

30 YEARS OF SMALL-ANGLE X-RAY SCATTERING

In the early days of x-ray diffraction, scattering close to the primary beam was a nuisance, to be disposed of with a large beam trap. Careful study of this scattering has yielded information on features intermediate in scale between that of the atomic arrangement in a crystal and that of the images in the electron microscope.

ANDRÉ GUINIER

EXPERIMENTAL AND THEORETICAL advances in the study of x-ray diffraction at small angles both started about 30 years ago. With the focusing crystal monochromator experimenters could obtain the intensity and resolution they needed to resolve the diffraction pattern close to the primary beam. Now many other methods allow a study of this kind of scattering. And application of the form-factor concept in scattering theory provided a statistical measure for the average size and shape of the small grains that are responsible for this kind of scattering.

The method, as a tool for investigation of material structures, must compete with electron microscopy. The detailed images produced in the electron microscope have no counterpart in scattering experiments. However, that same detail is often too intricate for easy reduction, and the advantage of small-angle scattering then lies in the easy and rapid availability of statistical information.

HISTORY

In the early 1930's one could say that there was no work on small-angle scattering. In fact, in the x-ray diffraction pattern the domain of small angles was

almost completely ignored. One reason for this neglect was that, generally, this region of the pattern was completely black from the many causes of parasitic scattering. This blackening was the same with and without a sample.

Another reason for neglect was that the chief interest lay in crystalline diffraction, and no crystals with very large cells were studied. The interesting region corresponded to a spacing of, say, less than 1 or 2 nm. Of course there were some exceptions—for instance the work of John D. Bernal and I. Fankuchen on the tobacco-mosaic virus and a paper by C. V. Raman on the small-angle scattering produced by some carbon black. B. E. Warren also made some observations on carbon black. But at this time (1936) nobody could imagine small-angle scattering as a subject for a thesis. Under the supervision of Charles Mauguin my work was to study what occurs in a diffraction pattern between the Bragg peaks. That was the beginning of the study of thermal scattering and other diffuse scatterings.

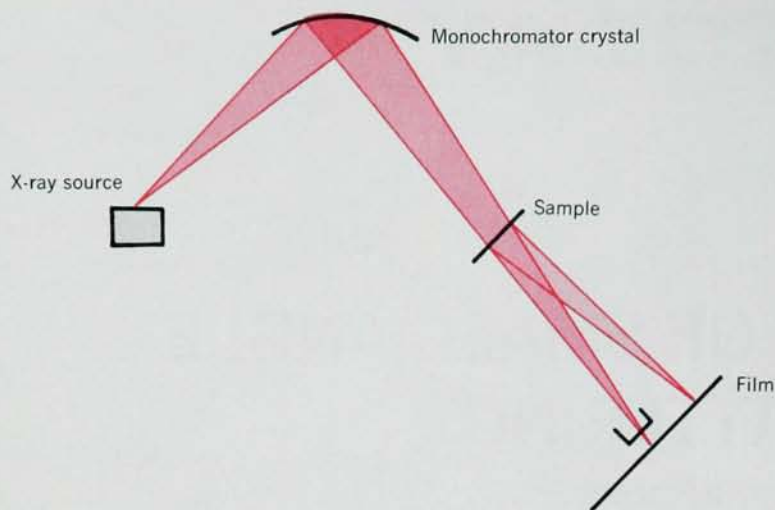
Focusing monochromator

Experimentally, we needed much clearer patterns than there were at

that time. We had to suppress, or at least diminish as far as possible, all causes of parasitic scattering. One of the chief causes was the presence in the incident beam of the continuous spectrum, in addition to the characteristic radiation. Therefore to isolate this useful characteristic radiation we



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FOCUSING X-RAY MONOCHROMATOR. The curved crystal produces a convergent beam with good intensity and resolution; without this feature exposure times were too long to be practical in small-angle scattering experiments. —FIG. 1

had to use a crystal monochromator. But unfortunately there was so much loss in intensity by crystalline reflection that, although the patterns were clear, they were very faint. Exposure times (only the photographic method was used) were much too long to be practical. Therefore I replaced the plane crystal by the curved crystal that had already been used with great success by x-ray spectroscopists. Figure 1 shows the arrangement schematically.

After some other improvements (for example, putting the diffraction camera in vacuum to avoid scattering by air and making very careful adjustment of the slits) it was possible to obtain a pattern with a very weak background. The improvement was particularly noticeable in the small-angle region. Thus I was led to study this part of the pattern. The focusing monochromator has another advantage; because the beam reflected by the crystal is rigorously converging, resolution of the scattering angle is much better than with an ordinary collimated beam even when the angle is small. Of course the direct beam should be trapped, but the blind re-

gion extends only to an angle of about 10–20 minutes of arc. Because the background of the pattern is almost completely clear, even faint scattering can be detected.

Small grains

With this apparatus I studied metal crystals to begin with. The general result was that, in the small-angle region, there was practically no scattering. Scattering at larger angles was studied at that time in France by Jean-Baptiste Laval—it is the thermal diffuse scattering. However, I did find some special samples that gave strong scattering restricted to an angular region less than a few degrees. I tried carbon black and found the effect that had been previously observed.

It soon became obvious that the real origin of this small-angle scattering lay in the existence of small grains. That was shown in a 30-year-old photograph (figure 2) that compares diffraction patterns from two species of amorphous silica. One is vitreous silica, and the other is a gel of silica. Their large-angle pattern is the same. The only difference is the appearance

of the small-angle scattering, which arises because the gel sample divides into small particles whereas the vitreous silica is homogeneous.

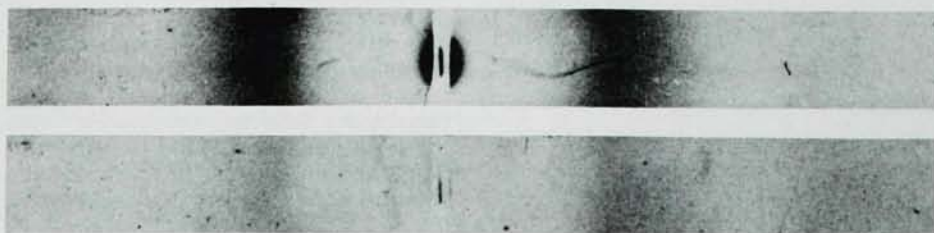
The patterns given by carbon black (figure 3) were at first very surprising. If you consider only one of these patterns it seems possible to measure a well defined angular limit for the scattering. But you find that, with variable exposure times, this limit changes. This result means that there is no definite angle corresponding to a discontinuity in the scattering; there is instead a rapid decrease of the intensity from the center up to large angles. It is not possible in this case to measure a line width in the manner usually done for a broadened line, because it is impossible to find the center or the maximum of the curve. So the only possibility is to find, experimentally, the law governing decrease of the scattered intensity with angle.

Another example of small-angle scattering was found some months later, with the interesting feature that the pattern did not have circular symmetry but was strongly anisotropic (figure 4). This work was with age-hardened aluminum-copper alloys. The streaks radiating from the center were dependent on the orientation of the sample. I was not at that time able to use single crystals, and the orientation of the different grains was not known. This qualitative observation showed, however, the possibility of anisotropic small-angle scattering.

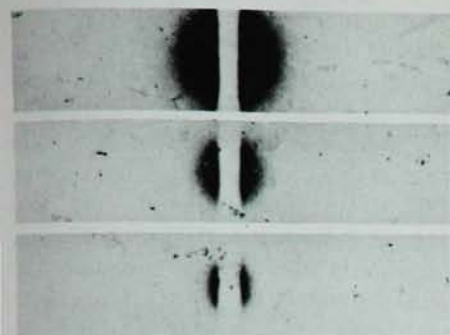
THEORY

Let me now review the theory of small-angle scattering in the present form. I will take the example of diffraction by a grain of limited size.

Consider a sample of matter in which we do not specify the order of the atoms but simply assume it to be statistically homogeneous. Then we cut a small grain from this sample and study the diffraction by this grain. The electron density in the grain can be represented, as suggested by P. P. Ewald in 1940, by the form-factor concept. If $\rho(\mathbf{x})$ represents the electronic density in the homogeneous matter, then in the small grain this density is represented by the product of $\rho(\mathbf{x})$ by the form factor $\sigma(\mathbf{x})$, a function that is zero outside the grain and unity inside it. Then we deduce the scattered amplitude by a Fourier transform that involves a convolution of the Fourier transforms of the form



SCATTERING IN SILICA. These 30-year-old photographs show small-angle scattering in silica gel (above) and the lack of such scattering in vitreous silica (below). The difference arises because the gel divides into small particles, whereas the vitreous sample is homogeneous. —FIG. 2



CARBON BLACK. These examples of small-angle scattering, taken for the same sample of carbon black with different exposure times, show that there is no sharp limit to the scattering. —FIG. 3

factor and of the electronic density. We call $\Sigma(s)$ the Fourier transform of the form factor. After some manipulation we find that the scattered intensity as a function of s is composed of two terms. (Here s is the usual scattering vector $(S - S_0)/\lambda S_0$ and S being the unit vectors along the incident and diffracted beam, and $s \approx 2\theta/\lambda$.)

$$I(s) = \rho_0^2 |\Sigma(s)|^2$$

+ a second term [a function of the Fourier transforms of $\rho(x)$ and $\sigma(x)$]

The first term

The first term is, apart from a scaling factor, proportional to the square of the average density of the matter multiplied by the square of the modulus of the function $\Sigma(s)$. The second term can be rather complicated, but we can neglect it for the moment. More important is that we have isolated the first term, which does not depend on the structure of matter on an atomic scale. It depends only on the shape and the size of the diffracting grain. This function is a centrosymmetrical function, decreasing from zero, in the Fourier space; in diffraction space it corresponds to a central peak of intensity decreasing from the zero angle. It becomes practically zero at an angle 2θ , which is the order of magnitude λ/D , D being one average dimension of the grain. Then, if we have a grain of microscopic (or even larger) dimensions, this angle is so small that we can not, even with special precautions, record the central peak. We are left with the second term, which represents the ordinary diffraction pattern at large angles. But if the grain is small enough (say, about 10 nm) this angle 2θ becomes of the order one degree, and small-

angle scattering is observable—some examples were shown above.

The separation of the scattered intensity into two terms is only a first approximation; we will now consider the second term more closely.

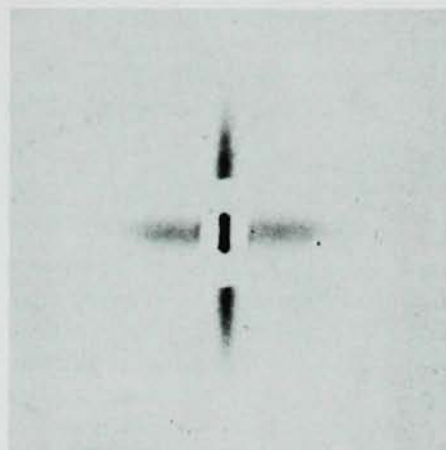
The second term

Imagine that the matter is completely homogeneous. (That is not physically possible because at the atomic scale matter can not be continuous.) Then the second term vanishes. Only the central peak is left. Consider instead a second, more realistic, case for which $\rho(x)$ is periodic—that is, the sample is a small crystallite. Then in the second term we have the Fourier transform of the periodic function, which gives rise to discrete peaks, the Bragg peaks. We find that all these peaks are broadened by exactly the same function as the direct beam. This is the well known effect of the crystallite size on the broadening of the Debye-Scherrer lines, or the crystalline spots in a single-crystal pattern.

Because the broadening is exactly the same for the center as for every other peak, in this case the small-angle scattering does not supply any different information from that gained by the study of the broadening of the Bragg peaks. However, there are some practical differences. The central peak, which can be called the 000 line, is very intense; in a powder every crystal participates in the central peak, whereas a very small proportion gives an hkl reflection. On the other hand, the experiment is more difficult with the central peak because we are unable to reach the maximum of the intensity curve. Therefore we cannot use the width of the line as in the ordinary treatment of line broadening.

If $\rho(x)$ is periodic, but not rigorously periodic, we have an especially interesting case. The sample is then a crystal with some defects. These defects can affect the width of the Debye-Scherrer line; the distortion of the crystal may produce a broadening of the line, but has no influence at all on the small-angle peak. We can thus separate the effect of the crystallite size and the distortion of the crystal, by comparing the broadening of a Debye-Scherrer line to the small-angle peak.

Finally we come to the last possibility: $\rho(x)$ neither constant nor regular. The sample is then amor-



ANISOTROPIC SCATTERING. Age-hardened aluminum-copper alloy shows these streaks radiating from the center of the pattern, with orientation depending on the orientation of the sample. The anisotropic scattering results from the formation of platelets ("Guinier-Preston" zones), which are clusters of copper plates, one atom thick. —FIG. 4

phous and gives a typical diffraction pattern of an amorphous material with broad rings. The scattering around the center, however, has exactly the same nature as in the previous cases. Thus the structure of matter does not influence the central peak, which is only dependent on grain size.

Radius of gyration

How can one use this general theory in the study of practical cases? It is not possible, of course, to operate on an isolated small grain. The sample is made of an ensemble of grains, forming a dilute system or a more or less close-packed system. If the grains are not spherical, their orientations are in general random. Under these conditions we can not deduce directly from the observed scattering the function $\Sigma(s)$ and the actual shape of one grain. We know only some average of this function for every value of s (equal to the scattering angle divided by the wavelength). To make the best use of these experimental data we have to take the theory further by choosing some model. The first model considered was the simplest—a very dilute system of identical particles, the separation between particles being large relative to their size. In these conditions we observe simply the sum of the scattering by individual particles, and experiment gives a true average of $|\Sigma(s)|$. It is thus possible to deduce one well defined parameter. This is the intensity curve (figure 5), which can be approximated (in its central re-

gion) by a Gaussian function. The coefficient of this Gaussian can be expressed in terms of a length R , which is called "the radius of gyration" of the particle.

$$I \propto \exp\left(-\frac{4\pi^2}{3} R^2 s^2\right)$$

As in mechanics, R is the square-root average of the distance of every atom from the center of mass of the particle. Thus, from the experimental intensity curve, it is possible to compute one parameter that, of course, does not give a total geometrical description of the particle, but is precisely defined.

This method of exploitation of small-angle scattering requires that the particles are well separated and well defined; if they are not all identical they must at least be similar with a very small range of sizes. This condition is realized, for example, by a solution of macromolecules. But for other samples the particles are not so well defined; for example, in a porous system such as carbon black, the particles can have all sizes and shapes. In this condition, the analysis of the intensity curves described above does not give good results.

Electron-density variations

We must start from a more general theory—the theory of diffraction by a substance in which there are irregular fluctuations of the electron density. We have said in a first approximation that small-angle scattering comes from the existence of small particles about 10 nm in size. In a more general way, we can say that a sample gives rise to small-angle scattering when the fluctuations of the density contain important terms with periods of between roughly 1 and 100 nm. Peter Debye was the first to connect these fluctuations of density with the small-angle scattering. In fact, it is simply an application of the general Patterson function used in crystallography. The local density, $\rho(\mathbf{x})$, at the point defined by the vector $\mathbf{x}$, is equal to the sum of the average density ρ_0 and a fluctuation term. Thus $\rho(\mathbf{x}) = \rho_0 + \Delta\rho(\mathbf{x})$. We consider now the product of $\Delta\rho(\mathbf{x})$ and the density fluctuation at a second point at a distance defined by the vector $\mathbf{x} + \mathbf{r}$. The average value of this product in the sample was called by Debye the "correlation function," $G(\mathbf{r}) = \langle \Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x} + \mathbf{r}) \rangle$. This expression is none other than a form of the Patterson function. Thus it is easy to understand that this correlation

function can be obtained from the Fourier transform of the scattered intensity, and this function contains all information given by the small-angle scattering. Unfortunately this function by itself is very difficult to interpret. Progress has been made in the application of Debye's general theory, trying to draw from the experiments some special parameters that have simple physical meaning for definite models.

The Porod law

One important contribution was supplied mainly by Gunther Porod in 1950. Porod assumes that the electron density in the sample does not vary continuously but may only take one of two values, for example ρ and zero. Between the two phases, matter and vacuum, there is a well defined interface. Porod has shown how it is possible to deduce from the small-angle experiment the specific surface of this interface, that is, the total area of the interface contained in the unit volume of the sample. Instead of using the central part of the scattering curve, Porod uses the wings (figure 5). He has shown that in these wings the product of s^4 by the scattered intensity tends to a constant, proportional to the specific surface of the particles. So, by studying the asymptotic decrease of the scattered intensity, it is possible to determine the specific surface in absolute value.

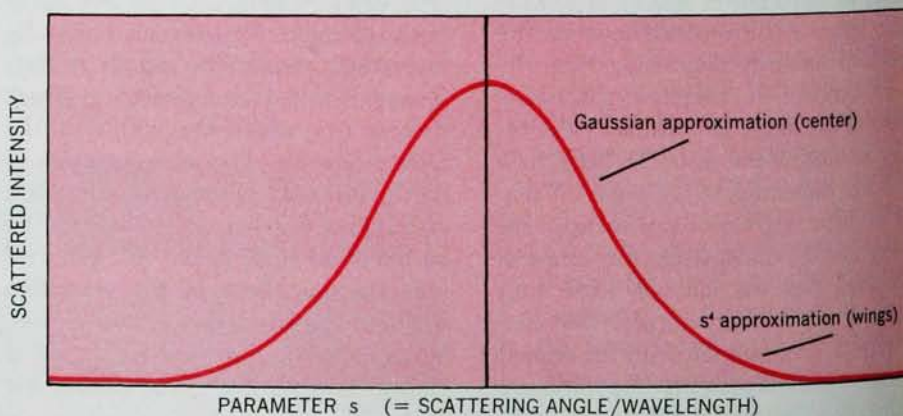
There have been important developments of the Porod theory, some of which are recent. For example, the limits of validity for the Porod law have been investigated. It was shown that the sample must have a clear, well defined interface between the two phases. The particles may have vari-

ous shapes and sizes, they may be in contact or isolated from each other, but the particles must have finite dimensions in all directions. If the sample is formed by an ensemble of very fine needles or very thin plates, the Porod law fails. Porod, and also Denise Tchoubar and Jacques Méring, were able to show that not only the limiting value but the manner with which the intensity reaches this limiting value depends on the nature of the interface, namely whether there are acute corners or only rounded surfaces.

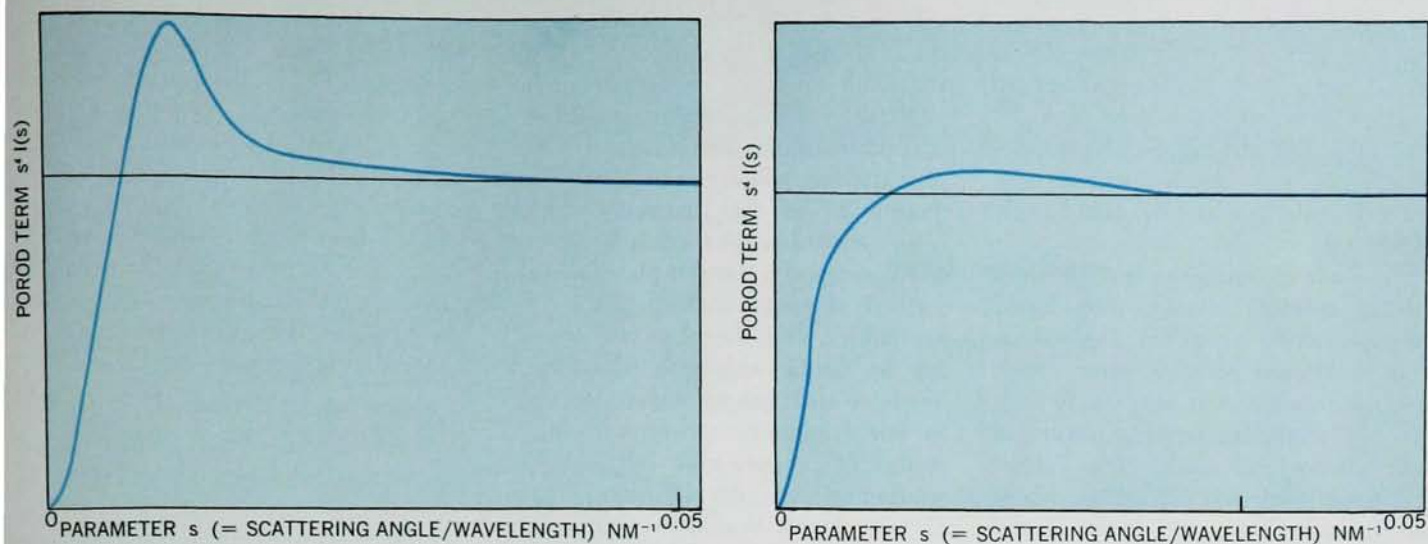
Figure 6 gives examples of the two cases. One sample is a suspension of particles that are of roundish form, and in this case the product reaches a constant asymptotic value after several oscillations, so that the asymptotic value is also the average value of this function. But in the other case, where the particles of magnesium oxide are cubes with well defined edges, the product $s^4 I$ shows very little oscillation, and the asymptotic value is not the average value of the function.

Further progress unlikely

These examples show that the theory of small-angle scattering has been refined and improved. However, I now have the feeling that it has practically reached its limiting state. It is very unlikely that any considerable progress will be made in the future. In fact, progress has been very slow in recent years; the theory is well connected with the general theory of diffraction, and there is little hope of going further. From the experimental point of view as well, small-angle scattering appears to have reached a steady value. The apparatus for small-angle scattering will certainly be continuously improved but no major change can be



INTENSITY CURVE for small-angle scattering. The central part can be approximated by a Gaussian function from which a radius of gyration is derived; an approximation for the wings is used in Porod theory. —FIG. 5



EFFECT OF GRAIN SHAPE on Porod's asymptotic function $s^{-4}I(s)$. Rounded particles (left curve) produce a curve that oscillates before settling towards the asymptote. Sharp-edged particles (right curve) show little oscillation in the asymptotic approach. —FIG. 6

foreseen, unless the power of x-ray sources is increased by a factor of 10 or 100, which is rather unlikely. Thus my conclusion is that, now it appears that small-angle scattering is a rather well established technique, the interest lies no longer in the progress of this technique but in the development of its applications.

APPLICATIONS

It is important that small-angle scattering be applied more and more in various fields in connection with other physical techniques. But it is also important that we know the kind of problem for which small-angle scattering is most advantageous or even unique.

Electron microscope

As I have already said, the normal range of particle sizes easily visible with small-angle scattering lies between 1 and 50 nm; this is just the range suitable for the electron microscope too. Let us recall that when the first experiments on small-angle scattering were made there was no electron microscope; the size of a molecule such as albumin or hemoglobin was first measured by x-ray scattering. Now of course the situation has completely changed, and the electron microscope has an obvious advantage; it gives direct images. By any diffraction technique, however, and in particular by small-angle scattering, we can not find the distribution of electron density directly. There are so-called "direct methods" for determining crystalline structure, but they are not applicable to the complicated and dis-

ordered structures of the samples that give small-angle scattering. Therefore, an electron microscope may give an image of the structure of a porous sample, whereas x rays supply only rather vague information on the statistics of the sizes and shapes of the pores.

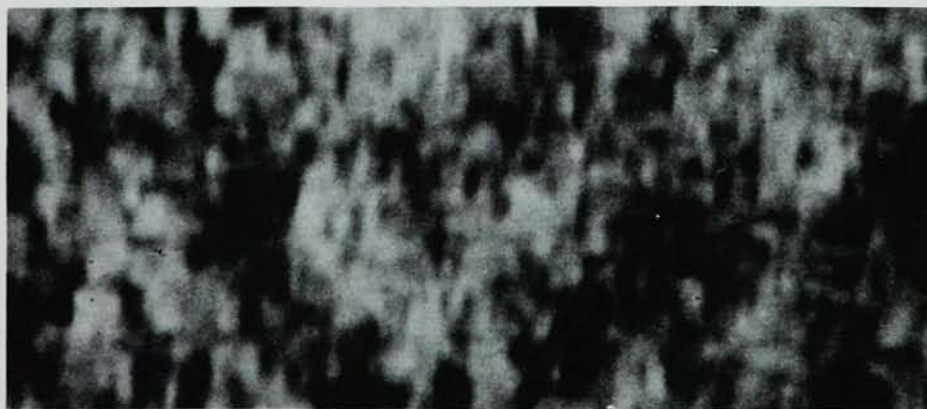
On the other hand, in some cases small-angle scattering can provide information that is not given by even the best electron microscope. I must emphasize these cases particularly, because the electron microscope is so much more popular than small-angle x-ray scattering.

Detection of platelets

One example is the study of the molecules of a colloidal solution. The preparation need not be dried. Another, very characteristic, example of the power of these techniques is investigation of the structures of age-hardened aluminum-copper alloys. In

these alloys hardening is the result of the formation of what metallurgists call the "Guinier-Preston" zones, which are clusters of copper in the form of platelets, one atom thick. These platelets, which produce a heterogeneity of electron density, are clearly visible by small-angle scattering (figure 4). The scattering is anisotropic and gives immediately the shape and orientation (parallel to 100 planes) of the platelets. Because these "particles" embedded in the aluminum crystal all have the same orientation, in this case we can deduce without ambiguity the dimensions of the platelet (10-nm diameter and 0.4-nm thick).

In contrast it was never possible to get good images of these platelets with the electron microscope. Figure 7 is a micrograph of the same alloy in the same state; there are certain irregularities of blackening, but it is very difficult to find that these irregularities are



ELECTRON-MICROSCOPE PHOTOGRAPH for the same alloy (aluminum-copper) as shown in figure 4, in the same age-hardened state. This picture does not provide the evidence for platelets that is so clear in the scattering data. —FIG. 7

oriented in two directions parallel to the 100 axes. It must be acknowledged that in such a picture alone you can not prove the existence of zones parallel to the 100 planes, whereas the conclusion was given immediately, without calculations, by small-angle scattering.

We have encountered another, very similar, example in neutron-irradiated lithium-fluoride crystals. The formation of lithium platelets after strong neutron irradiation is very easily seen in x-ray scattering but has never yet been shown with an electron microscope, although the size of the platelets is well within the range of the microscope resolving power.

Because the information given by x rays is contained in the Patterson function, it can define only a statistical view of the structure of the object. When average data of this type are needed, x rays must be employed rather than the electron microscope. Let us consider a metallic solid solution—that is, a single-phase alloy with a definite crystal lattice, but two (or more) species of atoms occupying the nodes of this lattice. Often these atoms are distributed at random, but sometimes they are not. The structure of the alloy is characterized by the statistics of the atom distribution. Clustering of one species of atoms can be detected by small-angle scattering and evaluated quantitatively. On the other hand, images from an electron microscope are generally not conclusive because they are much too intricate.

Double Bragg diffraction . . .

Unfortunately there is a phenomenon that prevents, or at best makes very difficult, many otherwise possible applications of small-angle scattering; it is double Bragg diffraction, pointed out about 12 years ago by W. W. Beeman. Suppose we have in the sample a crystal suitably oriented to give Bragg diffraction from one given plane, and suppose also that the diffracted beam falls on a second crystal. If that second crystal is parallel to the first a new diffracted beam will occur in the direction of the primary beam. If, alternatively, there is a small tilt angle between the two crystals, the second diffracted beam is not exactly in the direction of the primary beam but is close to it. This scattering depends on the mosaic structure, that is, the probability of having two crystals with a certain angle of tilt. For usual crys-

tals, the double Bragg reflection produces a small-angle scattering decreasing from the zero angle. A similar effect arises with amorphous samples.

There is no way to avoid this cause of scattering, which can be of the same magnitude as the scattering arising from electron-density inhomogeneities. For example if a metal is plastically deformed, the cold working distorts the crystallites, and the observed scattering by double reflection is changed. We have encountered such an example in our laboratory recently during a study of copper-zinc alloy. We wanted to study the diffusion of zinc. If this alloy is heated in vacuum the zinc evaporates, and if the treatment is long and hot enough one finally obtains almost pure copper. The metal contains many cavities, visible with the optical microscope, formed by the departure of the zinc. Our problem was to study the beginning of this phenomenon when only submicroscopic cavities exist and to follow their growth. We found, in this early stage, that the alloy gives small-angle scattering, but we could not decide without any other information whether the scattering was a result of the cavities or whether it was an effect of double Bragg scattering.

. . . defeated with neutrons

There is now a chance of answering this question positively, with neutrons instead of x rays. For neutrons one can choose a wavelength large enough to be more than double that of the largest spacing in the crystal. Thus there is no Bragg reflection at all. More generally, it is now certain that small-angle scattering of neutrons can give very interesting results, as is shown for example by Tasso Springer and W. Schmatz's work. We have compared the results with x rays and neutrons (for similar samples), and it appears that, in some cases, neutrons are more powerful than x rays. Because double scattering can be eliminated, small-angle scattering produced by dislocations in a metallic crystal is detectable. This was an insoluble problem for x rays because of the background from double Bragg reflections.

An advantage of combining neutron and x-ray scattering is that the two measurements lead to two equations if there are several species of atoms. The ratios of the scattering factors could be very different. In this way one could study ternary alloys, and

the composition of clusters could in principle be determined.

Small-angle neutron scattering can be made easier by collimating the neutrons in long guides in which they are totally reflected; these can be 30 meters long or more. One advantage of such long guides is that the experiment can be performed far from the reactor; the background intensity may then be very low, eliminating the need for heavy protection.

Electrons and other waves

We could perhaps use other types of waves for small-angle scattering experiments—electron beams, for example. Electron-diffraction devices now exist that permit measurement of electron scattering at angles of a few seconds of arc. How could such devices be useful, considering that an ordinary electron microscope can produce images that contain more information than a diffraction pattern does? The answer is the same as for x rays; statistics of the irregularities in the specimen show up more directly in a diffraction experiment than in a true image.

We can conclude, therefore, that x-ray small-angle scattering is a somewhat different technique from other x-ray techniques, because its purpose is not the study of structure on an atomic scale. It is really an application of x-ray optics. The basic theory uses general laws of diffraction and interference in optics—the laws are valid whatever the wavelength. For example the scattering of light by macromolecular solutions is based on the same equations as x-ray small-angle scattering. The important parameter is the ratio of the wavelength to the dimensions of the diffracting object.

We find the same general principle with very short wavelengths, for example the waves associated with high-energy particles for which the diffracting particles must be very small, perhaps as small as a nucleon. Thus the scattering of high-energy electrons by protons provides information on the form factor of the proton, just as the scattering of 0.1-nm x-ray beams may be useful for particles 10-nm in size and ordinary light for particles with dimensions of a few microns.

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