# Extinction in X-ray crystallography.

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## Historical introduction.

EXTINCTION is the increase in absorption that is to be expected when Bragg reflection of X-rays takes place in single crystals, and the corresponding decrease in intensity of reflection observed.

The increase of absorption was directly observed in 1914 in two ways. Using the ionization spectrometer, W. H. Bragg[1] found that the amount of radiation transmitted by a crystal section was notably decreased when the transmitted beam had suffered reflection from a set of crystal planes. A photographic method was used by Rutherford and Andrade,[2] who allowed a divergent beam of $\gamma$-rays to traverse a rocksalt crystal and who observed a pattern of absorption lines on a photographic plate so placed as to receive the transmitted radiation. Neither of these methods was developed to give quantitative measurements owing to the difficulty of making allowance for the divergency and inhomogeneity of the radiation, and the imperfections of the crystal.

Early observations on the intensity of X-ray reflection were much more informative, although at first very puzzling. Ionization spectrometer methods were used, reflections being observed from the surface or through the thickness of large single-crystal plates, which were chosen to be as perfect as possible. Darwin[3] had calculated in 1914 the intensity and angular width of the reflection to be expected from a perfect crystal, and in 1918, independently and by a different method, Ewald[4] obtained similar results. Comparison with experiment showed that the actual intensities observed were always *greater* than those expected from the calculation, however carefully the crystal specimens might be selected. Further experiment showed that the Bragg reflection from a crystal surface could be *increased* to a considerable extent by

[1] W. H. Bragg, Nature, London, 1914, vol. 43, p. 31.
[2] E. Rutherford and E. N. da C. Andrade, Phil. Mag., 1914, ser. 6, vol. 28, p. 263.
[3] C. G. Darwin, Phil. Mag., 1914, ser. 6, vol. 27, p. 675.
[4] P. P. Ewald, Ann. Physik, 1918, vol. 54, p. 519.

grinding or polishing the surface, a process which undoubtedly produced a fairly deep layer of somewhat disorientated crystallites. It seemed at first surprising that the X-ray reflection from a mosaic of partly dis-alined crystallites should be many times more intense than that from a much more perfect crystal, but this observation was in complete agreement with later theoretical findings, for Darwin showed that the reflection from a 'perfectly imperfect' or completely mosaic crystal would, in fact, be up to forty or more times as intense as that from an 'ideal' or perfectly monolithic crystal.[1] Observed values were found to fall between the two extremes, but were usually much nearer to the 'mosaic' value.[2] From an X-ray point of view, most crystals are comparatively imperfect.

To the earlier workers, this influence of crystal *texture* was not only difficult to understand fully, but was also definitely an obstacle to be overcome, before the more interesting questions of atomic arrangement and scattering power could be effectively investigated. We are now getting to the stage, however, where the question of crystal texture is of interest in itself, and extinction is once again receiving consideration, but from quite another angle.

### The nature of the problem.

What does, in fact, happen to a beam of parallel, monochromatic X-rays when it is incident on the face of a crystal? That depends on the wave-length of the rays, the nature, texture, and structure of the crystal, and the angle of incidence. If the angle of grazing incidence is sufficiently small, total reflection will take place from either crystalline or non-crystalline solids. The critical angle is given by the formula $\frac{1}{2}\theta_c{}^2 = 1\cdot35.10^{10}.\rho\lambda_o{}^2$ where $\theta_c$ is expressed in radians, $\rho$ is density in gr./c.c., and $\lambda_o$ the incident wave-length in cm. Hence for soda-glass and CuK$\alpha$ radiation $\theta_c = 14'$; for steel and CrK$\alpha$, $\theta_c = 38'$. For angles of incidence greater than $\theta_c$ the rays will enter the crystal and will be bent away from the normal in doing so. The refractive index $\mu$ is only a little less than unity, the amount of defect $(1 - \mu)$ being given by $1\cdot35.10^{10}.\rho\lambda_o{}^2$, provided that $\lambda_o$ is not near to any of the characteristic wave-lengths of atoms in the crystal (or more strictly, provided that the frequency of the incident waves is not near to any of the resonance frequencies of the component atoms). $(1 - \mu)$ is therefore of the order of

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[1] C. G. Darwin, Phil. Mag., 1922, ser. 6, vol. 43, p. 800.
[2] W. L. Bragg, C. G. Darwin, and R. W. James, Phil. Mag., 1926, ser. 7, vol. 1, p. 897; R. W. James, Zeits. Krist., 1934, vol. 89, p. 295.

$10^{-5}$ or $10^{-6}$, and may be neglected except in precision work, where it has chiefly to be considered in the case of dense crystals and long wave-lengths.

The X-rays on entering the crystal lose energy, partly by transformation, partly by scattering. Some energy may be used in ionizing atoms, with the production of $\beta$ rays, and this energy may reappear as fluorescent X-radiation of longer wave-lengths than that producing it. Some energy is used up in giving momentum to free or freed electrons and this is accompanied by the emission of scattered radiation also of longer wave-lengths (Compton effect), incoherent with the primary radiation. Some energy reappears as heat, due to increased vibration of atoms or molecules. X-rays are also scattered by the outer electrons of the atoms; since the atoms are always vibrating about their mean positions or may even be displaced permanently from the regular lattice points; and since in any case the electron clouds are extended, and not concentrated at the exact lattice points, a good deal of this scattered radiation is incoherent or only approximately coherent, and it forms a general background of diffuse, uneven but weak scattering which cannot be altogether avoided however the crystal is orientated. The fact that the atoms in a crystal are, on the whole, regularly arranged, however, means that *under certain conditions* the scattered radiation from these atoms will be coherent and will interfere constructively to give discrete diffracted (selectively reflected) beams. The total angle of diffraction within the crystal, $2\theta$, is given by the Bragg relation $n\lambda = 2d \sin \theta$, where $d$ is the spacing of the set of crystal planes on which the primary beam is incident in the crystal at angle $\theta$, and $\lambda$ is the wave-length in the crystal. The main transmitted beam, which corresponds to $n = 0$, is reduced both by this selective reflection and by ordinary absorption, the latter term being understood to include all the other effects described above: conversion into $\beta$-rays or fluorescent X-radiation, Compton effect, heating, and incoherent scattering effects.

The ordinary absorption is, relatively speaking, easy to deal with. Except in the neighbourhood of an absorption edge, it is comparatively straightforward to measure. It *must*, however, be measured under conditions where coherent constructive interference cannot take place. *This means that a single crystal must be used and the orientation must be such that the Bragg relation is not satisfied or even nearly satisfied for any set of planes.*

Let us suppose, however, that the absorption is measured, using a single crystal, in a direction corresponding to which some selective

reflection *is* taking place. Clearly the absorption will appear to be much greater than its normal value, because the transmitted beam will have been reduced not only by conversion into $\beta$ rays, &c., but also by the redirection of energy into the reflected beam. By how much the absorption is increased depends principally upon the *texture* of the crystal. If the crystal is perfect the absorption along those directions in which selective reflection takes place may be thirty or even a hundred times as large as the ordinary value. It is so large that the transmitted beam does not penetrate far into the crystal, whose lower layers, therefore, do not get a chance to scatter or to reflect the X-rays at all. This enormously enhanced absorption in a single crystal which has an extended perfect arrangement of atoms is called *primary extinction*. Now, why should primary extinction diminish the *reflected* beam, as it certainly does? In non-mathematical language, the reason is this: A perfect crystal reflects X-rays almost perfectly over a *very limited range* of angle on each side $(\theta \pm s)$ of the Bragg angle $\theta$, where $s = q\lambda/2\pi d \cos \theta$ ($q$ = fraction of the incident amplitude reflected from a single plane) and is of the order of a few seconds of arc. [In practice this formula must be modified to allow for the finite width of an X-ray line, for the fact that the crystal is finite and for differences in the diffraction curves for the two polarized components of the reflected beam.] The rays suffer a change of phase of $\pi/2$ on reflection, and therefore of $\pi$ on double reflection. A doubly reflected ray travels in the same direction as the incident ray, but tends to interfere with it destructively because of its opposite phase. A triply reflected ray travels in the same direction as the once-reflected ray but is again of opposite phase and therefore tends to reduce its intensity. The transmitted beam therefore loses energy both by the reflection of energy away in other directions and by the existence of scattered radiation parallel in direction but opposite in phase to itself. The reflected beam loses energy also through multiple reflection which redirects energy away from its own direction, or into its own direction with opposite phase. It is only in a perfectly regular crystal that these phase relationships, which together with the ordinary absorption result eventually in a complete annihilation (or extinction) of the transmitted beam, can exist. But this is not all. The lower parts of the crystal are not reached by X-rays at the correct angle for reflection and do not therefore make any contribution to the reflected beam. The enhanced absorption effectively limits the reflecting power of the crystal to a 'skin', whose depth depends on the angle and intensity of reflection, but which is of the order of some $10^{-4}$ cm. If the crystallites

in a mosaic or powder are of smaller dimensions than this, then primary extinction is unimportant because the whole of the crystallite will be reflecting; in a sense, it will all be 'skin'. But if the thickness over which the crystal arrangement is perfect is larger than this, then some of the crystal will be quite ineffective for reflection purposes.

Darwin has shown that the ordinary formula for the intensity of reflection from the face of a crystal can be modified to allow for primary extinction by the introduction of a factor[1] tanh $mq/mq$ where $m$ = number of perfect planes occurring in regular succession and $q$ is defined as before. The expression is not strictly applicable unless $mq$ is small, and a somewhat different expression is necessary for other conditions of reflection, for example, through a thin plate,[2] but it will give an indication of the correction to be applied. The expression is almost *independent of wave-length*, because $q = 2Ne^2.d^2F(hkl)/mc^2$ (neglecting the polarization factor), where $N$ is the number of pattern units/unit volume, $d$ the spacing, $F(hkl)$ the structure factor, and $e, m, c$ have their usual meanings. Table I gives the value of the expression for the first five orders of reflection from the cleavage face of rocksalt crystals of various thickness.

TABLE I.

| $n.$ | $hkl.$ | $d$ (Å.U.) | $q.$ | $m$ for $D$(cm.) $D = 10^{-3}.$ | $10^{-4}.$ | $10^{-5}.$ | (tanh $mq$)/$mq$ $D = 10^{-3}.$ | $10^{-4}.$ | $10^{-5}.$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 200 | 2·814 | $2·05 \times 10^{-4}$ | $3·55 \times 10^4$ | $\times 10^3$ | $\times 10^2$ | 0·14 | 0·85 | 1·00 |
| 2 | 400 | 1·407 | 0·30₇ ,, | 7·10 ,, | ,, | ,, | 0·46 | 0·98 | 1·00 |
| 3 | 600 | 0·938 | 0·08₁ ,, | 10·65 ,, | ,, | ,, | 0·81 | 1·00 | 1·00 |
| 4 | 800 | 0·703 | 0·02₆ ,, | 14·20 ,, | ,, | ,, | 0·90 | 1·00 | 1·00 |
| 5 | 10.0.0 | 0·563 | 0·00₉ ,, | 17·75 ,, | ,, | ,, | 0·99 | 1·00 | 1·00 |

Table II gives the primary extinction factor for the first five observable reflections from a diamond plate.

TABLE II.

| $hkl.$ | $q.$ | $m$ for $D = 10^{-3}.$ | $10^{-4}$ cm. | (tanh $mq$)/$mq$ $D = 10^{-3}.$ | $10^{-4}$ cm. |
|---|---|---|---|---|---|
| 111 | $9·84 \times 10^{-5}$ | $4·87 \times 10^4$ | $\times 10^3$ | 0·21 | 0·93 |
| 220 | 2·85 ,, | 7·95 ,, | ,, | 0·45 | 0·98₂ |
| 113 | 1·22 ,, | 9·32 ,, | ,, | 0·71 | 0·99₅ |
| 004 | 1·09 ,, | 11·24 ,, | ,, | 0·68 | 0·99₄ |
| 331 | 0·65 ,, | 12·25 ,, | ,, | 0·83 | 0·99₈ |

An alternative and rather useful form of the expression tanh $mq/mq$ is $(1 - m^2q^2/3 + 2m^4q^4/15 - 17m^6q^6/315 + ...)$ which shows the sharp

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[1] Hyperbolic tangent, tanh $x = (e^x - e^{-x})/(e^x + e^{-x})$.
[2] I. Waller, Ann. Physik, 1926, vol. 79, p. 261.

dependence of the extinction factor upon both $\mathbf{m}$ and $q$. It is clear, however, from the examples given that the *primary extinction* factor is only of importance when the thickness $D$ of perfectly regular atomic arrangement is greater than about $10^{-4}$ cm. and *chiefly affects intensely reflecting planes* ($q$ large) *especially when these are of small spacing* ($\mathbf{m}$ large). In order to be sure that primary extinction is eliminated, it is usual to powder the specimen so finely that the maximum particle size is less than, say, $0.5 \times 10^{-4}$ cm., or, in the case of reflection from a crystal face, to grind the face with a fine abrasive. Immersion in liquid air will also greatly diminish the primary extinction in a single crystal in some cases, although it may not remove it altogether, because the crystal tends to break up on a large scale as well as on a small one, and to disintegrate before the small-scale breaking up is complete.

Irregularities of atomic arrangement in crystals may take different forms. The crystal planes may be warped or distorted, or the spacings may not be quite uniform. The crystal may be composed of a mosaic of tiny perfect crystallites, nearly but not quite parallel to each other; or the crystallites may be parallel but separated by discontinuities at the inter-surfaces. In all these cases, and especially the last, multiple reflection may occur, but the phase relationships which led to destructive interference for both transmitted and reflected beams in the case of a large perfect crystal can no longer exist, because the continuity of arrangement has gone. In all such cases, however, the ordinary linear absorption will be increased in directions corresponding to which there is selective reflection. Energy $Q$ having been removed from the incident beam to form the reflected beam, the amount left to be transmitted will be smaller than if such selective reflection had not taken place. The factor by which $\mu$ is increased on account of selective reflection $Q$ is $gQ$, where $g$ is a constant of the crystal and is independent of the wavelength $\lambda$.[1] If multiple reflection occurs so that energy is redirected into the direction of the transmitted beam (though not now with any phase relationship), then an expression of the form $\mu' = \mu + gQ - g'Q^2 + \ldots$ may be necessary, where $g'Q^2$·and higher terms depend not only on the texture of the crystal but also on other experimental factors. This increase of absorption due to selective reflection is known as *secondary extinction*, and it leads to a decrease of the intensity of reflection, because although the transmitted beam does reach the lower layers of the crystal, yet it is not so strong as if no selective reflection had already

[1] R. W. James and E. M. Frith, Proc. Roy. Soc. London, Ser. A, 1927, vol. 117, p. 62.

occurred in the upper layers. The proportion, $\rho$, of the energy of the incident beam which is reflected away in a given time is, in fact, inversely dependent upon the absorption coefficient $\mu$, and if $\mu$ is increased to $\mu'$, $\rho$ will be decreased. For reflection from a crystal face of a deep crystal, $\rho = Q/2\,\mu'$ where $Q$ is not the theoretical intensity of reflection, but is the actual intensity (i.e. the theoretical value corrected for primary extinction; ($Q_0$ tanh $\mathbf{m}q)/\mathbf{m}q$ in this case). For reflection through a crystal plate, thickness $t_0$, $\rho = Qt.e^{-\mu't}$ where $t = t_0\sec\theta$; and the *maximum* value of $\rho$ will be found for a plate in which the length of path $t = 1/\mu'$, so that $\rho_{\mathrm{max.}} = Q/e\mu'$ (always less, therefore, than the reflection from a face, $Q/2\mu'$). $\mu'$ may be measured directly for any given reflection and wave-length by plotting $\rho$ against $t_0 = t/\sec\theta$; $\mu'$ corresponds to the value of $t_0$ for which the curve has its maximum and for which, therefore, $1/(t_0 \sec\theta) = \mu' = \mu + gQ - g'Q^2 \ldots$ . In order to find $g$, $g'$, &c., this procedure would have to be carried out for more than one set of crystal planes. Using this method for a particular NaCl crystal, Bragg, James, and Bosanquet[1] found $g = 320$, $g'$, &c., negligible.

### *Comparison of primary and secondary extinction factors.*

Writing $\rho = Q/2\mu'$ and $\rho = Qt.e^{-\mu't}$ in the forms $(Q/2\mu).\mu/(\mu+gQ)$ and $(Qt.e^{-\mu t})e^{-gQt}$, it is possible to compare the effect of secondary extinction in the two different sets of experimental conditions and also to see how the secondary compares with the primary extinction factor for reflection from a face. Neglecting polarization, as before, $Q_0$ may be expressed as $\frac{1}{2}(q^2\lambda \tan\theta)$ and therefore, although $q$ is almost independent of $\lambda$, $Q_0$ is not. This introduces an important difference between the two kinds of extinction: *secondary extinction varies with wave-length; primary extinction is almost independent of it.* For a given wave-length, crystal texture and experimental method will decide which is the more important. A second important distinction is that while *primary extinction depends only on perfect crystallite size, secondary extinction depends not only on perfect crystallite size, but also, in the case of transmission, on the over-all size of the crystal.* The dependence on perfect crystallite size occurs because if primary extinction exists, it will powerfully affect the value of the secondary extinction through its influence on $Q$. For a perfect single crystal of linear dimensions, say, $0.5 \times 10^{-4}$ cm. or less, primary extinction is negligible, and it is equally negligible for a single mosaic crystal composed of crystallites of this size. For a perfect crystal

[1] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag., 1921, ser. 6, vol. 42, p. 1.

(or a conglomerate of perfect crystallites) $10^{-3}$ cm. in size, primary extinction is already very important and for a perfect crystal $10^{-2}$ cm. or larger, the expression (tanh $\mathbf{m}q$)/$\mathbf{m}q$ is no longer a sufficiently good approximation to be used, and it is better to use Darwin's original formula for the intensity of reflection from a perfect crystal.

For a perfect single crystal of linear dimensions $10^{-4}$ or even $10^{-3}$ cm., secondary extinction is negligible, but it is *not* negligible for a larger mosaic crystal composed of crystallites of this size, though it will be more important for the conglomerate of smaller than for that of larger crystallites.

Table III shows the relative effect of secondary extinction in the case of (*a*) transmission, (*b*) reflection, from a crystal face, for NaCl crystals 0·1 and 0·01 cm. thickness which are composed of crystallites, say, $10^{-5}$ cm. diameter, so that primary extinction is negligible.

TABLE III.

| | CuKα. | | | MoKα. | | |
|---|---|---|---|---|---|---|
| *hkl.* | $e^{-gQ 0\cdot 1}$. | $e^{-gQ 0\cdot 01}$. | $\dfrac{\mu}{\mu+gQ}$. | $e^{-gQ 0\cdot 1}$. | $e^{-gQ 0\cdot 01}$. | $\dfrac{\mu}{\mu+gQ}$. |
| 200 | 0·05 | 0·74 | 0·84 | 0·51 | 0·93 | 0·71 |
| 400 | 0·64 | 0·96 | 0·97 | 0·88 | 0·99 | 0·93 |
| 600 | 0·86 | 0·99 | 0·99 | 0·98 | 1·00 | 0·99 |
| 800 | ...... not observable | | | 1·00 | 1·00 | 1·00 |
| 10.0.0 | ...... | | | 1·00 | 1·00 | 1·00 |

It is not, strictly speaking, correct to take the same value of $g$ (320) for the two experimental methods, but the results will at least show the trend of the correction. In practice, $g$ should be determined for the crystal and conditions used, but this is by no means easy.[1]

Table IV shows the relative effect of primary and secondary extinction for reflection from the face of a NaCl crystal composed of crystallites (*a*) $10^{-3}$, (*b*) $10^{-4}$ cm. diameter, for the same two radiations.

TABLE IV.

| | Primary $\left(\dfrac{\tanh \mathbf{m}q}{\mathbf{m}q}\right)$. | | Secondary $\left(\dfrac{\mu}{\mu+gQ_0\dfrac{\tanh \mathbf{m}q}{\mathbf{m}q}}\right)$. | | | |
|---|---|---|---|---|---|---|
| | CuKα or MoKα. | | CuKα. | | MoKα. | |
| *hkl.* | $D = 10^{-3}$. | $10^{-4}$ cm. | $10^{-3}$. | $10^{-4}$. | $10^{-3}$. | $10^{-4}$ cm. |
| 200 | 0·14 | 0·85 | 0·97 | 0·86 | 0·94$_5$ | 0·74 |
| 400 | 0·46 | 0·98 | 0·99 | 0·97 | 0·97 | 0·93 |
| 600 | 0·81 | 1·00 | 0·99 | 0·99 | 0·99 | 0·99 |
| 800 | 0·90 | 1·00 | — | — | 1·00 | 1·00 |
| 10.0.0 | 0·99 | 1·00 | — | — | 1·00 | 1·00 |

[1] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag., 1921, ser. 6, vol. 42, p. 1.

## Primary and secondary extinction in powders.

Primary extinction is negligible if the crystallites in a powdered specimen are less than about $0.5 \times 10^{-4}$ cm. diameter. Secondary extinction is never negligible on transmission through a thick specimen composed of fine crystallites, although it will be reduced to a minimum by giving the crystallites a random orientation. As long as energy is deflected from the transmitted beam by selective reflection, secondary extinction must exist. Whether the powder is used in the form of a cylinder, a briquette, foil, or sheet, selective reflection will always take place, and the absorption measured in a certain thickness of such a powder will always (allowance being made for difference of density due to faulty packing) be greater than that measured in an equal thickness of single crystal in such a direction that no Bragg reflection occurs.[1] Other things being equal, the secondary extinction for a powder composed of large crystallites is *less* than that for a powder composed of small crystallites, because primary extinction will have reduced the amount of energy selectively reflected away. Comparative measurements have been made by B. W. Robinson for anthracene single crystals[2] and powders.[3] He measured the linear absorption coefficients using $CuK\alpha$ monochromatized radiation; for the powders his measurements were made in and at right angles to the direction of compression, and corrected to the single crystal density. His results were:

| | |
|---|---|
| Single crystal ... ... ... ... ... ... | 0.503 per mm. |
| Roughly powdered briquette ... ... ... ... | 0.508 „ |
| Briquette of fine precipitated powder, composed of particles $1\cdot2 \times 10^4$ Å.U. diameter, very uniform ... ... | 0.547–0.558 „ |

Unit area, thickness $t$, of a powder plate, reflects away a proportion of the incident beam equal to $\Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta).t$, where $Q_0$ is the energy reflected away per unit volume per unit energy of the incident beam, by a very small crystal element; $p$ is the number of planes in the form contributing to each reflection, and $\theta$ is the Bragg angle. This will be equivalent to an additional linear absorption $\epsilon$ where $1 - \Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta).t = e^{-\epsilon t}$. $\epsilon$ is therefore of the order of $\Sigma\Sigma\frac{1}{2}(Q_0 p \cos\theta)$. For diamond powdered finely, this would mean an increase of linear absorption coefficient from $13.5_0$ to $13.8_8$ per cm. for $CuK\alpha$ and from $1.79_3$ to $1.93_6$ per cm. for $MoK\alpha$ radiation.

[1] R. Brill, H. G. Grimm, C. Hermann, and C. Peters, Ann. Physik, 1939, vol. 34, p. 418.

[2] B. W. Robinson, Proc. Roy. Soc. London, Ser. A, 1933, vol. 142, p. 422.

[3] B. W. Robinson, ibid., 1934, vol. 147, p. 467.

This leads to the question as to whether the absorption coefficient values given in such lists as those of the International Tables for Crystal Structure Determination (Berlin, 1935, vol. 2, pp. 575–585) are the correct values to use for single-crystal work. The evidence suggests that, in general, they are not, for practically all the original measurements were made on powdered material, either in the form of briquettes or of metal foil or sheet. As will be shown later, however, the error introduced by using these values is not serious compared with those due to *unsuspected* crystal perfection. The allowance for secondary extinction in the reflecting power of a powdered specimen is made automatically if the coefficient of linear absorption *measured on the specimen itself* enters into the formula for reflection (as it does in the case of reflection from the surface of a powder briquette). Unlike secondary extinction in a mosaic single crystal, secondary extinction in a powdered specimen is independent of the particular reflection considered, because the rays incident on any little block within the specimen will previously have suffered loss of energy by selective reflection in *all* the possible directions. The allowance for secondary extinction must therefore be included in all cases (low or high orders) where absorption is important at all. For instance, the effect of absorption is very marked in the intensity contours of the Debye–Scherrer lines from cylindrical powder specimens and necessitates careful allowance in work where precision measurements of spacing are required, since the apparent maximum of intensity is by no means at the geometrical centre of each line. Here again the effect of secondary extinction should be included by making absorption measurements on the specimen itself, or on a similar powder.

*Study of extinction by use of a divergent X-ray beam.*

The effect of primary and secondary extinction is particularly notable in *transmission* photographs of single crystals, using a widely divergent beam of characteristic X-radiation.[1] On such photographs there is a background of general plus characteristic radiation on which are *white* lines marking those directions in which differential absorption has occurred, on account of radiation having been reflected away (fig. 1). These lines, however, are not always visible; sometimes the background appears to be uninterrupted by any sort of pattern. The lack of a pattern may be due to incorrect exposure or to unsuitable thickness of the crystal specimen. These can be adjusted by trial or by calculation.

[1] K. Lonsdale, Nature, London, 1943, vol. 151, p. 52; 1944, vol. 153, pp. 22, 433; Phil. Trans. Roy. Soc. London (in press).

Even with a correct exposure and suitable crystal dimensions, however, the pattern of absorption lines may be absent either because the crystal is too perfect (primary extinction), or because it is too imperfect (extinction effects smeared out in all directions). It might be imagined that since primary extinction involves a greatly enhanced absorption co-efficient, the absorption lines would be particularly noticeable for a perfect crystal. But it must be remembered that although absorption is *complete* in the particular directions for which total Bragg reflection
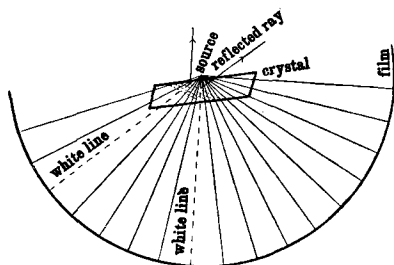


FIG. 1.                    FIG. 2.

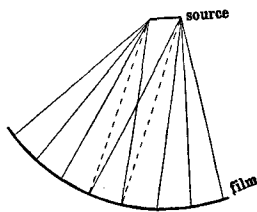FIG. 1. Production of secondary extinction pattern using single crystal and divergent beam.
FIG. 2. Reduction of contrast of sharp absorption in a particular direction, by transmitted rays from another part of extended source.

occurs in an extended perfect crystal, those directions are limited to a few seconds of arc and the proportion of the incident beam absorbed *or* reflected is very small indeed. Also if the source of divergent X-rays is an area instead of an exact point, a sharp absorption in any particular direction will tend to be obscured by transmitted rays of slightly different direction coming from other parts of the source (fig. 2).[1]

In the case of diamond the integrated intensity of reflection $\rho$ from the (111) face of a perfect crystal, using $CuK\alpha$ radiation, is about $4 \times 10^{-5}$, whereas the corresponding quantity for a mosaic diamond is about $2 \times 10^{-3}$, fifty times as large. The absorption line in the first case (primary extinction) will be much less noticeable than that in the second (secondary extinction). In fact the divergent-beam patterns of white lines are secondary extinction patterns. It is possible to prove this experimentally. If a crystal of an organic compound, such as hexamine or oxalic acid dihydrate, is found to give no divergent-beam pattern,

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[1] I am indebted to Dr. W. Ehrenberg of Birkbeck College, London, for this suggestion.

it is possible to make a pattern appear by dipping the crystal into liquid air, a process which would certainly decrease the crystal perfection (R. Brill, *et al.*, 1939, loc. cit.) in an irreversible way. A faint pattern can usually be made more intense by the same procedure. Anthracene is one of the crystals which has been found, by this method, to possess considerable initial perfection in some cases; and this perfection, as has been mentioned before, is not entirely removed by the liquid-air treatment, which does not always have time to break up the crystal on a really small scale before it disintegrates through cracking.

The texture of such crystals as diamond and calcite is not affected by sudden changes of temperature, but it is notable that clear water-white diamonds of obvious perfection do not give a divergent-beam pattern, whereas less perfect specimens (particularly those diamonds known as type II) give good patterns, and the patterns from really distorted diamonds, in which the absorption lines are broad, are usually the most intense of all. The completely mosaic kind of diamond known as *boart* gives no pattern because in this case (as for a powder) all the absorption lines are so broad as to cover the whole film; they are not localized.

Unfortunately, the difficulty of monochromatizing a divergent beam puts *measurement* of secondary extinction by this method out of the question, but the method does give a qualitative idea of the kind and amount of extinction present in any given crystal specimen, and it has shown that both primary and secondary extinction are factors to be reckoned with, even in such relatively soft crystals as those of organic compounds.

*Summary.*—The total absorption and the total scattering from a single crystal or from a crystalline powder are both affected, by primary and secondary extinction, to an extent which varies with crystal texture. The dependence of each on wave-length of X-rays, on perfect crystallite size, and on over-all size of specimen is considered. It is concluded that secondary extinction for a fine powder is greater than that for a coarse powder and that the linear absorption coefficient measured on powdered briquettes or on metal foil is not the correct value to use for single crystal work. Divergent beam transmission photographs give much qualitative information about crystal texture.