

Personal Reminiscences

A. GUINIER

When I began to think of scientific research in 1935, it was Ch. Mauguin whose advice I asked for the choice of a subject. Honestly, I would find it hard to tell today what first took me to Mauguin. I had never taken courses in mineralogy, but it was common knowledge that Mauguin, who had himself come from chemistry, was a good patron also for a physicist. Anyway, looking back today over a span of 25 years, I can appreciate how very much to the point and profound were the first directives he gave me, and if I find my name figuring in this collection of reminiscences it is so because Ch. Mauguin had a feeling for the importance which the physics of solids would acquire in future beside crystal structure analysis, and of the rôle X-ray diffraction was bound to play in this new branch of science.

For the last two or three years a young physicist, J. Laval, had been making measurements in Mauguin's laboratory which at the time were very original. Their aim was to find the intensity of X-ray scattering between the directions of Bragg reflections. The measurements were made with an ionization chamber and the scattered intensity was so weak that Laval had to go to the very limit of sensitivity of his electrometer. He had, by that time, found very remarkable results which one was far from understanding.

While Laval continued his experiments Mauguin wanted the same problem attacked by a different method. For that reason he asked me to fix up a device for registering photographically the phenomena Laval had discovered.

In the then usual Debye-Scherrer diagrams the background intensity between the powder lines was caused by unwanted side effects, such as the non-monochromatism of the primary radiation, the scattering by the air in the camera, etc., and these effects also masked the simple scattering by the sample. One had therefore to get rid of these background producing causes, and at the same time it became

essential to work with a primary beam of the highest intensity, since the aim was to study scattering a thousand times weaker than the normal scattering in powder lines.

The answer to this came with the use of curved crystal monochromators for the purification of the X-rays given out by the tube. The techniques of curved crystals were well known in Paris through the spectrographic work of Y. Cauchois, and furthermore, Laval already used them. In theory the combination of a curved crystal monochromator and a diffraction camera of the focussing type, like that of Seemann-Bohlin, should give powder diagrams of great intensity combined with high resolution. The attempt was, in fact, satisfactory, and the decisive success came by placing the target focus of the X-ray tube in the position of the point source on the circumference of the camera, and by making the focus as small as possible. Since we were using demountable X-ray tubes, it was possible to modify the cathode until a much finer target focus was achieved than in the then available sealed-off tubes which were built for high load rather than small focus.

This is the origin of the diffraction camera now called Guinier camera. Its use has spread mainly in Europe where several variants have been constructed, as by Hägg in Sweden, De Wolff in the Netherlands, and Jagodzinski in Germany. In U.S.A. it became known at a time when the counter diffractometer had already produced a considerable improvement of the powder method, so that it is not much used there nowadays.

But what I was aiming at was not so much the improvement of powder diagrams than the study of the diffuse scattering by crystals. Soon Laval and I continued research along different lines: while he made a fundamental study, experimental and theoretical, of the diffuse scattering of perfect crystals in thermal vibration, I studied diffuse scattering due to imperfections of the crystal structure. The first examples of this I obtained on substances which I had occasion to examine in my camera in 1937/38.

The camera with monochromator permitted the study of scattering at very low angles, down to some ten minutes of arc—which had been quite impossible in the usual cameras. No wonder therefore that even in the very first trials on various samples I could observe details which had not previously been detected. Some samples gave in the immediate neighbourhood of the direct beam a diffuse spot, often of high intensity and limited to an angular range of the order of a degree. At that time B. E. Warren had observed the same for carbon black and

had attributed it to the state of dispersion of the scattering matter. Simple experiments convinced me that small-angle scattering is indeed characteristic for the division of matter into submicroscopic particles ($< 1000 \text{ \AA}$) and does not depend on the atomic structure. Thus it is observed for very small crystals in colloidal metals as well as for amorphous particles (silica gel) and colloidal solutions (albumen).

A simple theory, valid for a sufficiently dilute system of particles, relates the decrease of intensity with scattering angle to the value of a parameter which is characteristic of the size of the scattering particles. This so-called Law of Guinier is successfully applied for instance in the study of protein solutions.

Nowadays small-angle scattering by any kind of particle is well understood in reciprocal space; it is a particular case of the broadening of diffraction spots for the case of very minute crystals. P. Debye and G. Porod have extended the simple theory to heterogeneous systems without the restriction to very dilute ones. Low-angle scattering is used extensively in the study of macromolecules and fine grain catalysts.

Small-angle scattering has also revealed a 'large scale structure' in many solid high-polymers. This structure is intermediate between a very irregular heterogeneity (which would produce continuous scattering) and strict periodicity (which would give sharp diffraction spots). At present there exist plenty of well-agreeing observations, but we do not as yet understand the origin and conditions of stability of such quasi-periodicities whose scale is out of proportion to that of the basic structural cell. One can only guess that there lies hidden here an important element for the full understanding of the structures and properties of bodies built from molecular chains.

As I was studying low-angle scattering in 1938, two metallurgists, Calvet and Jacquet, asked me to make an X-ray examination of aluminium-copper alloys of which they were studying the changes during age-hardening. With his new method of electrolytic polishing Jacquet achieved to detect precipitates at an earlier stage of age-hardening than his predecessors. Calvet and Jacquet gave me samples, age-hardened at room temperature, in which they could not yet find any precipitation. These samples gave rise to a problem: what structural change could explain a considerable change in the mechanical properties, while even the most meticulous microscopical study revealed no change of the alloy before and after the ageing?

By good luck the samples of Calvet and Jacquet were of such coarse grain that in my camera only three or four grains were hit. If they were kept fixed during the exposure to a monochromatic X-ray, the patterns

contained, besides the usual diffraction spots of the Al-structure, very faint spots or radial spikes, which could not be explained by the ordinary diffraction theory whatever the crystal lattice might be. On rotating the sample, some of these spots wandered like spots on a Laue diagram even though the rays used were strictly monochromatic. I was very happy when I observed these unexpected spikes, for I felt that I had hit upon a diffraction phenomenon characteristic for the hardened crystal for which the other experimental methods had failed.

The essential features of the observations became understandable if one assumed that the AlCu crystal contains a series of small bits of (100) planes which produce specular reflection of the X-rays. Knowing that the copper atoms have the tendency to separate out, it was natural to surmise that the little reflecting flakes are formed by the segregation of copper. The detailed study of the reciprocal space of a single crystal soon showed that this model was too simple and that the copper-rich flake produces distortions of the adjoining aluminium planes.

The same observations on AlCu and a very similar interpretation were published simultaneously and independently by G. D. Preston, then of the National Physical Laboratory. Preston, however, did not continue this line of research after the interruption by the war.

This was the first example of a structure which is found in many oversaturated solid solutions in the course of their returning to stable equilibrium. The atoms of the excess solute do not segregate at once to form a well crystallized second phase, but they gather in small regions, of the order of some ten Ångström across and imprisoned in the crystal. These regions where the solid solution becomes heterogeneous and which are finally accompanied by smaller or greater distortions of the adjoining matrix crystal, are called the 'Guinier-Preston Zones.'

A structure of this kind corresponds to a state which is called pre-precipitation, and many examples are known. The interpretation of the initial X-ray results has now been confirmed by direct pictures obtained with the electron microscope. Furthermore, one has observed similar structures in crystals subjected to neutron irradiation; in this case what segregates out are the point defects caused by the irradiation, be they empty sites or interstitial atoms.

In a more general way, 'G. P. Zones' are a particular example of destroyed periodicity, and it is well known that such imperfections play an important rôle in the physics of solids. As another example let us mention the imperfect ordering, or antiphase domains, of alloys that are capable of being perfectly ordered. X-rays are sensitive to such lack

of periodicity, provided a sufficient number of atoms is affected. The G. P. Zones of AlCu were a particularly favourable example because the flake form, by enhancing diffuse scattering along a line in reciprocal space, led to a relatively large intensity. Many other alloys, studied under the conditions we had originally, would have not let us observe anything.

Dislocations are, as defects, too rare and too small for producing abnormal scattering. Like many others, we looked for them in vain. However when dislocations pile up along subboundaries they effectively produce a disorientation between the adjoining sub-grains. In 1948 I showed that a modification of the simple Laue method, known as the Guinier-Tennevin method, permits the study of disorientations of the order of half a minute of arc. This method, together with microscopic observation, allowed to make visible the polygonized state of a metal which occurs during the annealing of the deformed crystals as long as true recrystallization does not occur.