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A New Source of Small-Angle X-Ray Scattering*

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Introduction

In the course of a photographic investigation of the small-angle scattering of x-rays from neutron irradiated diamond single crystals, an anomalous scattering was observed. The anomalous scattering most frequently appears as streaks within a range of several degrees of the direct beam. In turning the crystal the streaks are observed to turn through the same angle and the intensity of the streaks depends upon the crystal orientation and neutron exposure. When the crystal is oriented so that a streak intercepts the direct beam, an intense diffuse scattering about the direct beam is also observed. This orientation is such that a Bragg reflection occurs.

The x-ray effects observed from diamond which has received a neutron exposure of less than 3×10^{20} neutrons/cm² ($E \geq 1$ MeV) are similar to those predicted for crystals containing point defects.¹ The point defects in this case are the interstitials and vacancies produced by the neutron irradiation. These effects are: sharp Bragg reflections which are shifted in position corresponding to the change in density, a reduction in the intensity of the reflections by a factor analogous to a temperature factor, and a diffuse scattering localized around the Bragg reflections somewhat analogous to a temperature diffuse scattering. It is this diffuse scattering that produces the anomalous small-angle scattering.

The anomalous scattering is explained as a multiple scattering involving the Bragg and diffuse scattering within the crystal. Two cases can be distinguished depending on the scattering sequence. The first case, which results in streaks, occurs when the direct beam is first diffusely scattered in such a direction as to be subsequently Bragg scattered. The intensity of the resulting reflection conics is determined by the distribution of the diffuse scattering and crystal orientation. The second case, which produces an ap-

parent small-angle scattering, occurs when the direct beam is first Bragg scattered and then subsequently is diffusely scattered into the region about the direct beam.

Experimental Conditions

The anomalous scattering was observed under a number of experimental conditions including crystal monochromatized radiation. However, all the photographs in the figures were made in an evacuated Kiessig small-angle camera using .00035 in. nickel filtered copper radiation from a Philips fine focus x-ray tube operated in full rectification at 40 kv and 20 ma. The pictures were recorded on Ilford industrial G film 100 mm in diameter developed for 6 min. at 20°C. The crystals were mounted on a small goniometer inside the Kiessig camera 17 mm behind the normal sample position so the crystal could be rotated about an axis from outside the camera. The pin hole slit system, K-15, which produces a beam about 1mm in diameter was used for all exposures.

Case I: Streaks

In order to observe the effects it is essential that the crystal have a large diffuse scattering near the Bragg reflections. Figure 1 is a transmission Laue of the diamond crystal used in this investigation. The crystal was exposed to 2.47×10^{20} neutrons/cm² (fast), and has a density 4.9% less than unirradiated diamond. In the photograph the direct beam is along the $[\bar{1}11]$ direction. The salient features of the photograph are the intense diffuse spots outside the (111) , $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$ Laue spots and the sharpness of the Laue spots. The three (111) reflections lie just outside the Ewald sphere of copper K_{α} radiation, and the diffuse scattering associated

with these reflections is cut by the Ewald sphere giving rise to the diffuse spots on the Laue pattern.

Figure 2 is a photograph of the small-angle scattering of the same crystal. The direct beam is directed slightly more towards $[111]$ than in Fig. 1. Three streaks are clearly evident and are in fact partial reflection conics from the $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, and $(1\bar{1}\bar{1})$ planes which are reflecting part of the diffuse scattering near the (111) , $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$ Laue spots of Fig. 1. These streaks are similar to the reflection conics observed in diamond by Grenville-Wells² and Norman³ produced by the Compton scattering acting as an internal radiation source. In the present observations, the diffuse source is of limited distribution and strongly dependent upon crystal orientation, so that the closer a point on the streak is to the direct beam the stronger its intensity.

This can be better understood with the aid of Fig. 3. S_0/λ is the direct beam which is diffusely scattered into the direction S/λ from a point g distant from the reflection B_{hkl} . The ray S/λ is traveling in a direction so as to satisfy the Bragg angle for the (hkl) reflection and is Bragg scattered into the direction S'/λ . The rays S/λ which satisfy the Bragg condition generate a cone whose axis is parallel to B_{hkl} with semi-cone angle $\pi/2 - \theta_{hkl}$ and whose apex is the center of the Ewald sphere. The locus of points, g , which contribute to the streak is the intersection of the cone with the Ewald sphere, and $g = S'/\lambda - S_0/\lambda$. Apart from polarization factors⁴ the intensity scattered into the streak is proportional to the interference function at $B_{hkl} + g$. If 2α is the angle between the direct beam and a point on the streak $g = \frac{2}{\lambda} \sin \alpha$. Taking $2\alpha_0$ as the smallest angle on the streak with the positive direction towards B_{hkl} we can write $\cos \{B_{hkl}, g\} = \frac{\sin \alpha_0}{\sin \alpha} \cos (\theta_{hkl} + \alpha_0)$. These two quantities enter into the expression for the diffuse scattering from point imperfections.

For a diamond crystal of N unit cells containing a fraction p of the atoms as Frenkel defects and assuming the displacements about an interstitial and vacancy are respectively $C_i \frac{F}{|r|^3}$ and $C_v \frac{F}{|r|^3}$, the diffuse scattering is given approximately as**

$$I_D = 8p(1-p)f^2N \left\{ \left[1 + a C_v \left(\frac{B \cos(B,g)}{g} + 1 \right) \frac{\sin 2\pi rg}{2\pi rg} \right]^2 + \left[1 + b C_i \left(\frac{B \cos(B,g)}{g} + 1 \right) \frac{\sin 2\pi rg}{2\pi rg} \right]^2 \right\} \quad (1)$$

where $a = -b = 4\pi(2/a_0)^3$ for reflections with even Miller indices and $a = b = 2\pi(2/a_0)^3(1-2p)$ for reflections with odd Miller indices. The cell edge is a_0 , and r is the distance of the closest atom to an interstitial or vacancy. Qualitatively Eqn. (1) accounts for many of the observed features of the streaks. It correctly predicts that the most intense point on the streak is that nearest the direct beam for which g is smallest. Since irradiated diamond expands $C_v + C_i$ is positive⁵ so that the most intense (111) streaks should be found when $\cos\{B,g\}$ is positive. This is indeed found to be the case as can be seen by comparing the $(\bar{1}\bar{1}\bar{1})$ streaks in Figs. 2 and 4. In Fig. 4 the (111) reflection

* This type displacement is expected in an elastically isotropic medium⁵ and C_i and C_v are the strength of an interstitial and vacancy. The anisotropy ratio, $C_{11} - C_{12}/2C_{44}$, is unity for a cubic isotropic medium. The elastic constant data for diamond give 0.628⁶, 0.667⁷ and 0.875⁸ for this ratio.

** The expression was derived using the results of Smirnov and Tikhonova⁹ grouping terms as Borie¹⁰ has done, and using Ekstein's^{11,12} approximation for the lattice sums involved.

lies outside the Ewald sphere so that $\cos \{B, g\}$ is positive and the $(\bar{1}\bar{1}\bar{1})$ streak is more intense than in Fig. 2 where the cosine is negative. The value of $2\alpha_0$ for Figs. 2 and 4 are -0.933° and 0.883° so that the only major difference is the cosine factor.

Case II: Apparent Small-Angle Scattering

When the crystal is oriented so that the streak and main beam intersect, a large anomalous scattering about the direct beam is observed as in Fig. 5. This corresponds to the (111) reflection being on the Ewald sphere and while this condition is to be avoided in practice the anomalous scattering is not double Bragg scattering.¹³ In Fig. 6 the direct beam, S_0/λ , is Bragg scattered into the direction S/λ . S/λ , playing the role of an incident beam, is diffusely scattered into the direction S'/λ from a point of g distant from B_{hkl}^- . All the points g which contribute to this diffuse scattering must lie on the Ewald sphere. The expression for g is the same as in the case of the streaks and $\cos \{B_{hkl}^-, g\} = -\sin \alpha \sin \theta + \cos \alpha \cos \theta \cos \beta$. β is the angle between the traces of the planes containing S'/λ and S_0/λ and S/λ and S_0/λ on the film. The $\cos \{B_{hkl}^-, g\}$ is generally positive in the region below the direct beam and the scattering in Fig. 5 is more intense in this region in qualitative agreement with Eqn. (1).

Summary

A parasitic source of small-angle scattering in single crystals, not previously reported, has been observed. It is a multiple scattering effect involving the diffuse scattering from point imperfections and the Bragg scattering. Two cases can occur depending on the scattering sequence. The first case occurs when the direct beam is first diffusely scattered in such a direction as to be subsequently Bragg scattered to produce reflection conics. The second case occurs when the direct beam is first Bragg scattered and subsequently diffusely scattered about the direct beam to produce an apparent

small-angle scattering. Similar effects should be observed in crystals with a diffuse scattering analogous to this. Thermal diffuse scattering is such a source, and we have observed the effect in KCl and phenanthrene. Figure 7 is a transmission Laue of phenanthrene in which the thermal diffuse sources giving rise to the reflection conics in Fig. 8 are identified. Fricke and Gerold have reported strong evidence for similar observations in copper and aluminum.¹⁴ Other diffuse sources which could produce similar effects are found in heterogeneous alloys with clustering or in crystals with stacking disorders. This parasitic source of small-angle scattering was discussed using only geometrical and kinematical considerations for the scattering processes, neglecting absorption. However, we feel that these considerations suffice to explain our observations, and to alert investigators to the possibility of observing similar effects.

References

1. D. T. Keating, Acta Cryst. 16, A113 (1963)
2. H. J. Grenville-Wells, Nature 168, 291 (1951)
3. N. Norman, Acta Cryst. 11, 1 (1958).
4. L. V. Azaroff, Acta Cryst. 8, 701 (1955).
5. J. D. Eshelby, J. Appl. Phys. 25, 255 (1954).
6. H. J. McSkimin and W. L. Bond, Phys. Rev. 105, 116 (1957).
7. S. Bhagavantam and J. Bhimasenachar, Proc. Roy. Soc. (London) A187, 381 (1946).
8. E. Prince and W. A. Wooster, Acta Cryst. 6, 450 (1953).
9. A. A. Smirnov, E. A. Tikhonova, Soviet Phys.- Solid State 3, 899 (1960).
10. B. Borie, Acta Cryst. 12, 280 (1959).
11. H. Ekstein, Phys. Rev. 68, 120 (1945).
12. W. Cochran, Acta Cryst. 2, 259 (1956).
13. A. Guinier and E. Guyon, J. Appl. Phys. 30, 622 (1959).
14. H. Fricke and V. Gerold, J. Appl. Phys. 30, 661 (1959).

Figures

- Fig. 1 Transmission Laue photograph of neutron irradiated diamond. The crystal to film distance was 39 mm and exposure time 90 min. The other exposure conditions are given in the text. The direct beam is along $[\bar{1}11]$. The intense diffuse scattering near the (111) , $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$ Laue spots and the sharpness of the Laue spots should be noted.
- Fig. 2 Small-angle scattering from neutron irradiated diamond. The crystal to film distance was 183 mm and the exposure time 20 hrs. The prominent streaks are reflection conics from the $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$ and $(1\bar{1}\bar{1})$ planes reflecting the diffuse scattering near the (111) , $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$ Laue spots of Fig. 1. The closer a point on the streak is to the direct beam the stronger its intensity ($2\alpha_0 = -0.933^\circ$).
- Fig. 3 Reciprocal space construction for streaks. The construction represents the condition of Fig. 2 with B_{hkl} outside the Ewald sphere. The direct beam, S_0/λ , is diffusely scattered in the direction S/λ which is Bragg scattered into the direction S'/λ to produce a point on the streak at the angle 2α from the direct beam.
- Fig. 4 Small-angle scattering from neutron irradiated diamond. The (111) reflection lies inside the Ewald sphere ($2\alpha_0 = 0.883^\circ$). The $(\bar{1}\bar{1}\bar{1})$ streak is more intense than in Fig. 2 where the (111) reflection is outside the sphere. All other conditions are the same as in Fig. 2.
- Fig. 5 Small-angle scattering from neutron irradiated diamond. The (111) reflection lies on the Ewald sphere ($2\alpha_0 = 0$). In addition to the streaks there is an apparent large small-angle scattering which is more intense below the direct beam than above. The other conditions are the same in Figs. 2, 4 and 5.
- Fig. 6 Reciprocal space construction for the apparent small-angle scattering. The construction represents the conditions of Fig. 5. The direct beam, S_0/λ , is Bragg scattered into the direction S/λ which is diffusely scattered into the direction S'/λ .

Fig. 7 . . Transmission Laue photograph of phenanthrene. The crystal to film distance was 83 mm and the exposure time was 15.8 hrs. The direct beam is 6.9° from $[001]$ towards $[\bar{2}0\bar{1}]$. The other conditions are given in the text. The most intense sources of thermal diffuse scattering are identified.

Fig. 8 Small-angle scattering from phenanthrene. The crystal to film distance was 183 mm and the exposure time 39.7 hrs. The reflection conics associated with the diffuse sources of Fig. 7 are identified (For the (201) streak $2\alpha_o = -0.62^{\circ}$).

FIGURE 1

FIGURE 2

$$|g| = \frac{2}{\lambda} \sin \alpha \text{ (Å}^{-1}\text{)}$$

$$\cos\{\vec{B}_{hkl}, \vec{g}\} = \frac{\sin \alpha_o}{\sin \alpha} \cos(\theta_{hkl} + \alpha_o)$$

FIGURE 4

FIGURE 5

$$\cos \{B_{\bar{h}\bar{k}\bar{l}}, g\} = -\sin \alpha \sin \theta + \cos \alpha \cos \theta \cos \beta$$

$$|g| = \frac{2}{\lambda} \sin \alpha$$

FIGURE 7

FIGURE 8