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A Comparison of X-ray Diffraction Methods in the Study of Imperfections

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Two groups of X-ray diffraction methods are used to study the imperfections present in the small silver halide crystals of photographic emulsions. One group reveals the possible existence of sub-units within the crystals. There is an unexplained discrepancy between the results for the (200) and (220) planes. A new experimental and theoretical approach has made possible the separate evaluation of misalignment and distortion within the grains. The method is a useful extension of existing techniques, and yields values which are also in agreement with results from other methods. These and the previous observations indicate the existence of substructures within the grains.

Introduction

The purpose of this paper is to give an account of the application of several different X-ray diffraction methods to the study of structural imperfections in the crystals of silver halide, with linear dimensions of the order of one micron, which are dispersed in gelatin in ordinary photographic 'emulsions'. For the investigation of internal imperfections X-ray diffraction methods have, of course, been used for many years. The investigations reported here differ from the customary crystallographic studies in that the specimen is composed of separated individual crystals (grains) which can be counted and regarded as the units under examination. This is an advantage in the study and evaluation of the diffraction patterns.

Some of the methods are here described for the first time, while others which are well known have not previously been applied to such specimens. From the results of the different methods there emerges a consistent account of the structure of the crystals, which has led to a clearer visualization of their imperfections. In addition, there is presented a quantitative comparison of the results obtained by using different diffraction methods in the examination of the same specimen. As such a comparative approach does not seem to have been presented in the literature, the results may be of interest to crystallographers. In view of the experimental difficulties, the agreement found between the different approaches is very satisfactory. It is also established that individual regions within the same grain can give rise to separate reflexions, although there is a discrepancy in the estimate of the number of these regions, depending on the crystal plane examined.

As already mentioned these investigations were carried out on the silver-halide grains present in a variety of commercial photographic emulsions. Theoretical and experimental considerations have shown that certain types of structural imperfection in silver-halide grains can act as electron traps, and it is therefore believed that structural disorder in the crystal lattice may be of importance in the mechanism of photographic latent-image formation. No direct evidence on internal imperfections in silver halide grains from investigations in which an electron microscope has been used has yet been reported in the literature, although some indication of surface imperfections has been given by examinations by combined carbon replica and gold shadowing techniques.

We shall now consider in turn the various methods used in the examination of the specimens. These usually consist of a diluted dispersion of grains in gelatin.

Laue photographs

In many ways the simplest method of obtaining information about structural disorder would appear to be a Laue diffraction photograph of a single grain. This approach is, however, almost impracticable because of the small dimensions of the grains, necessitating very long exposures. For example, only a few diffraction spots were obtained, in spite of 100 hr exposure in a Hilger Microfocus X-ray unit (focal spot 100×140 μ) with a lead-glass capillary of 3 μ diameter. (The specimen was centred with a microscope.) The spots obtained were too few to allow indexing by stereographic methods. However, some of the Laue spots showed elongation into asterism streaks. This is a clear indication of either bending of the crystals or mosaic formation.

Laue photographs of larger single crystals of tabular form with diameters in the range 20–30 μ were successfully obtained and showed clear evidence of the formation of twinned crystals (Berriman & Herz, 1957). This does not, however, prove that such twinning occurs in the smaller non-tabular grains of commercial photographic emulsions.

Microbeam techniques

Since the Laue method appeared to be impracticable the less direct microbeam technique (Hirsch & Kellar,

1950) was adopted, in order to ascertain whether the grains were perhaps subdivided into a number of blocks, each acting as a unit.

In our experiments a known small number of grains (about 150) was exposed in a transmission camera using a Hilger Microfocus unit, with a lead-glass capillary of 90 μ diameter. Spotty Debye–Scherrer rings were produced. The mean number of spots expected is N_e, given by

$$N_e = \tfrac{1}{2}pN \cos\theta(d\theta + \Delta) \qquad (1)$$

where p is the multiplicity factor and θ the Bragg angle of the plane considered, $d\theta$ is the angular divergence of the incident X-ray beam, and Δ is a range of angles over which reflexion is possible owing to departure from exact monochromatism, variations in lattice spacing (distortion) and lack of angular resolution if the crystals are very small. N is the number of grains irradiated. If the observed number of spots exceeds N_e significantly, then this can be interpreted as evidence in favour of subdivision of the grains. In carrying out these experiments it was important to ascertain whether structural changes occurring during the unavoidable exposure to X-rays could influence the results. Accordingly patterns were made with the specimen at liquid-nitrogen temperature, at which the mobility of silver ions in the lattice is very greatly reduced. These results were identical with those carried out at room temperature. It was also important to avoid wide fluctuations in relative humidity, since this causes a change in the swelling of the gelatin, which in turn changes the lattice spacing in the crystals (Berry, van Horn & Griffith, 1954; Herz, 1960). A relative humidity of 50% was chosen, and exposures were made with the specimens close to room temperature.

To use equation (1) the values of $d\theta$ and Δ in particular must be known. The determination of $d\theta$ is difficult, mainly because of the internal reflexions occurring within the lead glass capillary. Its value was found to be $1{\cdot}3 \times 10^{-3}$ radian. From the experiments no direct assessment of Δ is possible, and it was assumed to be small compared with $d\theta$. This assumption led to a mean number of 12 substructures per grain for the (200) planes in high speed X-ray emulsion grains (Herz & Grounsell, 1958). The same procedure applied to the 220 ring gave 7 substructures per grain. This is a surprising result, for although the assumption that Δ is small may be wrong, it is easy to see from equation (1) that provided Δ is the same for both sets of planes, the same number of substructures per grain should be derived if we accept the validity of the model, *i.e.* that each grain consists of an aggregate of independent units.

So far our considerations have been based on a model in which a grain consists of a number of sub-units misaligned with respect to each other. There is, however, an alternative model for which the same experimental results would be expected. Suppose the grains are single crystals whose lattice planes show appreciable bending which may result in the formation of mosaics of very small dimensions and relative misalignment. It is now no longer true that the normals associated with each lattice plane in the crystal lie within an extremely small solid angle. Equation (1) is derived by calculating the expected number of normals occurring within the solid angle for which reflexion is possible. Since there is now a wide range of normal directions for each bent plane the number of normals in the solid angle for reflexion is increased, and this will also lead to a greater number of spots in the ring. It is important to point out here that if bending occurs over an angular range which is appreciable compared with that of the divergence of the beam it is possible for the application of equation (1) of the still microbeam method to lead to numerical results which are in error even though the value of Δ may be accurately known.

In order to obtain further information, another approach was made, by a method described by Andrews & Johnson (1959). In this the term $(\Delta + d\theta)$ is eliminated by the use of two photographs in which the specimen is oscillated through two different angles. These were 2·5° and 5° and the corresponding exposure times for each pattern were 5 and 10 hr respectively. Apart from the multiplicity factor, Bragg angle and oscillation angles, the only other information necessary is the number of grains irradiated. Although it is fairly easy to count the number of grains within the geometrical area of the capillary on a diluted single-grain layer of emulsion, experience has shown that this is not in fact the whole area illuminated. To avoid uncertainty a platinum pinhole smaller in diameter than the lead-glass capillary was placed in contact with the emulsion, which limited the irradiated area to a known value. Consistent results were obtained in this way and the mean number of sub-structures per grain for the (200) plane of the same type of X-ray emulsion grain was found to be 3.

It may be argued that again the presence of bending may give rise to error in the Andrews & Johnson method. However, experiments described in the next section show that in this specimen (L of Table 1) angular bending of the lattice planes amounts to

Table 1. *Results of oscillation experiments*

Specimen	Position I	Position II	Position III	Misalignment χ_T	Distortion $100(\delta_1+\delta_2)/d$
A	0·30	0·21	0·18	12·0′	0·04
B	0·29	0·20	0·19	11·7	0·02
C	0·77	0·29	0·28	33·7	0·26
D	0·83	0·34	0·31	35·4	0·40
E	0·20	0·20	0·18	7·2	0·02
F	0·49	0·29	0·24	19·6	0·26
G	0·37	0·26	0·21	14·5	0·18
H	0·76	0·23	0·23	34·7	0·10
J	0·80	0·23	0·21	36·8	0·10
K	0·35	0·24	0·19	30·7	0·12
L	0·26	0·21	0·20	10·1	0·04

only 10′, which is very small compared with the angles of oscillation in the Andrews & Johnson method. Therefore, the number of extra reflexions caused by the presence of bending is only a very small fraction of those due to the oscillation and moreover, since the difference of the results of two oscillations is taken, the extra reflexions will be subtracted out. We therefore believe that the experimental results are to be attributed to the presence of substructures.

From the paired measurements it is of course also possible to evaluate $(\Delta+d\theta)$. By subtracting the result for $2\frac{1}{2}°$ oscillation from that for 5° oscillation we find the number of spots for exactly $2\frac{1}{2}°$ oscillation. This may then be subtracted from the result for the nominal $2\frac{1}{2}°$ oscillation, which in fact includes the additional contribution from $(\Delta+d\theta)$. It will be obvious that the effect of statistical fluctuations will be greatly enhanced as a result of the two subtractions. For this reason the calculation can only give the order of magnitude of $(\Delta+d\theta)$. In the next section a more accurate method of finding this value is given.

It was expected that the number of substructures per grain would be the same, irrespective of the plane index or ring chosen for examination. Our previous results indicated that this might not be so and it was decided to check the number of substructures per grain by means of the 220 ring. The Andrews & Johnson technique showed again different numbers of substructures per grain for 200 and 220 rings, namely 3 and 1·6 respectively. In view of the importance of this discrepancy a fuller investigation was carried out and further experimental evidence and discussion will be found below (p. 270).

Combination of oscillation methods

By an investigation of the diffraction spots we may obtain further information about misalignment (or bending) and distortion within the regions of the grains giving rise to reflexion.

In these experiments the specimen received radiation collimated by a capillary of 120 μ diameter from a focal spot of dimension $100\times140\,\mu$. The specimen oscillates as in Barrett's (1937) method over a total angle of 2·5°, which therefore is also the range of angles over which radiation strikes the specimen. Two alternatives may now be adopted. The film is either fixed or oscillates with the specimen, thus keeping their relative positions fixed. The latter is called position I; the former position II. Results from these paired experiments supplement each other and allow the effects of distortion of lattice spacing and misalignment of crystal planes to be separated. This approach does not seem to have been adopted before. It has been applied in this paper to experiments on various types of commercial emulsions.

Since the angular size of a spot in the radial direction can readily be obtained from the patterns, it will be convenient to deduce approximate theoretical values

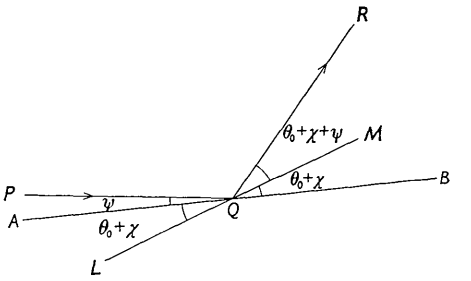

Fig. 1. The geometry of the microbeam exposure.

for this quantity from reasonable simplifying assumptions. The crystal (Fig. 1) is supposed to be situated at Q and the beam is incident along AB. Consider a particular reflexion, most of the planes of which are assumed to have a Bragg angle of θ_0. LM represents a set of planes at an angle $(\theta_0+\chi)$ to AB, the angle χ representing a small misalignment. PQ is an incident ray making a small angle ψ with the axis of collimation, and is reflected by the planes LM along QR. If the wavelength of the incident beam were exactly λ and the lattice spacing exactly d, the Bragg condition would be

$$\lambda/d=2\sin\theta_0\,. \tag{2}$$

However, if the incident radiation covers a range of wavelengths $(\lambda-\beta_1)$ to $(\lambda+\beta_2)$ and the lattice spacings vary between $(d-\delta_1)$ and $(d+\delta_2)$, reflexion will in general be possible only between the limits specified by the inequality

$$\left(\frac{\lambda+\beta_2}{d-\delta_1}\right)\geq 2\sin(\theta_0+\chi+\psi)\geq\left(\frac{\lambda-\beta_1}{d+\delta_2}\right). \tag{3}$$

Since χ and ψ are small compared with θ_0, and β_1, β_2 and δ_1, δ_2 are all small compared with λ and d respectively, the inequality (3) may be written, to a good approximation,

$$\Delta_1\geq(\chi+\psi)\geq-\Delta_2 \tag{4}$$

where

$$\begin{aligned}\Delta_1&=\left(\frac{\beta_2}{\lambda}+\frac{\delta_1}{d}\right)\tan\theta_0\\ \Delta_2&=\left(\frac{\beta_1}{\lambda}+\frac{\delta_2}{d}\right)\tan\theta_0\,.\end{aligned} \tag{5}$$

The reflected ray QR makes an angle $(2\theta_0+2\chi+\psi)$ with AB. Suppose χ_M and χ_m are maximum and minimum values of χ, and ψ_M and ψ_m those of ψ. The problem of determining the angular size φ of a spot in the radial direction is therefore to find the range of values of $(2\chi+\psi)$ subject to the condition (4) and the conditions

$$\begin{aligned}\chi_M\geq\chi\geq\chi_m\,,\\ \psi_M\geq\psi\geq\psi_m\,.\end{aligned} \tag{6}$$

If the specimen and recording film oscillate together (position I, Fig. 2) in effect the specimen is irradiated

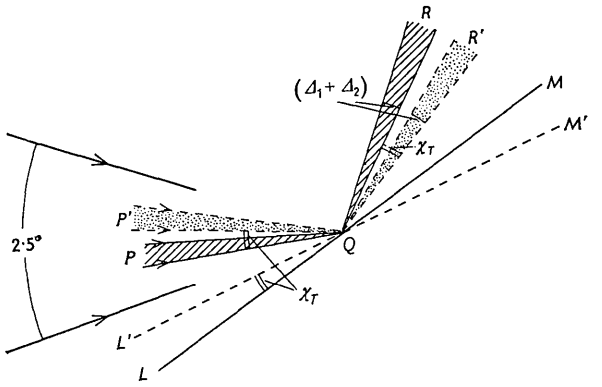

Fig. 2. Position I. Specimen and film oscillate together. The incident beam has an effective divergence of 2·5°. LM and $L'M'$ represent extreme positions of the misaligned planes in a grain with total angular separation χ_T. Reflexion by plane LM occurs within an angular range $(\Delta_1+\Delta_2)$ about QR, and similarly $L'M'$ reflects about QR' which is at an angle χ_T to QR. The total angular range for reflexion is $(\Delta_1+\Delta_2+\chi_T)$.

from a wide range of angles so that the limits on ψ are wide. Thus the quantity $(\chi+\psi)$ can attain the extremes given by the inequality (4) even though χ itself may have only a small range. Considering the variable part of the angle of reflexion, which we may write $\chi+(\chi+\psi)$ it will be seen that its maximum and minimum values are therefore $\chi_M+\Delta_1$ and $\chi_m-\Delta_2$ respectively. Writing χ_T for the range $\chi_M-\chi_m$ it follows that in these circumstances the range of φ is given by

$$\varphi_1=\Delta_1+\Delta_2+\chi_T\,. \tag{7}$$

If now the specimen alone oscillates (position II, Fig. 3) this corresponds in effect to a wide range of values of χ. Inequality (4) may be written

$$\Delta_1-\psi\geq\chi\geq-\Delta_2-\psi\,, \tag{8}$$

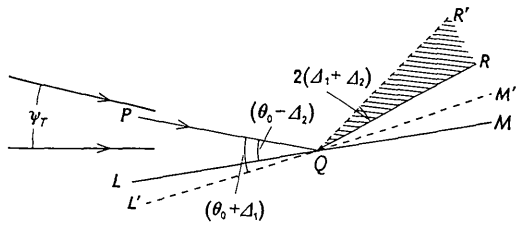

Fig. 3. Position II. Specimen oscillates and film is stationary. PQ is an incident ray and lattice planes LM and $L'M'$ have Bragg angles $(\theta_0-\Delta_2)$ and $(\theta_0+\Delta_1)$ respectively. As the specimen rotates, all positions within these extremes will reflect the ray PQ into the angle RQR', which equals $2(\Delta_1+\Delta_2)$. If ψ_T is the total divergence of the incident beam, the total angle over which reflexion occurs is therefore $2(\Delta_1+\Delta_2)+\psi_T$.

and when the range of values of ψ is inserted it is clear that the limits on χ are

$$\Delta_1-\psi_m\geq\chi\geq-\Delta_2-\psi_M\,. \tag{9}$$

If in $\chi+(\chi+\psi)$ we insert the maximum and minimum values of each part, the upper and lower limits are $\Delta_1-\psi_m+\Delta_1$ and $-\Delta_2-\psi_M-\Delta_2$ respectively. Thus

$$\varphi_2=2(\Delta_1+\Delta_2)+\psi_T \tag{10}$$

where ψ_T represents the whole range of values of ψ.

If there is no oscillation (position III) the derivation of the angular size in accordance with conditions (4) and (6) leads in general to a number of different expressions, depending on the relative magnitudes of ψ_T, χ_T and $(\Delta_1+\Delta_2)$. In order to keep the account brief, we shall make use of the experimental observation that in all cases of interest

$$\varphi_1\geq\varphi_2\,, \tag{11}$$

that is

$$\chi_T\geq\Delta_1+\Delta_2+\psi_T\,. \tag{12}$$

With this information the appropriate value of the range of φ can be deduced as follows. The extremes in the inequality (9) give the largest range of values of χ for which reflexion is possible, *i.e.* $\Delta_1+\Delta_2+\psi_T$. Now it is known from experiment that in fact χ_T exceeds this quantity (see inequality 12). Since χ_T exceeds the total range for which reflexion is possible, it therefore follows that the result φ_3 when specimen and film are stationary must be the same as that in the previous case since the additional range of χ cannot contribute to the reflexion. Hence

$$\varphi_3=\varphi_2\,. \tag{13}$$

The experimental result may now be examined with reference to the arguments presented above. In Table 1 we list the mean radial lengths, in millimetres, of spots for the (200) ring of a series of photographic emulsion specimens. In all cases the geometry of the experimental set-up was identical, so that the listed values are directly comparable and proportional to the angles φ_1, φ_2 and φ_3.

It will be seen from these results that the values of position I are always greater than or equal to those of position II, as has already been mentioned in the theoretical arguments. In many cases the differences are very large. It was predicted theoretically that in these circumstances the values for positions II and III should be equal and it will be seen that they are in fact fairly close although those of position II are in general slightly higher than those of position III. The slight discrepancy may perhaps be due to errors in the relative exposure conditions. The exposures for position II must necessarily be longer than those of position III to compensate for the oscillation of the specimen. If the effective exposure in position II is too low in comparison with that of position III, some of the faintest spots in the position II pattern would escape measurement, so that the mean size would be increased.

In order to deduce values of χ_T and $(\Delta_1+\Delta_2)$ from equations (7) and (10), it is necessary to know

the value of ψ_T. This was found from a consideration of the geometrical conditions. These are such that the whole focal spot ($100 \times 140\,\mu$) of the X-ray tube is visible from each grain. Converting this area into solid angle at the grain of the specimen we obtain a value of the effective divergence ψ_T which is the angle at the apex of the cone of rays within the solid angle. From this the value of ψ_T was found to be $1{\cdot}3 \times 10^{-3}$ radians. Because of the possibility of internal reflexion within the lead-glass capillary used as a collimator, exposures were taken to give images of the illuminated area at different distances from the end of the capillary in order to check the above value. The result gave almost the same value as that mentioned before, so that with the capillary used in this case internal reflexion can in effect be neglected. In Table 1 values of the misalignment χ_T in minutes are given in the fifth column. From the value of $(\Delta_1+\Delta_2)$ we can find the contribution due to distortion by subtracting the contribution due to wavelength spread. In the patterns the spots arising from the Cu $K\alpha_1$ and $K\alpha_2$ components of the incident beam overlap so that the main part of the wavelength spread must be attributed to the differences between the two components, which is 0·00384 Å. In addition there is the intrinsic width of each of the $K\alpha$ lines, which is 0·00058 Å (Compton & Allison, 1935). The total spread $(\beta_1+\beta_2)$ is therefore 0·00442 Å. Hence for Cu $K\alpha$ radiations of wavelength 1·54 Å,

$$\frac{\beta_1+\beta_2}{\lambda} = 0{\cdot}00287\,. \qquad (14)$$

It will be seen in the last row of Table 1 that the value of $100(\beta_1+\beta_2)/\lambda$, *viz.* 0·287, is often much larger than $100(\delta_1+\delta_2)/d$ so that wavelength spread in these cases contributes the major part of the total $(\Delta_1+\Delta_2)$. It is very satisfactory that in these circumstances no negative values occur.

It may be mentioned that very similar results for distortion were obtained by F. Willets (private communication) with an entirely different approach, using line broadening as a method of measurement. These and other details will be further discussed below.

Monochromatic convergent-beam method

Instead of utilizing the full spread of a line focus of an X-ray tube (as was done by Berry, 1956) so that each crystal received X-rays from a wide range of angles, the specimen was placed in the focal spot of a bent quartz monochromator where it also received radiation from a wide angle, which was again 2·5°. In these circumstances, owing to the fact that the specimen is only irradiated by monochromatic radiation, less scatter is obtained in the background of the diffraction pattern than is obtained with white radiation. More important is the fact that spots obtained are due either to $K\alpha_1$ or to $K\alpha_2$ wavelengths as both cannot overlap in the production of a diffraction spot. This is because the separation of the $K\alpha$ doublet in the focus of the monochromator is greater than the diameter of the largest grain examined, and hence each crystal reflects either $K\alpha_1$ or $K\alpha_2$ radiation. The facts mentioned led to a very high resolution of the diffraction spots and to high contrast against a relatively low background.

Owing to the wide angle of the incident monochromatic beam, we have in effect position I as previously defined, and it is to be expected that the radial lengths of the spots are given by the expression (7). However, the wavelength spread in this case is only 0·00058 Å, since the crystals receive either $K\alpha_1$ or $K\alpha_2$ radiation. This means that the value of $(\Delta_1+\Delta_2)$, (*i.e.* distortion plus wavelength spread) is now much smaller than in the oscillation method.

If, therefore, we subtract from the previous oscillation results for position I (φ_1) a value 0·05 mm, which corresponds to $\tan\theta_0 d\lambda/\lambda$ where $d\lambda$ is equal 0·00384 Å, we obtain a value directly comparable with the streak length observed in the monochromatic convergent beam experiments. This comparison is shown in Table 2 for the four specimens examined.

Table 2. *Comparison of results from convergent beam and oscillation experiments*

Specimen	*C*	*E*	*K*	*L*
Mean streak length (conv.)	0·65	0·17	0·21	0·22
$\varphi_1 - 0{\cdot}05$ (oscill.)	0·72	0·15	0·30	0·21

Considering the very different conditions of the two experiments the agreement is quite satisfactory.

Asterism

The oscillation and monochromatic convergent beam results may also be compared with those obtained by examination of asterism streaks, which appear when microbeam patterns are given twice to four times the normal exposure. These streaks arise from the white radiation, that is, they are Laue spots elongated by misalignment. This means that in the inequality (4) both Δ_1 and Δ_2 are very large, so that the only limitations on χ and ψ are those in inequality (6). Hence, the maximum and minimum values of $(2\chi+\psi)$ are $(2\chi_M+\psi_M)$ and $(2\chi_m+\psi_m)$ respectively. The range over which reflexion occurs is therefore given by

$$\varphi = 2\chi_T + \psi_T\,. \qquad (15)$$

The asterism streaks were measured close to the 200 ring, although of course the streaks do not necessarily arise from (200) planes. Nevertheless if the effective misalignment is the same for planes of different index the value of φ will not alter and so the streak length will only vary with the Bragg angle because of the effect of the geometry of the camera. Hence, from the observed value of φ and the value of ψ_T ($1{\cdot}3 \times 10^{-3}$ radian) the value of χ_T can be

derived. A comparison of the results obtained by the asterism measurements and those from the oscillation experiments is shown in Fig. 4.

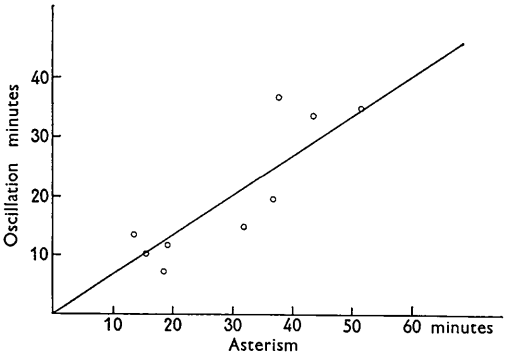

Fig. 4. The correlation between results obtained from oscillation and asterism measurements.

In view of the many experimental difficulties the scatter in the results is not unduly large. The fact that χ_T from the asterism streak is generally longer than χ_T from the oscillation measurements is probably due to the loss of the smallest and faintest asterism streaks caused by the increased background resulting from heavy exposures.

The 200/220 discrepancy

It has been mentioned above that an inconsistency is found in the number of spots occurring in the 200 and 220 rings, which could be interpreted as a difference in the number of substructures. This difference occurred in the still microbeam method as well as that of Andrews & Johnson. Furthermore, F. Willets (private communication) found a similar discrepancy to exist for AgCl and NaCl crystals. As this discrepancy was entirely unexpected, a considerable amount of time has been spent in trying to establish its cause. Unfortunately no definite solution of the problem has yet been found although hypothetical explanations for the effect are considered. In the following some of the arguments, and experimental results of these investigations are given.

Perhaps the most likely explanation is that weak diffraction spots merge into the background fog which is increased by the longer exposure times required for the 220 ring (see further discussion below). For this reason such spots may not be visible, and escape counting. It is, however, not easy to demonstrate the correctness of this explanation by any convincing experiments.

A number of other possibilities have been examined as alternatives. For example, the most obvious cause of the discrepancy would be that there is preferred orientation on the grains. To examine this possibility, a specimen was placed with its plane at an angle of 80° instead of 90° to the incident beam. This did not affect the results.

It was conjectured that perhaps the problem was in some way peculiar to silver-halide crystals. Accordingly experiments were carried out on other face-centered crystals, of which aluminum is an example. Again the same discrepancy was found.

Next, the effect of variation of exposure time was considered. According to equation (1) the number of spots to be expected in a given ring depends on the multiplicity factor for the corresponding planes. The factors are 6 and 12 for the 200 and 220 planes of a face-centred cubic lattice. Since the values of $\cos\theta$ (see equation (1)) are not very different, we should therefore expect approximately twice as many spots in the 220 ring as in the 200 ring. A survey of 66 patterns has been made and the ratios of numbers of spots in the 220 and the 200 rings has been plotted against the frequency of their occurrence. The peak of the histogram was found to be at 1·2 instead of the expected 2. Now the ratio of intensities of the spots is theoretically and experimentally about 1:2, so that we might argue that the exposure time required for the 220 ring should be practically twice that required for the 200 ring. When the exposure time for the 220 ring was increased to twice its value for the 200 ring, the peak of the histogram increased slightly to 1·4. It will be realized that this experimental work was extremely time-consuming, individual exposures being as much as 40 hr or more, so that a large number of results could not be obtained. However, sufficient patterns were obtained to make it appear unlikely that the discrepancy could be attributed to the effect of exposure time.

Another possibility is the occurrence of double reflexion of spots which would otherwise appear in the 220 ring, causing them to fall elsewhere. Although this may perhaps occur for certain reflexions by the (220) planes when the crystal is in a special orientation, it seems unlikely to be able to account for the disappearance of half the expected number of spots in the 220 ring.

A rather speculative explanation of the discrepancy may be that one of the members of the joined crystallites (if substructures are assumed to be present) is in a preferred orientation. (A similar argument would hold for twinned crystals.) If this is the case, the plane of contact is parallel to the same index-planes in the adjacent substructures. Therefore if this set of planes is in a position for reflexion, the two substructures will give rise to a single diffraction spot. Instead of two random chances for reflexion there will only be one for this arrangement of two substructures. This will only be true for the planes parallel to the plane of contact; the other planes of the two substructures are not influenced by this attachment. Hence the multiplicity factor is reduced for the particular crystallite and the particular index under consideration. It is, however, difficult to

imagine that the factor is reduced by the required amount.

In our view, the discrepancy of the results for the two rings deserves further experimental study. It is a pity that other workers do not appear to have examined more than a single ring in each pattern.

Conclusions

The work described in this paper is concerned with two broadly different aspects of structural disorder in photographic emulsion grains. It was very desirable to have the results from a variety of experimental methods applied to a wide range of specimens so that intercomparison was possible. This has involved experimental work over a very long period.

The microbeam method revealed results which could be interpreted as a subdivision of the grains. Results of the other experiments, *viz.* the oscillation, monochromatic convergent beam and asterism methods, revealed the existence of misalignment and distortion within individual regions of the grains. Analysis shows that the range of angle of misalignment for eleven different types of specimen is between 7′ and 37′ and the percentage distortion between 0·02 and 0·40. It is important to stress that the agreement between the widely different methods (summarized in the Tables and Fig. 4) is very satisfactory. A similar range of values has also been found by Berry (1956). F. Willets of this laboratory has also carried out distortion measurements with line broadening techniques, using standard deviation as a measure of line breadth (Pitts & Willets, 1961). The values of distortion in various types of emulsion obtained on the one hand by Willets's method and on the other by the various methods previously described are not only of the same order but even numerically very near in some cases.

It remains to discuss the reliability of the results obtained. The peculiar discrepancy occurring between the (200) and (220) planes has already been discussed. In view of the experimental conditions, in particular the long exposure times, it is impracticable to repeat observations a sufficient number of times to derive accurate estimates of error, but the general self-consistency of the results and the plausible values obtained lend strong support to the view that systematic errors have been avoided.

The new technique involving the combination of three positions of film and specimen in microbeam oscillation experiments is a very useful method which allows a separation to be made between angular misalignment of the lattice planes and variation of lattice parameter (distortion) and gives the magnitude of each. Such a separation permits a much clearer visualization of the average characteristics of the imperfections present in crystals of the specimen.

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