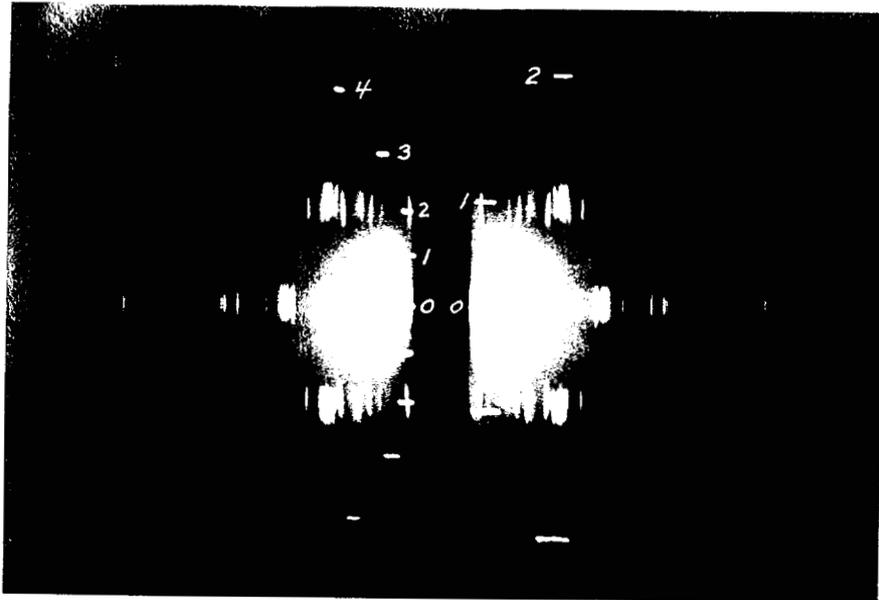


Figure 3.

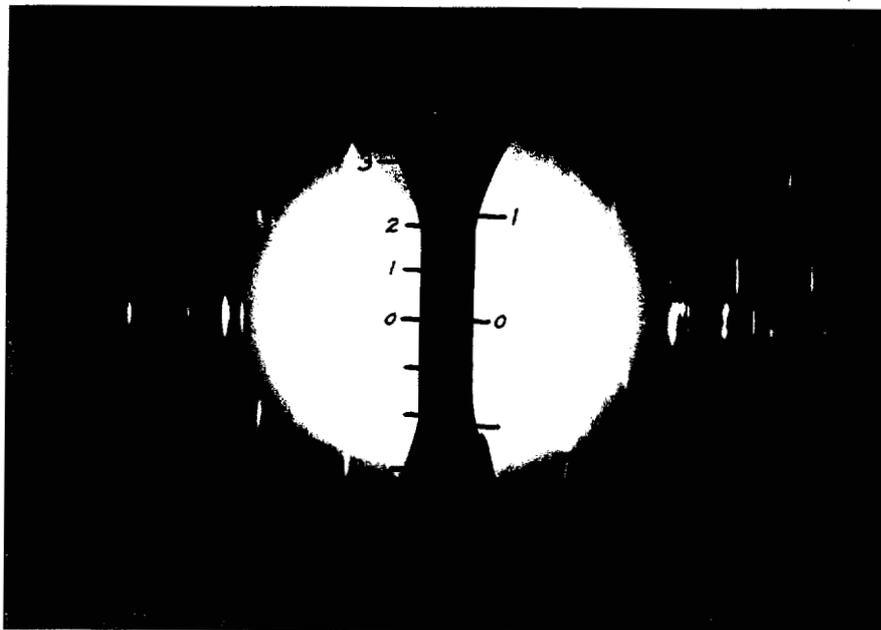


Figure 4.

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