Acta Cryst. (1956). **9**, 35

The Anomalous X-ray Background Scattering from β-Tin

By S. C. Prasad and W. A. Wooster

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 12 *July* 1955)

White tin shows anomalous diffuse X-ray scattering corresponding to points in reciprocal space distributed over volumes large compared with those associated with thermal diffuse scattering. A detailed study has been made of the volumes surrounding the reciprocal-lattice points 400 and 103, and it is shown that the scattering volume is in the form of plates passing through the points 400 and 103 and normal to the x and z axes respectively. A tentative explanation of the phenomenon is given in terms of static distortions of the lattice.

Introduction

In studying the elastic constants of β-tin by diffuse X-ray reflexions (Prasad & Wooster, 1955) it was found that anomalies existed in the intensities of the background scattering. When the intensity of first-order thermal scattering, I, is plotted against $1/R^2$, where R is the distance of the scattering volume element from the nearest reciprocal-lattice point (relp), a straight line is obtained. The value of I on this straight line for a zero value of $1/R^2$ is taken as the contribution of the background. Table 1 gives values of this background for three relps and various directions (rekhas) passing through the relps. In most crystals so far examined the background intensity for a given relp is independent of the rekha passing through it, but in β-tin this is not the case.

Table 1. *Background intensity*

	Rekha parallel to					
Relp	[100]	[010]	[001]	[110]	[$\bar{1}$10]	[$1/\sqrt{2}, 0, 1/\sqrt{2}$]
400	20	120	110	20	—	—
440	60	60	118	20	20	—
103	114	—	42	—	—	42

For the relp 400 there are in Table 1 two rekhas lying in the plane parallel to (100) which have high background intensities. For the relp 440 there are three similar rekhas, parallel to [100], [010] and [001] respectively. In the following paragraphs it will be shown that these are isolated observations corresponding to a diffusely scattering 'plate' passing through 400 and perpendicular to [100]. All directions passing through the relp 400 and lying in this plate have a high background intensity. For the relp 103 there is one such direction, namely [100], represented in Table 1. This, again, is a special case of the general result that all directions passing through 103 and lying in a plane parallel to (001) have an abnormally high background scattering.

The experiments of Arlman & Kronig (1943), using a Laue photograph with X-rays travelling along the [001] axis, showed diffuse bridges joining some of the reciprocal points. The present work extends these early two-dimensional observations by making a three-dimensional survey round two relps.

Experimental method and results

A Geiger-counter spectrometer of conventional pattern (Ramachandran & Wooster, 1951) was used throughout this work. Volume elements of reciprocal space centred on planes passing through or near the relps 400 and 103 were explored. Three single crystals were grown separately and faces parallel to (100), (103) and (110) were cut on the crystals, using the technique described earlier (Prasad & Wooster, 1955). The intensities to be measured were all of the same order as the natural background due to Compton scattering, cosmic rays, etc. Counting was carried on for three separate periods of five minutes for each of several hundred reciprocal volume elements. The intensity of the incident X-ray beam was standardized by reference to the integrated reflexion of the appropriate relp. A correction, usually known as the 'skew correction', was applied to take account of the fact that the angles of incidence and reflexion were not in general equal. The angles subtended by the slit in front of the Geiger counter during the survey of the anomalous background were 0·5° in a horizontal plane and 2·5° in a vertical plane respectively. However, divergence corrections were found to be unnecessary because the accuracy of the individual observations was not more than 10% and the effect to be measured varied slowly from point to point. A section of the results obtained is plotted in Fig. 1.

The contour numbers give the total counts in a five-minute interval. The broken lines occur where the background is principally due to the usual thermal diffuse scattering. The data obtained from these regions has been used in finding the elastic constants of β-tin (Prasad & Wooster, 1955).

The main feature of the distribution shown in Fig. 1(*a*) is a continuous 'plate' of reciprocal volume ele-

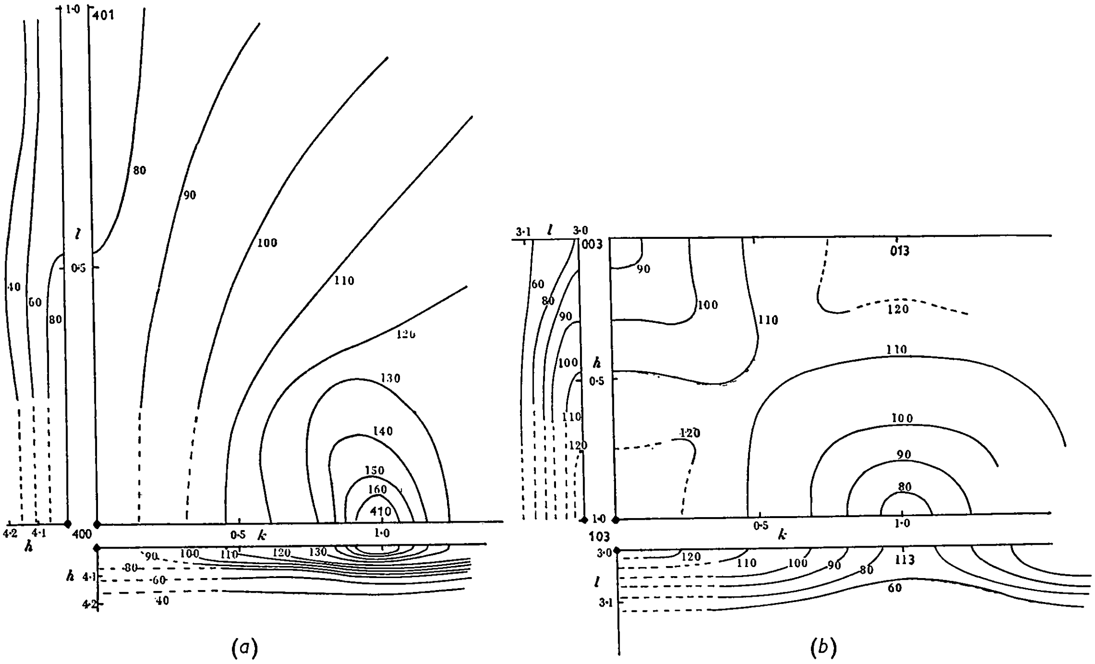

Fig. 1. The intersections with the three coordinate-planes of surfaces corresponding to given diffuse scattering powers. (a) The distribution round the point 400; (b) the distribution round the point 103.

ments which scatter diffusely, extending from 400 to 410 and beyond, in the direction of the y axis, and from 400 to 401 and beyond, in the direction of the z-axis. The Bragg reflexion 410 is not allowed by the space-group ($I4/amd$) but the diffuse intensity rises to a maximum at this point. A similar 'plate' may be seen in Fig. 1(b) having its plane normal to the z axis and passing through the 103 relp. The reflexion 113 is forbidden by the space group but the diffuse intensity is a minimum at this point. A less complete survey of reciprocal space round the relp 440 was also carried out and it revealed two 'plates' passing through 440 and perpendicular to the x and y axes respectively. It should be noted that these observations are consistent with those of Arlman & Kronig (1943), who obtained a photograph in which the 'plates' parallel to (100) and (010) appeared as diffuse lines forming a square net.

Possible explanations of the anomalous scattering

Arlman & Kronig (1943) suggested that the diffuse lines on the Laue photograph were due to distortions of the lattice. Later, Bouman, Arlman & van Reijen (1946) endeavoured to explain them in terms of thermal diffuse scattering. The present work shows that the volume within which thermal diffuse scattering contributes an appreciable fraction of the observed effect is small. In Fig. 1 the broken lines show how far thermal diffuse scattering extends. Another origin of the effect must therefore be sought, and we shall assume that some static distortion of the lattice is responsible.

If the effect were due to foreign atoms or vacant sites these would have to form rods parallel to the x, y and z axes. The reciprocal equivalents of such rods are diffuse plates and the plane of each plate is perpendicular to the corresponding rod. The diffuse intensity in such a 'plate' falls off as the distance from the nearest relp increases. This is not the case for the relp 410 between the relps 400 and 410. An alternative static distortion of the lattice is one in which transverse waves of various wavelengths and amplitudes are frozen in. Thus, for example, a transverse wave having its wave normal directed along an axis $[0kl]$ and its displacement vector along [100] would give rise to a scattering point in the 'plate' through the

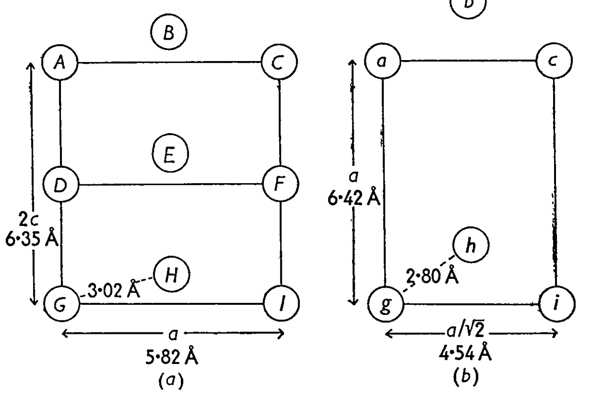

Fig. 2. (a) Distribution of atoms of β-tin on the (100) plane. (b) Distribution of atoms of α-tin on the $(\bar{1}10)$ plane.

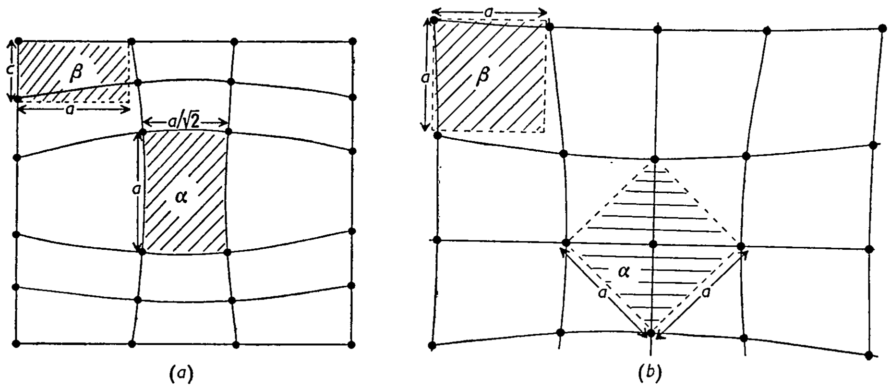

Fig. 3. Distortion of the lattice (*a*) on the *yz* plane, (*b*) on the *xy* plane, due to an island of α-tin in the β-tin matrix.

relp 400. If k and l take all integral and non-integral values and the wavelength varies over the range 10–400 Å approximately, the observed 'plate' would be approximately obtained. Such an infinite series of waves of distortion of the lattice can be caused by the existence of a small foreign island within the crystal. If the atomic arrangement in this island is not the same as that of the surrounding matrix a disturbance of the kind described above can be caused.

It now remains to examine the possibility that either of these two explanations applies to β-tin. Since the transformation point of β-tin to α-tin is at 18° C., the temperature close to which the present observations were made, it is necessary to consider the possible coexistence of the two atomic arrangements.

The structure of α-tin is the same as that of diamond with $a = 6{\cdot}42$ Å, and with a distance between nearest neighbours of 2·80 Å. The structure of β-tin is body-centred tetragonal with $a = 5{\cdot}82$, $c = 3{\cdot}175$ Å. A remarkable relation exists between the two structures. If α-tin be given a homogeneous deformation so that its c axis is compressed from 6·42 to 3·175 Å and its a and b axes are extended from 6·42 to 8·23 Å, the deformed α-structure would be identical with the β-structure. The decrease in volume so produced is 18%. Usually such large homogeneous deformations would not be considered as having any relevance, but in the range of temperature near to a transition point it may not be unreasonable to imagine a continuous transition from β- to α-tin, at any rate within very small volume elements. Fig. 2 shows the distributions of atoms over the (100) plane of the β structure and the (110) plane of the α structure. The difference between $6{\cdot}42(c_\alpha)$ and $6{\cdot}35(2c_\beta)$ is small enough to permit the two structures to exist in normal regular alignment at an interface. The difference between 4·54 Å ($a/\sqrt{2}$ for α-tin) and 5·82 Å (a for β-tin) is 22% and this is rather large, though orientated overgrowths in some other crystals occur with up to 16% difference in corresponding cell dimensions (Friedel, 1926). We shall assume the existence of an island of α-tin within the matrix of β-tin. At the interface parallel to (100) of the β-form the atoms *A B C G H I* (Fig. 2(*a*)) will be replaced by atoms *a b c g h i* (Fig. 2(*b*)) of the α-form. The atoms *D E F* will be unbonded on one side and act as anomalous scattering centres. All over the bounding surface of the island there will be atoms such as *D E F* which will scatter differently from the normally bound atoms. Without entering into speculations concerning the distribution of such atoms over the interface, it may be suggested that the anomalous diffuse reflexions could be due to the presence of these atoms. Alternatively, we may assume that there is a continuous change in the atomic arrangement in going from the island of α-tin into the matrix of β-tin. If this were so the distortions of the lattice would be represented in the (100) and (001) planes by the diagrams of Fig. 3. The diagrams show an island consisting of no more than one unit cell of the α-form. This is not a necessary limitation and is adopted only for simplicity in representation. The displacement of the lattice rows could be resolved into a series of static transverse waves. Again, without knowing the shape of the α-region it is not possible to evaluate the corresponding transverse waves, but they could be of the kind necessary to explain the observed anomalous diffuse scattering.

One of the authors (S. C. P.) feels a great pleasure in recording his gratitude to the Government of Bihar, India, for the grant of a research scholarship and the leave for the period in which this work has been carried out.

References

Arlman, J. J. & Kronig, R. (1943). *Physica*, **10**, 795.

Bouman, J., Arlman, J. J. & Reijen, L. L. van (1946). *Physica*, **12**, 353.

Friedel, G. (1926). *Leçons de Cristallographie*, p. 526. Paris: Berger-Levrault.

Prasad, S. C. & Wooster, W. A. (1955). *Acta Cryst.* **8**, 682.

Ramachandran, G. N. & Wooster, W. A. (1951). *Acta Cryst.* **4**, 335.