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Determination of Elastic Constants of Crystals from Diffuse Reflexions of X-rays.
I. Theory of Method

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This paper describes the use of a Geiger-counter spectrometer for measuring the intensity of the very weak beams of X-rays diffusely reflected from crystals in directions close to, but not coincident with, those corresponding to Bragg reflexions. The reflected beam, being diffusely scattered, is limited by the dimensions of the various slits, and corrections are necessary to allow for the effects of divergence in the beams. Corrections for Compton scattering, for the effects of white radiation and for the mosaic texture of the crystal are also given. The theoretical principles by which the observations may be related to the elastic constants are discussed, and a particular method of selecting the experimental data to give the ratio of elastic constants of cubic crystals is indicated. The main part of the diffuse scattering is due to X-rays which have been scattered from only one elastic wave. A small part is due to X-rays which have been scattered from two elastic waves, and in an appendix is given the analysis by which a correction for the second-order diffuse scattering may be made.

1. Introduction

The principle of the present method of determining elastic constants is based on the theory of thermal diffuse reflexions put forward originally by Waller (1923, 1925, 1928). According to this theory the diffuse reflexions are produced as a result of the superposition of the thermal waves, generated by atomic vibrations, on the static periodicity of the crystal. As a result of this, the regular periodicity of the crystal is modulated by each thermal wave giving rise to a series of dynamic stratifications corresponding to each set of static lattice planes (*hkl*). These dynamic stratifications are inclined at small angles to their associated lattice planes. It is thus possible to get a coherent reflexion from these dynamic stratifications, but at angles not satisfying the Bragg condition with respect to the static lattice planes. The strength of this dynamic reflexion obviously depends on the amplitude of modulation, that is, on the amplitude of the corresponding thermal wave. The latter is again dependent on the frequency of the wave, being smaller the higher the frequency, owing to the partition of energy among the different modes of vibration. On the other hand, the geometry of the dynamic reflexion, i.e. the angles of incidence and reflexion with respect to the static planes, depends on the wave-length and direction of propagation of the wave. Thus, by proper choice of the geometry, it is possible in principle to pick out for observation the dynamic reflexion due to a particular thermal wave having a definite wave-length and a definite direction of propagation. From a measurement of the intensity of this reflexion, the frequency of the wave can be calculated. Combining the two measurements, the velocity of the wave can be obtained. If now it is assumed that these waves are the same as the elastic sound waves in the crystal, but of much higher frequency, then, knowing the velocity of propagation of the waves for different directions of travel, it is possible to calculate the elastic constants of the crystal by the established theory of elasticity. This is the main principle of the present method, though many other factors have to be considered.

2. Experimental method

The practical problem affecting all this work is the measurement of the ratio of the intensity of a strong incident beam of monochromatic X-rays to that of a weak reflected beam of the same wave-length.

The intensity of the X-ray beam was made as constant as possible by using a sealed copper-anode tube (CA–6 G.E.C.) and a source of high tension operated by a machine-set depending on the frequency but not on the voltage of the mains supply. A bent-crystal monochromator (Wooster, Ramachandran & Lang, 1949) was used to produce a beam having a divergence of 30′ and of high intensity. Harmonics of the characteristic radiation, of wave-lengths 1·54/2 and 1·54/3 A., were either eliminated by using a sufficiently low voltage on the X-ray tube or else allowed for in the final determination of the diffuse intensity. The crystal was mounted on a goniometer (Wooster & Martin, 1936) (Fig. 1) consisting of a frame carrying two worm wheels *B* and *C*, *B* being geared to rotate at twice the speed of *C*. The upper worm wheel carries the Geiger–Müller tube, *D*, in a screened box, *E*, and the lower worm wheel carries the crystal. The movement of the Geiger–Müller

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tube can be coupled to that of the crystal through a 2 : 1 spur gearing so that they may be moved together from one reflecting position to another. The crystal is mounted on a vertical circle, *F*, within which is a standard goniometer head, *G*, providing the usual two rotations and three translations, for setting the crystal. The adjustments possible with the vertical circle were found helpful in making the various corrections described below as well as in bringing the crystal into the correct orientation. Two disks *H*, *I*, each carrying six nickel absorption screens, were mounted between the monochromator and the first collimating slit, *a*, of the goniometer.

It was of great importance to determine the intensity of the incident beam with an accuracy of ±1 %. This was achieved by a monitor consisting of an air-filled ionization chamber, and will be the subject of a separate publication. An argon-filled Geiger–Müller counter was used to record the intensity of the Bragg reflexion and also of the diffuse reflexion. A pressure of 60 cm. argon and a length of 17 cm. was used, and quenching was achieved with ethyl alcohol at 1·5 cm. pressure. The plateau extended over 100 V. and the slope of the plateau was 1·5 % for 100 V.

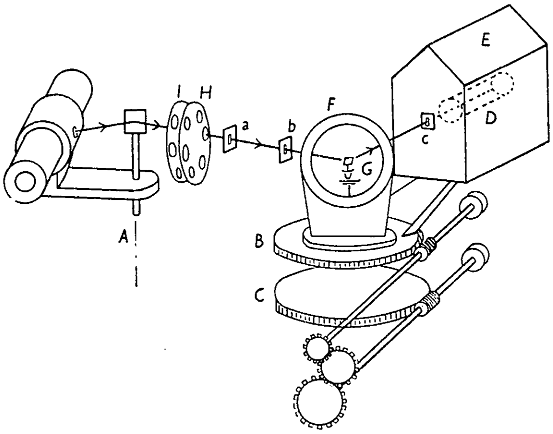

Fig. 1. Component parts of Geiger-counter spectrometer: *A*, axis about which X-ray tube and monochromatising crystal pivot; *B*, *C*, worm wheels supporting counter-box (*E*) and vertical circle (*F*); *D*, Geiger–Müller tube; *G*, goniometer head; *H*, *I*, disks supporting absorption screens; *a*, *b*, *c*, limiting slits.

The electronic counting apparatus consisted of three parts, namely, a background suppressor, a scaler and an averaging meter. The X-ray tube was operated on unrectified a.c., and all the X-rays were produced and recorded during about one-third of each cycle. The background suppressor (Wooster *et al.*, 1948) rendered the counting system inoperative for the two-thirds of each cycle during which X-rays were not produced. The background count was by this means reduced to one-third of its natural value, and the signal/noise ratio thereby increased by a factor of three. The scaler was based on the system described by Rotblat, Sayle & Thomas (1948), though some of its parts were omitted. The averaging circuit was constructed according to the design given by Friedman (1945). The indication of the microammeter was not used for quantitative measurement of intensity and was employed only in finding the crystal setting corresponding to a Bragg reflexion.

3. The orientation of the crystal and the Geiger–Müller tube

In this work it is essential to measure the intensity of the X-rays diffusely reflected from a known volume element in reciprocal space. This volume element is always near to a reciprocal point which corresponds to a strong Bragg reflexion; its position is determined by the setting of the crystal and the Geiger–Müller tube, and its size by the divergence of the incident and reflected beams. The angle of incidence is denoted by i and the angle of total deflexion of the X-rays by ϕ, so that, when a Bragg reflexion occurs from a face parallel to the atomic planes, $i=\frac{1}{2}\phi=\theta$, where θ is the usual Bragg angle. In Fig. 2 Q represents a reciprocal-lattice point and Q' any point near to it. O is the origin of the reciprocal lattice, and reflecting circles of radii $1/\lambda$ are drawn through O and Q, and O and Q' respectively.

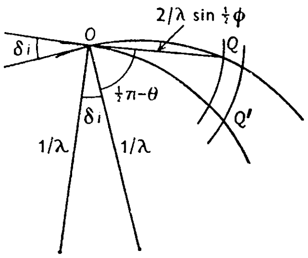

Fig. 2. Two reflecting circles passing through reciprocal points Q, Q' and the corresponding angular relations.

According to the usual construction for reflecting circles, the incident X-rays reflected from Q make an angle of $\frac{1}{2}\pi-\theta$ with OQ. The angle between the diameters of the reflecting circles passing through Q and Q' gives the change, δi, in angle of incidence necessary to make Q' fall on the reflecting circle. In Fig. 2 circles with centres at O are drawn through Q and Q'. These represent the positions of all points in reciprocal space with the same two ϕ values as Q and Q', since the angle of deviation is given by the angle which the line joining Q or Q' to the centre of the corresponding limiting circle makes with the direction of the incident X-rays. It is therefore possible to construct a chart (Fig. 3) consisting of (*a*) circles passing through O having their diameters inclined at any desired angle, e.g. 1°, to one another; and (*b*) circles concentric about O having radii such that they correspond to deviations of any whole number of degrees. For a deviation of ϕ the radius is $(2/\lambda)\sin\frac{1}{2}\phi$ when the radius of the reflecting circle is $1/\lambda$. When such charts are superimposed on a drawing of the reciprocal lattice, based on the relation $d^*=1/d$ and drawn to the same scale as the reflecting circle, the i, ϕ values of any point can be read off. These values can be transferred to the goniometer, and the intensity of the diffusely reflected X-rays then corresponds to the diffuse reflecting power of the particular point in reciprocal space chosen on the drawing. For convenience the whole range of i, ϕ values is covered in three charts of which Fig. 3 represents the last; the ranges covered are $\phi = 20$–$47°$, 42–$70°$ and 66–$100°$. In addition to i and ϕ, a third angular co-ordinate, ψ, is sometimes required. This angle, ψ, gives the tilt of the normal of the reflecting lattice planes to the horizontal plane, and is required in evaluating one of the corrections described below. When it is required to set the angle ψ accurately, the normal to the reflecting planes is made to lie in the plane of the vertical circle, which then bisects the angle between the incident and reflected rays. Rotation of the vertical circle in its own plane then rotates the normal to the lattice planes through the angle defined as ψ.

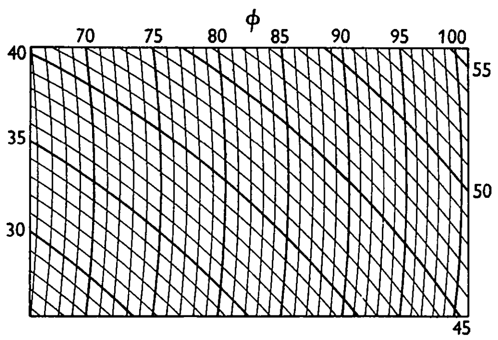

Fig. 3. Chart of i, ϕ values in reciprocal space.

4. Measurement of X-ray intensities

4.1. *Measurement of the diffusely reflected beam*

The flux of diffusely reflected X-rays entering the Geiger–Müller tube through the observing slit is of the order of 20–100 counts/min. The natural background, after reduction by the apparatus described in § 2, was about 15 per min. To obtain an accurate estimate of the extra counts produced by the diffuse reflexions, the following procedure was adopted. Each observation was made over a period of 5 min., during which period the monitor was automatically switched on. This pair of readings from the scaler and the monitor was repeated over several 5 min. periods until more than a thousand counts had been made. Every few measurements the background count was taken over a 5 min. period. The mean of the background counts during a session was taken and subtracted from each of the observed counts to give the number of counts due to the diffuse reflexions alone. The readings of the monitor were used to correct for variations in incident intensity. Since each observation of diffuse flux is based on not less than a thousand counts, the statistical accuracy was $\pm 3\%$.

4.2. *Absolute measurement of the incident flux*

To determine the elastic constants it is necessary to measure the absolute value of the incident flux. For this purpose the incident beam should be reduced to about the same intensity as the diffuse beam, since the Geiger–Müller tube does not possess a linear response at high counting rates. It is impracticable to carry out this reduction by means of absorption screens alone, as the reduction factor is of the order of 10^6 and small amounts of radiation of wave-lengths $\frac{1}{2}\lambda$, $\frac{1}{3}\lambda$, etc., in the monochromatized beam lead to large errors. Consequently, the integrated reflexion was used as an intermediate standard. For the material of the absorption screens nickel is preferable to aluminium. Although the mass absorption coefficient for Cu $K\alpha$, the wave-length of which radiation is denoted by λ, is nearly the same for both nickel and aluminium, nickel absorbs X-rays of wave-length $\frac{1}{2}\lambda$ to the same extent as it absorbs λ, while aluminium absorbs $\frac{1}{2}\lambda$ much less. The ratios of the mass absorption coefficients for nickel and aluminium for the wave-lengths $\frac{1}{2}\lambda$ and $\frac{1}{3}\lambda$ are both approximately 9·0.

The integrated reflexion is given by the expression $J\omega/I_0$, where J is the 'integrated flux', i.e. the total flux of X-rays reflected by the crystal as it is turned through the Bragg setting at a constant angular velocity, ω, with an incident flux of intensity I_0. The procedure adopted for introducing the integrated flux as an intermediate standard involved four separate measurements with the Geiger–Müller tube. During the first two measurements the voltage on the X-ray tube was so low that radiation $\frac{1}{2}\lambda$ was not excited; the third and fourth measurements were taken with the normal voltage on the X-ray tube. The measurements may be summarized as follows:

Low voltage on X-ray tube:

(1) Incident intensity, using absorption screens with a factor of up to 1000.

(2) Integrated flux, using no absorption screens.

High voltage on X-ray tube:

(3) Integrated flux, using absorption screens having a factor of up to 1000.

(4) Diffuse reflexion, using no absorption screens.

The error in using the integrated flux as an intermediate standard is small and arises from the radiations $\frac{1}{3}\lambda$ and $\frac{1}{4}\lambda$ present in the beam at normal working voltages. The intensity of the radiation $\frac{1}{2}\lambda$ is irrelevant, since the absorption coefficient of nickel for this wave-length is the same as for radiation λ. The intensity of the third and higher orders was 0·05 % of the total X-ray intensity, and a small correction has been made on this account. Because of the difficulties inherent in the use of absorption screens, the absolute measurements of the ratio of diffuse flux to the incident flux were probably correct only to 15 %.

5. Corrections to the measurements

5.1. *Compton scattering*

Before applying the measured intensity of the diffuse flux to the calculation of the elastic constants certain corrections must be applied. The first of these is for the Compton scattering. All material gives rise to incoherent scattering of X-rays due to the Compton effect, and the Geiger–Müller tube responds equally to this radiation as to the coherently reflected diffuse X-radiation. Fortunately, the variation of the intensity of Compton scattering with angle is slow compared with the corresponding variation of the radiation in which we are interested, so that it can be allowed for by subtracting the same quantity from every measured value of the diffusing power round any given lattice point. The magnitude of this correction is small for most inorganic substances but becomes large for organic materials. The method of correcting for this constant contribution is described in §9.

5.2. *Geometrical corrections*

The second set of corrections arises partly from the geometry of the apparatus and partly from the imperfections of the crystal and the deviation from strictly monochromatic character of the X-ray beam. The geometrical corrections to the observed intensity are of two kinds: one, called a 'skew correction', is due to the angles of incidence and reflexion being unequal; the other, called a divergence correction, arises from the variation of the volume of reciprocal space which contributes to the reflexion as i and ϕ are varied.

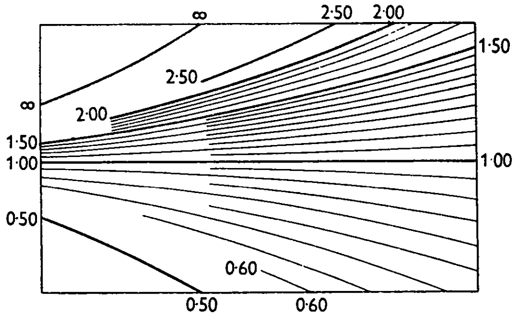

Fig. 4. Chart of absorption correction for the range $\phi = 20$–$47°$.

It may be shown (Laval, 1939) that if the observed diffuse intensity reflected within a given solid angle by a crystal plate, having the reflecting atomic planes parallel to the surface, is $I_{d'}$, and the diffuse intensity which would have been observed from the same portion of reciprocal space if the angles of incidence and reflexion had been equal is I_d, then

$$I_d = I_{d'} \cdot \frac{1}{2}\left(1 + \frac{\sin i}{\sin(\phi - i)}\right).$$

When $\phi = 2i$, obviously $I_d = I_{d'}$. The factor

$$\tfrac{1}{2}\{1 + \sin i/\sin(\phi - i)\}$$

is called the 'skew correction'. Standard charts for this correction have been prepared giving the value of the correction as a function of i and ϕ (Fig. 4). They are constructed to cover the same three regions of reciprocal space as the i, ϕ charts on which they may be directly superposed.

5.3. *Divergence corrections*

These corrections arise from the fact that, owing to the divergence of the incident and reflected beams, a measurement of diffuse reflexion corresponds to a range of values of i and ϕ, and not simply to the values set on the goniometer. Three divergences have to be taken into account: of the angle of incidence i; of the angle of deviation ϕ; and of the vertical divergence, arising from the angular spread of the incident beam in the vertical direction and the finite vertical dimension of the observing slit. As a result of these divergences, the measured value of the diffuse structure intensity is a mean value over a small element of volume surrounding the reciprocal point being studied. The necessity of making these corrections has been pointed out by Olmer (1948). In the present investigation, however, the method of making the correction is somewhat different from that adopted by Olmer. Here, the corrections for the three factors mentioned above are made separately, and are denoted by

i-correction, for divergence of angle of incidence;
ϕ-correction, for divergence of angle of deviation;
and ψ-correction, for vertical divergence.

The principle by which each of the divergence corrections is made is the same and may be described as follows. Suppose that we require the ψ-correction to any given observation of diffuse intensity. Keeping i and ϕ constant, the value of ψ is changed by tilting the crystal, about a horizontal axis lying in its own face, at various angles up to a few degrees on either side of its normal vertical setting. In each of these positions the diffuse intensity is recorded. The crystal and a Geiger–Müller tube are now set to allow the peak of the Bragg reflexion to enter the tube. Again keeping i and ϕ constant, ψ is varied over a sufficiently large range to include the entire Bragg reflexion. We can now plot two curves $F(x)$ and $\mathscr{S}(\delta)$ giving the variation of the diffuse reflecting power with angle x and the variation of the intensity of the Bragg reflexion with the departure, δ, from the normal Bragg setting. If x_0 is the angle at which the diffuse reflexion is being observed, and if

$$g(\delta) = \tfrac{1}{2}\{F(x_0 + \delta) + F(x_0 - \delta)\} - F(x_0),$$

it can be shown by an elementary approximation that the correction to be subtracted from the observed value of $F(x_0)$ is given by

$$\int_0^{\Delta} g(\delta)\, \mathscr{S}(\delta)\, d\delta \Big/ \int_0^{\Delta} \mathscr{S}(\delta)\, d\delta,$$

where Δ is the maximum value of δ for which $\mathscr{S}(\delta)$ is greater than zero. This expression has been derived on the assumption that $\mathscr{S}(\delta)$ is the same for $+\delta$ as for $-\delta$, a condition which is usually fulfilled. A simplification can be introduced experimentally in the determination of the ψ-correction. When diffuse reflexion is received from a region of reciprocal space surrounding a point A, Fig. 5, the vertical divergence permits reflexion from a certain line A_1A_2 of the isodiffusion surface to be recorded. Other observations of the intensity of diffuse reflexion are made corresponding to points B and C. Since the isodiffusion surfaces are similar figures it is necessary to permit reflexion from all points on lines B_1B_2 and C_1C_2 to be recorded if the same fractional error is to be introduced as was obtained at point A, i.e. if the ψ-correction is to remain the same. If the distances QA, QB, QC are R, R', R'' respectively, then

$$A_1A_2 : B_1B_2 : C_1C_2 = R : R' : R''.$$

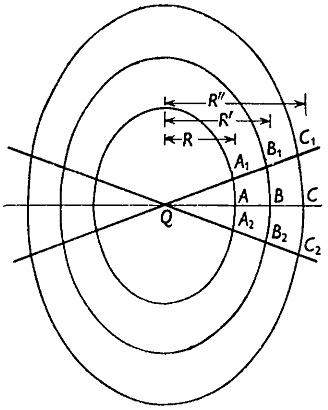

Fig. 5. Diagram showing that for a constant ψ-correction the slit height must be proportional to the distance of the reciprocal point from the reciprocal-lattice point Q.

Since the origin of the reciprocal lattice is a long way off in comparison with the length QA, the change in ψ in going from A_1 to A_2 must be proportional to A_1A_2, i.e. to R. The permitted change in ψ is also proportional to the slit height. Thus, to keep the ψ-correction the same it is necessary to make the slit height, both in front of the crystal and in front of the Geiger–Müller tube, proportional to the distance of the reciprocal point under observation from the nearest reciprocal-lattice point. When the i-correction is to be made, ϕ and ψ are kept constant, but i is varied around the value corresponding to the region in reciprocal space which is being studied. In the second observation i is varied with the chamber set to receive the Bragg reflexion. Thus the two curves for $F(x)$ and $\mathscr{S}(\delta)$ are again obtained. A similar procedure is adopted for finding the ϕ-correction. Finally, all these corrections are added together.

5.4. *White-radiation and mosaic-structure corrections*

It will be convenient at this point to introduce three terms, namely, 'relp', 'rel-vector' and 'rekha'. The term 'relp' signifies any *re*ciprocal-*l*attice *p*oint; 'rel-vector' refers to the line joining such a point to the origin of the reciprocal lattice; and 'rekha' (Sanskrit = ray, to be pronounced rèkha) is a term applied to any line drawn through a reciprocal-lattice point.

Unlike the skew correction and the divergence corrections, which have to be made for every measurement, the corrections considered in this subsection arise only for measurements made at points along certain rekhas. Thus, if the crystal is appreciably mosaic, then the Bragg reflexion would extend over a range of angles on either side of the peak, e.g. along the arc BQB' in the section shown in Fig. 6. Thus, enhanced values would be observed for the diffuse flux for points lying on rekhas close to the rekha AQA'. If this additional flux is not large compared with the true diffuse flux, then it can be eliminated by interpolation from measurements along neighbouring rekhas. This procedure of interpolation is called the correction for mosaic structure.

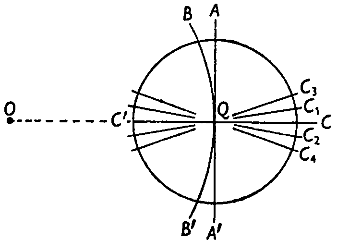

Fig. 6. Diagram showing the rekhas AQA' and CQC' affected respectively by mosaic structure and white radiation.

The white-radiation correction is important for the rekha $C'QC$, i.e. the rekha lying along the rel-vector OQ, and is similar to the mosaic-structure correction, since it is intended to correct for a slightly enhanced diffuse reflexion observed for points along the rekha. The enhancement is due to the small amount of white radiation diffusely reflected by the monochromatizing crystal into the collimator, which could, however, be specularly (Bragg) reflected by the crystal under study. The enhancement is generally less than 10 %, and it can be corrected by interpolation from measurements at points such as C_1, C_2, C_3, C_4 (Fig. 6) lying on the same circle as C, but on rekhas at ±10° and ±20° to the rel-vector, or at other angles, as suitable. It is, however, important to make this correction for every measurement lying on this rekha.

6. Theoretical principles

The complete mathematical theory of diffuse reflexions was first given by Waller (1923, 1925, 1928). Since then, various papers have appeared on the subject, particularly since the experimental discovery of the phenomenon in 1939 by workers in various parts of the world (for a review of the experiments, see Lonsdale (1943)). A review of the theoretical papers may be found in an article by Born (1943), where he has also given a complete derivation of the theory on the basis of quantum mechanics. This particular form of the theory is not, however, suited for the determination of elastic constants, for it aims at expressing the intensity of diffuse reflexion in terms of the interatomic force constants. What is required for the present investigation is a formulation that connects the intensity with the macroscopic elastic properties of the crystal. This has been done in papers by Laval (1939, 1943) and by Jahn (1942). Of these, the former discussed the problem for a general crystal having any number of atoms per unit cell, but did not connect the final formulae explicitly with the elastic constants. The latter has done this, but only for the special case of a monatomic lattice. Jahn has not, however, obtained formulae for absolute intensities of diffuse reflexion. In this paper, these two aspects of the theory have been combined, so that the formulae are applicable to a crystal of any symmetry and having any number of atoms per unit cell.

The intensity of X-rays diffusely reflected by the crystal may be described by means of the quantity 'diffuse structure intensity' defined as the ratio of the intensity of X-rays diffusely reflected per unit cell of the crystal per unit solid angle in the given direction to that scattered by a single free electron under the same conditions. It may be denoted by D. As is well known, if unit intensity of polarized X-rays, having amplitude components p_1 and p_2 normal and parallel respectively to the plane of incidence, is incident on a free electron, then the intensity scattered by it at an angle ϕ per unit solid angle is given by ϵ^2, where

$$\epsilon=\frac{e^2}{mc^2}\sqrt{(p_1^2+p_2^2\cos^2\phi)}. \tag{1}$$

Obviously, the intensity of X-rays diffusely reflected by a unit cell of the crystal under the same conditions is $D\epsilon^2$. The diffuse structure intensity, D, is thus analogous to the square of the structure amplitude, F^2, for Bragg reflexions. The intensity of X-rays diffusely reflected at any particular setting can be considered to be made up of different components called 'first order', 'second order', etc., according as it has interacted with one, two or more thermal waves respectively (Laval, 1939). The diffuse structure intensity of first, second, etc., order may be denoted by D_1, D_2, etc., respectively. These are of diminishing order of magnitude, and, in the present work, we shall consider only the first- and second-order components.

Laval (1939) has shown that the first-order diffuse reflexion from an element of reciprocal space round a point P is produced only by elastic waves having their wave-vectors $\mathbf{R}_\alpha$, equal to $\pm QP$, where Q is the relp nearest to P (Fig. 7). Similarly, it can be shown that the second-order diffuse reflexion from P is produced only by the combined action of pairs of waves, the wave-vectors $\mathbf{R}_\alpha$, $\mathbf{R}_\beta$ of which add vectorially to $\pm QP$ (Fig. 8).

For a given wave vector $\mathbf{R}_\alpha$, there are in the crystal a number of waves with different frequencies, which may be classified as 'acoustical' and 'optical' waves. The former have low frequencies for long wave-lengths, while the latter have relatively high frequencies and are therefore much less effective in producing diffuse reflexions, owing to their small amplitudes. In what follows we shall consider theoretically only the effects of acoustical waves. The method of correcting for the effect of optical waves is indicated in §9.

The following expressions, valid for a region of reciprocal space close to a relp, may be derived for the components of the diffuse structure intensity from the equations of Laval (1939):

$$D_1=\frac{kT}{\tau}\,|\,F_T\,|^2\,\frac{q^2}{R^2}\sum_{\alpha=1}^{3}\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)}{\rho V_\alpha^2}, \tag{2}$$

$$D_2=\frac{k^2T^2}{2\tau^2\rho^2}\,|\,F_T\,|^2\,q^4\sum_\alpha\sum_\beta\frac{1}{N}\,\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)}{V_\alpha^2R_\alpha^2}\,\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\beta)}{V_\beta^2R_\beta^2}, \tag{3}$$

where k is Boltzmann's constant, τ is the volume of the unit cell, F_T is the structure amplitude at temperature T, ρ is the density, $\mathbf{q}$ is the rel-vector OQ and $\mathbf{R}$ the vector QP in Fig. 7, and $\boldsymbol{\xi}_\alpha$ and V_α are respectively the amplitudes and velocities of the three acoustical waves having the wave-vector $\mathbf{R}$. N is the number of unit cells in the crystal. Thus, for a definite direction of the wave-vector $\mathbf{R}$, the intensity of first-order diffuse reflexion is centro-symmetrical with respect to the relp and is inversely proportional to R^2. This is so because $\boldsymbol{\xi}_\alpha$ and V_α depend only on the direction of the wave-vector, but not its magnitude.

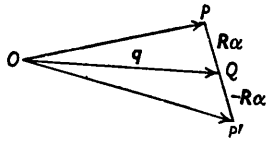

Fig. 7. Vector diagram showing connexion between $\mathbf{q}$ and $\mathbf{R}_\alpha$.

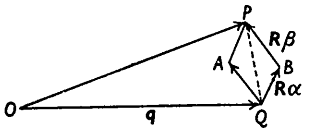

Fig. 8. Vector diagram showing how second-order diffuse reflexion occurs with a proper combination of waves.

The result that D_1 is proportional to $1/R^2$ for a particular rekha $\mathbf{R}$ is of fundamental importance to the present investigation.

In view of the close relationship between the direction of a rekha and that of the elastic waves in the crystal, it is convenient to have the same axes of reference to define a rekha as those used for the elastic constants of the crystal. As is well known, a set of orthogonal coordinate axes is used in crystal elasticity even for non-cubic crystals, and the same axes may be used to define the orientation of the rekha. Thus, a rekha will be denoted by the symbol $[ABC]_{hkl}$, where A, B, C are numbers proportional to the direction cosines with respect to the axes of reference and h, k, l are the indices of the relp with which it is associated. The direction cosines (u, v, w) would obviously be given by

$$(A,B,C)/\sqrt{(A^2+B^2+C^2)}.$$

In general, the direction of a rekha is arbitrary and the parameters A, B, C are not rational. However, in a cubic crystal, if the direction of a rekha happens to be parallel to a zone axis, then A, B, C are rational and are in fact proportional to the zone indices.

When there is no ambiguity, the indices h, k, l may be dropped in describing a rekha. Also for brevity, $[ABC]_{hkl}$ may be written $[\mathbf{R}]_{\mathbf{q}}$, i.e. the rekha parallel to $\mathbf{R}$ associated with the relp $\mathbf{q}$.

7. Evaluation of the rekha constant

In equation (2) for D_1, all the terms except the summation are known or can be readily evaluated. The calculation of the sum $\sum_{\alpha=1}^{3}\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)/\rho V_\alpha^2$ is a problem in crystal elasticity, and an explicit evaluation for cubic crystals has been obtained by Jahn (1942), following earlier work by Faxen (1923), Waller (1923, 1925) and others. The sum is a function of the elastic constants c_{rs} of the crystal and of the indices A, B, C, h, k, l of the rekha. For simplicity, we may write (2) as

$$D_1=\frac{kT}{\tau}\,|F_T|^2\frac{q^2}{R^2}K[ABC]_{hkl}, \tag{4}$$

where

$$K[ABC]_{hkl}=\sum_{\alpha=1}^{3}\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)}{\rho V_\alpha^2}. \tag{5}$$

The function $K[ABC]_{hkl}$ is a characteristic constant of the rekha for the particular crystal and may be called the 'rekha constant'; its value is given by

$$\begin{aligned}K[ABC]_{hkl}={}&P^2(A^{-1})_{11}+Q^2(A^{-1})_{22}+R^2(A^{-1})_{33}\\&+2PQ(A^{-1})_{12}+2PR(A^{-1})_{13}+2QR(A^{-1})_{23},\end{aligned} \tag{5a}$$

where P, Q, R are the direction cosines of the rel-vector hkl with respect to the orthogonal co-ordinates used to define the rekha, and $(A^{-1})_{ij}$ are the elements of the matrix A^{-1} inverse to the matrix A_{ij}, whose elements are given by

Comparing the diffuse structure intensities of first and second order, the following facts may be noticed:

(*a*) D_2 varies as T^2, while D_1 varies as T. Thus, the second-order diffuse reflexion will be more important, the higher the temperature.

(*b*) D_2 and D_1 are both proportional to $|F_T|^2$, but the variation with $\mathbf{q}$ is different; D_2 is proportional to q^4, while D_1 varies as q^2. Thus the second order is relatively more important for a higher relp (i.e. larger hkl) than for a lower one.

(*c*) D_2 varies as $1/R$, while D_1 varies as $1/R^2$. Thus, the second order is relatively less important the closer is the point of observation to the associated relp.

8. Intensity of diffuse reflexion from a crystal plate

From the definitions of the previous sections, the energy diffusely reflected per unit cell of a crystal per unit solid angle per unit incident intensity is $\epsilon^2(D_1+D_2)$, if only diffuse reflexions of first and second order are taken into account. We shall now consider the flux of X-rays diffusely reflected from a crystal plate. Suppose that the incident X-rays make an angle i with the surface of the crystal plate and that the diffusely reflected X-rays suffer a total deviation ϕ. If I_0 is the total flux of incident rays, and $I_{d'}$ the observed intensity of diffuse flux, then a quantity, I_d, called the 'skew-corrected' diffuse flux, has already been given (§ 5.2):

$$I_d=I_{d'}\cdot\frac{1}{2}\left\{1+\frac{\sin i}{\sin(\phi-i)}\right\}. \tag{8}$$

If Ω is the solid angle subtended at the crystal by the observing slit before the Geiger–Müller tube, then

$$\frac{I_d}{I_0}=\frac{\epsilon^2(D_1+D_2)\,\Omega}{2\mu\tau}, \tag{9}$$

where μ is the linear absorption coefficient and τ is the volume of the unit cell.

$$\begin{aligned}
A_{11}&=c_{11}u^2+c_{66}v^2+c_{55}w^2+2c_{56}vw+2c_{15}wu+2c_{16}uv,\\
A_{22}&=c_{66}u^2+c_{22}v^2+c_{44}w^2+2c_{24}vw+2c_{46}wu+2c_{26}uv,\\
A_{33}&=c_{55}u^2+c_{44}v^2+c_{33}w^2+2c_{34}vw+2c_{35}wu+2c_{45}uv,\\
A_{12}&=c_{16}u^2+c_{26}v^2+c_{45}w^2+(c_{25}+c_{46})\,vw+(c_{14}+c_{56})\,wu+(c_{12}+c_{66})\,uv,\\
A_{13}&=c_{15}u^2+c_{46}v^2+c_{35}w^2+(c_{36}+c_{45})\,vw+(c_{13}+c_{55})\,wu+(c_{14}+c_{56})\,uv,\\
A_{23}&=c_{56}u^2+c_{24}v^2+c_{34}w^2+(c_{23}+c_{44})\,vw+(c_{36}+c_{45})\,wu+(c_{25}+c_{46})\,uv.
\end{aligned}$$

This expression can be simplified for crystals of higher symmetry, for particular relps, and for special directions of the rekha.

It is shown in the Appendix that

$$D_2=\frac{\pi^3}{2}\frac{(kT)^2}{\tau}\,|F_T|^2\frac{q^4}{R}K'[ABC]_{hkl}, \tag{6}$$

where

$$K'[ABC]_{hkl}=\sum_{\alpha=1}^{3}\frac{\cos^4(\mathbf{q},\boldsymbol{\xi}_\alpha)}{\rho^2V_\alpha^4}. \tag{7}$$

$K'[ABC]_{hkl}$ is a function only of the elastic constants and of the six indices of the rekha $[ABC]_{hkl}$.

9. The study of diffuse reflexion at points along a rekha

As mentioned earlier, equation (4) gives the diffuse structure intensity at a point close to a relp. An improvement in the correspondence between the observed and theoretical values is obtained by taking averages of the values for points P and P' at equal distances on opposite sides of the relp along the same rekha. This is due to the fact that a small constituent term of D_1, not included in (4), changes sign on going from P to P', whereas the main contribution depends only on R^2. In all the measurements discussed below such an average will be assumed to have been taken.

In the equation

$$D_1=\frac{kT}{\tau}\,|\,F_T\,|^2\frac{q^2}{R^2}K[ABC]_{hkl},$$

the right-hand side consists of four types of factor:

(*a*) the factor kT/τ, which is a constant for a particular crystal and for a fixed temperature;

(*b*) the factor $|\,F_T\,|^2 q^2$, which varies from relp to relp, but is a constant for a particular one;

(*c*) the factor $1/R^2$, which shows how the intensity of diffuse reflexion varies with the distance from the relp along any particular rekha; and

(*d*) the factor $K[ABC]_{hkl}$, which shows how the intensity varies with the direction of the rekha for constant R^2.

Thus, if Q is the relp in Fig. 9, then along any one of the rekhas, such as AA', the intensity varies as $1/R^2$.

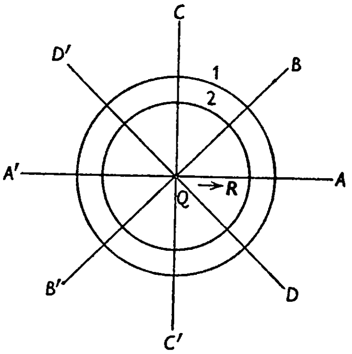

Fig. 9. Diagram showing several rekhas intersecting in Q and passing through two circles.

On the other hand, the intensities at points of intersection of one of the circles, e.g. 1, with the various rekhas will vary as the values of the constants K for these rekhas. Consequently, if we consider two points at the same distance along two rekhas $[A_1B_1C_1]_{hkl}$ and $[A_2B_2C_2]_{hkl}$ associated with the same relp, then

$$\frac{D_1[A_1B_1C_1]_{hkl}}{D_1[A_2B_2C_2]_{hkl}}=\frac{K[A_1B_1C_1]_{hkl}}{K[A_2B_2C_2]_{hkl}}. \tag{10}$$

This expression may be written

$$\left[\frac{A_1B_1C_1}{A_2B_2C_2}\right]_{hkl}.$$

Evidently, the quantity $[A_1B_1C_1/A_2B_2C_2]_{hkl}$ is a function only of the indices A_1, B_1, C_1; A_2, B_2, C_2; h, k, l of the two rekhas, and of the elastic constants, all other quantities in (4) dropping out completely. We may describe this function by the term 'K-ratio'. Experimentally, this quantity may be determined by measuring the values of D at two points at the same distance along the two required rekhas and finding their ratio. However, this requires a knowledge of the intensity of first-order diffuse reflexion due to acoustical waves only. The observed intensity has therefore to be corrected for the presence of other components, such as Compton scattering, fluorescent radiation, diffuse reflexion of second order from acoustical waves and diffuse reflexion due to optical waves.

The intensities of the Compton scattering, fluorescent radiation and scattering due to optical waves vary little over the region of reciprocal space included in the observations made about any one relp. Further, such variation as there is can be eliminated by taking the mean value of the intensities of X-rays scattered from reciprocal volumes at equal distances on opposite sides of the relp. The value of I_1, the diffuse intensity due to first-order scattering from the elastic waves, is found by plotting I_d, the observed diffuse intensity, against $1/R^2$. The points so plotted lie, within the accuracy of the measurement, on a straight line, which cuts the axis of I_d at a point corresponding to the constant contribution of the Compton, fluorescent and optical scattering. This quantity can be subtracted from the observed intensity to give the sum of the intensities, I_1 and I_2, due to first- and second-order elastic scattering. The ratio of I_2 to I_1 can be shown to be

$$\frac{I_2}{I_1}=\frac{\pi^3}{2}kTq^2R\,\frac{K'[ABC]_{hkl}}{K[ABC]_{hkl}}. \tag{11}$$

If the observed diffuse intensity, after allowing for Compton and other constant contributions, is assumed to be entirely due to the first-order elastic scattering, preliminary values of the elastic constants may be calculated. These can be used to obtain $K'[ABC]_{hkl}$ and $K[ABC]_{hkl}$ and hence the ratio I_2/I_1. The correction to I_d on account of I_2 can then be applied and a more accurate set of elastic constants obtained. If necessary this process of successive approximations may be applied again.

10. Optimum conditions for the investigations

The first requisite is obviously that the diffuse flux to be observed should be as large as possible. Since the diffuse structure intensity D_1 is proportional to $q^2\,|\,F_T\,|^2$, i.e. to $|\,F_T\,|^2/d^2$, other conditions remaining the same, it is best to choose for study the neighbourhood of those relps for which this quantity is the largest.

The convenient range of suitable Bragg angles is 20–50°. The lower limit arises from the fact that the skew correction for the outer circles becomes appreciably different from unity if the angle of reflexion is smaller than 20°, and a slight missetting of the crystal is liable to produce large errors. The upper limit arises from two causes. The first is the mechanical limit to the movement of the instrument, which only goes up to $\phi=110°$, so that θ should be less than 50°. Secondly, the formulae of Laval, used in this paper, are based on the assumption that the amplitudes of atomic vibration are small compared with the lattice spacing. The mean amplitude of thermal vibrations at room temperature is of the order of 0·2 A. for most crystals (Lonsdale, 1948). We may therefore assume that 1 A. is a safe lower limit for the lattice spacing. The Bragg angle corresponding to 1 A. with Cu $K\alpha$ is 50°, which is fortunately just within the limit set by the instrument.

Considering next the wave-length of X-rays to be used, it is preferable to work with as long a wave-length as possible for several reasons. First, the scale of the reciprocal lattice is increased with a longer wave-length, so that, for the same angular separation from the Bragg setting, points in reciprocal space closer to the relp can be studied. Secondly, by using a longer wave-length, the lattice spacings of the planes for which the Bragg angle is between 20 and 50° can be made larger than the lower limit of 1 A. For instance, if Mo $K\alpha$ is used, then for d to be greater than 1 A. the Bragg angle must be less than 25°, which is rather small; with Cu $K\alpha$, however, θ can be as large as 50° under the same conditions. A third advantage of using a longer wave-length is that the intensity of Compton radiation, which is important with materials of low atomic number, is thereby reduced. The fourth consideration is concerned with the present set-up in which argon-filled Geiger–Müller counters are used and in which the pressure of gas cannot conveniently exceed 1 atm. Consequently, to get a fairly good efficiency, wave-lengths much smaller than Cu $K\alpha$ cannot be used. There is, of course, an upper limit to the wave-length also, of about 2 A., set by absorption in air, etc. It would appear that the K radiation of one of the elements Fe, Co, Ni, Cu is the most suitable for use; actually Cu $K\alpha$ radiation was employed.

APPENDIX

Intensity of the second-order diffuse reflexion from elastic waves

It has been shown (Laval, 1939) that the second-order diffuse structure intensity D_2 is given by the expression

$$D_2=\frac{k^2T^2}{2\tau^2\rho^2}\,|F_T|^2q^4\sum_\alpha\sum_\beta\frac{1}{N}\,\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)}{V_\alpha^2R_\alpha^2}\,\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\beta)}{V_\beta^2R_\beta^2},\qquad(12)$$

where the summation is to be made over all pairs of acoustical waves for which the vectorial sum of the wave-vectors $\mathbf{R}_\alpha$, $\mathbf{R}_\beta$ is equal to $\pm QP$, where QP is the vector joining the relp, Q, to the centre of the reciprocal volume element P, associated with the scattered radiation.

Suppose that D_2 is to be evaluated for the point P in Fig. 10. Q is the relp and let $\overrightarrow{QP}=\mathbf{R}$, so that all possible combinations of $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ satisfying $\mathbf{R}_\alpha+\mathbf{R}_\beta=\mathbf{R}$ have to be taken into account. Since both $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ have to be equal to a vector within the first Brillouin zone of the crystal, the following construction can be made (Laval, 1939):

In Fig. 10, let $Q_1Q_2Q_3Q_4$ be the first Brillouin zone around Q and let $P_1P_2P_3P_4$ be a similar figure with P as centre. Then all $\mathbf{R}_\alpha$ (e.g. $\overrightarrow{QC}$) must have their termini C inside $Q_1Q_2Q_3Q_4$, and similarly all $\mathbf{R}_\beta$ (e.g. $\overrightarrow{CP}$) must have their origin C inside $P_1P_2P_3P_4$, since they must end at P. To satisfy both conditions, C must lie within the volume common to both figures, shown shaded in Fig. 10. Consequently the summation in (12) has to be performed over this volume. Replacing the sum by an integral

$$D_2=\frac{k^2T^2}{2\tau\rho^2}\,|F_T|^2q^4\sum_\alpha\sum_\beta\times\iiint\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\alpha)}{V_\alpha^2R_\alpha^2}\,\frac{\cos^2(\mathbf{q},\boldsymbol{\xi}_\beta)}{V_\beta^2R_\beta^2}\,d\tau^*,\qquad(13)$$

where $d\tau^*$ is an element of volume of reciprocal space. The integral can in principle be evaluated by numerical or graphical methods, but this is extremely laborious, and it is impracticable to undertake the evaluation for every rekha of a crystal that is investigated. However, if some approximations are made, the expression may be integrated analytically. If the point P lies close to a relp, as is the case in our investigations, then D_2 is in general less than 10 % of D_1. The use of rather crude approximations is therefore justified in evaluating D_2, since the measurement of D_1 is itself expected to be accurate only to about 3 %.

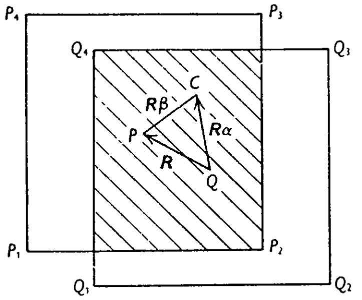

Fig. 10. The area of reciprocal space (shown shaded) within which the points C can lie for the second-order reflexion.

Now, an appreciable part of the integral (13) comes from the region of reciprocal space close to the line QP in Fig. 10. This is because of the presence of the factor $R_\alpha^2R_\beta^2$ in the denominator, which has a minimum value when $\mathbf{R}_\alpha=\mathbf{R}_\beta=\frac{1}{2}\mathbf{R}$. Consequently, we may replace the numerators by the corresponding expression for the wave-vector $\mathbf{R}$, and similarly the velocities V_α and V_β may also be replaced by the corresponding velocity for the direction $\mathbf{R}$. Representing the three waves for the wave-vector $\mathbf{R}$ by the indices $\gamma=1,2,3$, we have

$$D_2=\frac{k^2T^2}{2\tau\rho^2}\,|F_T|^2q^4\sum_{\gamma=1}^{3}\frac{\cos^4(\mathbf{q},\boldsymbol{\xi}_\gamma)}{V_\gamma^4}\iiint\frac{1}{R_\alpha^2R_\beta^2}\,d\tau^*,\qquad(14)$$

with the condition that $\mathbf{R}_\alpha+\mathbf{R}_\beta=\mathbf{R}$. Further, when QP is small compared with the dimensions of the Brillouin zone, the integral may be extended to infinity so as to cover the whole of reciprocal space. This again introduces only a small error, as will be shown below.

The integral in (14) may best be evaluated by taking spherical polar co-ordinates (r, θ, ϕ) for the point C. Take Q as the origin and QP as the original position of the radius vector, so that the angle CQP is θ. Then the integral in (14) is equal to

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{r^2} \frac{1}{(r^2 - 2rR\cos\theta + R^2)} r \sin\theta \, dr \, d\theta \, d\phi, \quad (15)$$

where clearly $R = QP$. Now

$$\frac{1}{\sqrt{(r^2+2rR\cos\theta+R^2)}} = \sum_{n=0}^\infty \frac{R^n}{r^{n+1}} p_n(\mu) \quad (r > R)$$

and

$$= \sum_{n=0}^\infty \frac{r^n}{R^{n+1}} p_n(\mu) \quad (r < R),$$

where $\mu = \cos\theta$ and $p_n(\mu)$ is the Legendre polynomial of order n (Jeffreys & Jeffreys, 1946). Using this substitution, and the well-known integral

$$\int_{-1}^{+1} p_m(\mu) \, p_n(\mu) \, d\mu = \frac{2}{(2n+1)} \delta_{mn},$$

we find that expression (15) is equal to

$$4\pi \left[\int_0^R \Sigma \frac{1}{(2n+1)} \frac{r^{2n}}{R^{2n+2}} dr + \int_R^\infty \Sigma \frac{1}{(2n+1)} \frac{R^{2n}}{r^{2n+2}} dr \right]. \quad (16)$$

The two terms within the square brackets are equal, each being equal to $\frac{1}{R} \sum_{n=0}^\infty \frac{1}{(2n+1)^2}$, so that (16) equals

$$\frac{8\pi}{R} \sum_{n=0}^\infty \frac{1}{(2n+1)^2}. \quad (17)$$

The integral (15) in fact extends only over the shaded volume in Fig. 10 and not over the whole of reciprocal space, as is supposed here. The effect of this may be estimated by considering what happens if the upper limit of r is not infinity, but is equal to the dimensions of the Brillouin zone. Suppose, for example, that this is five times the length R, then the second term of (16) will be reduced by about one-fifth, while the first term is unaffected, so that the total integral is reduced by about 10 %. This error is not important, considering the other approximations which have been made.

Now $$\sum_{n=0}^\infty \frac{1}{(2n+1)^2} = \frac{3}{4} \sum_{n=1}^\infty \frac{1}{n^2} = \frac{3}{4} \zeta(2),$$

where $\zeta(x)$ is the Riemann ζ function of (x). From Jahnke & Emde (1945), $\zeta(2) = \frac{1}{6}\pi^2$, so that the integral (15) is found to be π^3/R, and

$$D_2 = \frac{\pi^3}{2} \frac{k^2 T^2}{\tau \rho^2} \frac{|F_T|^2 q^4}{R} \sum_{\alpha=1}^{3} \frac{\cos^4(\mathbf{q}, \xi_\alpha)}{V_\alpha^4}. \quad (18)$$

Analogously to (5), we may define

$$K'[ABC]_{hkl} = \sum_{\alpha=1}^{3} \frac{\cos^4(\mathbf{q}, \xi_\alpha)}{\rho^2 V_\alpha^4}, \quad (19)$$

so that D_2 can be written in the form (6).

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