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Counter Diffractometer — The Effect of Dispersion, Lorentz, and Polarisation Factors on the Positions of X-ray Powder Diffraction Lines

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The variation of sin θ over a diffraction line in the back-reflection region is such that the centroids of spectral and observed profiles do not correspond exactly in the Bragg equation. The discrepancy has been called dispersion error.

The modification of the line-profile due to the Lorentz factor causes a similar error. Previous derivations of the Lorentz factor have distinguished between the so-called 'polychromatic' factor for single crystals and the 'monochromatic' factor for powder work. Neither are applicable in this case since a 'polychromatic' factor for powder work is required due to the finite spread of wavelengths in the characteristic lines. The new Lorentz factor is calculated, giving

$$P(\psi)\delta\psi \propto F(\lambda)\delta\lambda \tan \psi/2 ,$$

where ψ is the diffractometer angle ($= 2\theta$), $P(\psi)$ the observed profile, and $F(\lambda)$ the spectral profile.

The polarization factor causes a somewhat smaller shift of the centre of gravity of the observed profile.

A theoretical treatment of these aberrations is given. To the first order, the Lorentz factor displaces the centroid by $(2V \tan^3 \bar{\theta})/\bar{\lambda}^2$ and the dispersion factor by an additional $(V \tan^3 \bar{\theta})/\bar{\lambda}^2$, both towards high 2θ, where V is the variance of the spectral profile over the range used, $\bar{\theta}$ is the mean diffraction angle and $\bar{\lambda}$ the mean wavelength. The total correction has been calculated and plotted on the assumption of Cauchy spectral profiles. It is additive to, and independent of, the normal corrections for geometrical aberrations and becomes larger than these at very high angles.

The total effect on the line profile can be corrected by replotting, if each reading is weighted by $(\cos \theta)^{3/2}$, but limitations of this and other replotting techniques, due to their dependence on the other aberrations present, are pointed out.

1. Introduction

Accurate measurements of lattice parameter are now possible with the counter diffractometer as the result of extensive studies over the past few years of all the major aberrations of the instrument.

One such aberration is due to the wavelength spread of the characteristic wavelength 'lines'. The non-linear transformation from the λ to the θ scale given by the Bragg equation causes a shift of the centroid of an observed profile from the value corresponding to the centroid of the spectral profile. This shift may be considered to be made up of a shift due to pure dispersion and a shift due to the Lorentz factor. A third, smaller, shift occurs due to the variation of the polarization factor over the line.

The effects of a distribution of lattice spacings and X-ray wavelengths on line positions have been studied by A. R. Lang (1956). The main conclusion drawn by this author is that the true line profile may be generated from the observed one by replotting against sin θ. Graphs are also given of displacement of centre of gravity assuming Gaussian line profiles.

The purpose of the present paper is to derive a more general expression for the shift of the centre of gravity due to these effects. This will allow corrections to be made, which are accurate to the order of $0{\cdot}001° \, 2\theta$, without the necessity for the replotting of the profiles. It will also permit present techniques of centre-of-gravity determination to be retained. A new method of weighting the individual step-by-step intensity readings is also described which will give the same result as replotting against sin θ. It is pointed out that corrections obtained by replotting techniques are not completely reliable since accurate corrections must be based on the spectral and not on the observed profiles.

2. The angular factor

2·1. *The interference function*

The interference function in reciprocal space $I_P(\mathbf{r}^*)$ for a powdered sample of equal-size crystallites may be generated by considering the single-crystal function $I_O(\mathbf{r}^*)$ oriented in all directions with equal probability. It will therefore be spherically symmetrical about the reciprocal lattice origin,

$$I_P(\mathbf{r}^*) = I_P(|\mathbf{r}^*|) = I_P(r^*) \qquad (1)$$

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and will be given by

$$\iint_{S(r^*)} I_O(\mathbf{r}^*)\,dS = \iint_{S(r^*)} I_P(r^*)\,dS = 4\pi r^{*2} I_P(r^*)\,, \quad (2)$$

where $S(r^*)$ is the spherical surface of radius r^*. If crystallites with a distribution of reciprocal lattice vectors ϱ_{hkl} are present in the sample, the corresponding interference function $J(r^*)$ will be obtained by the superposition of the individual functions,

$$J(r^*) = \sum_{\varrho} I_P(r^*) = \frac{1}{4\pi r^{*2}} \sum_{\varrho} \iint_{S(r^*)} I_{O\varrho}(\mathbf{r}^*)\,dS\,. \quad (3)$$

If a continuous distribution $G(\varrho)$ of ϱ_{hkl} may be assumed

$$J(r^*) = \frac{1}{4\pi r^{*2}} \int_{\varrho} G(\varrho) \iint_{S(r^*)} I_{O\varrho}(\mathbf{r}^*)\,dS\,d\varrho\,. \quad (4)$$

If, further, the crystallites are sufficiently large, $I_{O\varrho}(\mathbf{r}^*)$ will be so sharp that $G(\varrho)$ may be considered constant over the range of ϱ near r^* for which $I_{O\varrho}(\mathbf{r}^*)$ is appreciable, and then

$$J(r^*) = \frac{G(r^*)}{4\pi r^{*2}} \int_{\varrho} \iint_{S(r^*)} I_{O\varrho}(\mathbf{r}^*)\,dS\,d\varrho\,. \quad (5)$$

Since the crystallites are identical, and since $\partial\varrho/\partial r^* = 1$ and $\delta S\,\delta r^*$ is an element of volume in reciprocal space, this may be transformed to

$$J(r^*) = p\,\frac{G(r^*)}{4\pi r^{*2}} \iiint_{\tau_{hkl}} I_O(\mathbf{r}^*)\,d\tau\,. \quad (6)$$

Where τ_{hkl} is the small volume in reciprocal space over which $I_O(\mathbf{r}^*)$ is effective, and p is the multiplicity factor. By a well-known result this reduces to

$$J(r^*) = p\,\frac{G(r^*)}{4\pi r^{*2}}\,Nv^*\,, \quad (7)$$

where N is the number of scattering centres in a crystallite and v^* is the volume of the reciprocal unit cell.

2·2. *The line profile*

We consider wavelengths in the range λ to $\lambda+\delta\lambda$ incident upon the sample while the diffractometer angle ψ $(=2\theta)$ changes at constant angular velocity ω to $\psi+\delta\psi$. If $F(\lambda)\,\delta\lambda$ is the incident intensity flux per second of X-rays in this wavelength range, the total incident flux in the time taken to transverse $\delta\psi$ will be

$$F(\lambda)\,\delta\lambda\,\delta\psi/\omega\,.$$

Now $J(r^*)$ represents the intensity flux diffracted per second per unit solid angle in real space, per unit incident energy, in terms of the scattering power of a single unit of the structure, under the diffraction conditions defined by $\mathbf{r}^*$. The total intensity passing through the receiving slit in the movement through $\delta\psi$ will therefore be

$$P(\psi)\,\delta\psi = \int_{\varepsilon_1}\int_{\varepsilon_2}\int_{\lambda} F(\lambda)\,\frac{\delta\psi}{\omega}\,\frac{1}{2}\left(\frac{e^2}{mc^2}\right)^2 \times |\mathscr{F}|^2(1+\cos^2\psi)J(r^*)\,d\lambda\,d\varepsilon_2\,d\varepsilon_1\,. \quad (8)$$

where ε_1 and ε_2 are the angles subtended by the dimensions of the receiving slit at the sample, and the other terms have their usual meaning. Using equation (7) we have

$$P(\psi)\,\delta\psi \propto \int_{\varepsilon_1}\int_{\varepsilon_2}\int_{\lambda} F(\lambda)\,\frac{G(r^*)}{r^{*2}} \times (1+\cos^2\psi)\,v^*\,d\lambda\,d\varepsilon_2\,d\varepsilon_1\,\delta\psi\,. \quad (9)$$

The integrand may be considered constant over the ranges of ε_1 and ε_2 subtended by normal receiving slits in the back-reflexion region, and since these angles are constant

$$P(\psi)\,\delta\psi \propto \int_{\lambda} \frac{F(\lambda)\,G(r^*)}{r^{*2}}\,v^*(1+\cos^2\psi)\,d\lambda\,\delta\psi\,. \quad (10)$$

If the distribution G is sharp compared with F

$$P(\psi)\,\delta\psi = \frac{(1+\cos^2\psi)}{r^{*2}}\,v^*F(\lambda)\,\delta\psi \int_{\lambda} G(r^*)\,d\lambda \quad (11)$$

$$= \frac{(1+\cos^2\psi)}{r^{*2}}\,v^*F(\lambda)\,\frac{\partial\psi}{\partial\lambda}\,\delta\lambda \int_{r^*} G(r^*)\,\frac{\partial\lambda}{\partial r^*}\,dr^* \quad (12)$$

$$\propto \sin(\psi/2)\,\frac{(1+\cos^2\psi)}{\cos(\psi/2)}\,F(\lambda)\,\delta\lambda \quad (13)$$

using the Bragg relationship between λ and r^*. Similarly, if the distribution F is sharp compared with G

$$P(\psi)\,\delta\psi = \frac{(1+\cos^2\psi)}{\sin^2(\psi/2)}\,v^*G(r^*)\,\frac{\partial\psi}{\partial r^*}\,\delta r^*\,\lambda^2 \int_{\lambda} F(\lambda)\,d\lambda \quad (14)$$

$$\propto \frac{(1+\cos^2\psi)}{\sin^2(\psi/2)\cos(\psi/2)}\,G(\varrho)\,\delta\varrho\,. \quad (15)$$

The first case is normally the one of interest for high-accuracy lattice parameter measurements. Modern technique for such work involves the determination of the centroid of the complete $K\alpha$ doublet, and the distribution $F(\lambda)$ then has a dominant effect. We shall therefore define the angular factor for this case from equation (13),

$$B(\psi) = \tan(\psi/2)(1+\cos^2\psi)\,. \quad (16)$$

3. Displacement of the centroid

3·1. *General theory*

A general treatment allows one to predict the error in the centroid of an observed profile and gives at the same time a weighting factor which will permit the elimination of the correction.

We suppose each intensity reading of the observed profile $P(\psi)$ to be multiplied by some function of ψ, say $\varphi(\psi)$, and the weighted mean value of ψ then calculated

$$\bar{\psi}_\varphi = \frac{\int \psi\varphi(\psi)P(\psi)\,d\psi}{\int \varphi(\psi)P(\psi)\,d\psi} . \tag{17}$$

Now the observed profile is generated from the spectral profile $F(\lambda)$ by the two relations

$$P(\psi)\,\delta\psi = B(\psi)F(\lambda)\,\delta\lambda \tag{18}$$

and

$$\psi = 2 \arcsin (\lambda/2d) = \psi(\lambda) , \tag{19}$$

where d is the mean lattice spacing. Using these two equations and for brevity writing

$$B(\psi) = B(2 \arcsin [\lambda/2d]) = B_1(\lambda) \tag{20}$$

and similarly

$$\varphi(\psi) = \varphi_1(\lambda) \tag{21}$$

we have

$$\bar{\psi}_\varphi = \frac{\int \psi(\lambda)\varphi_1(\lambda)B_1(\lambda)F(\lambda)\,d\lambda}{\int \varphi_1(\lambda)B_1(\lambda)F(\lambda)\,d\lambda} . \tag{22}$$

Defining new functions g and f by the equations,

$$\varphi_1(\lambda)B_1(\lambda) = g(\lambda) \tag{23}$$

and

$$\psi(\lambda)g(\lambda) = f(\lambda) \tag{24}$$

equation (22) becomes

$$\bar{\psi}_\varphi = \frac{\int f(\lambda)F(\lambda)\,d\lambda}{\int g(\lambda)F(\lambda)\,d\lambda} . \tag{25}$$

We may expand f and g about $\lambda = \bar{\lambda}$ by Taylor's theorem, thus,

$$\bar{\psi}_\varphi = \frac{\int \{f(\bar{\lambda})-(\bar{\lambda}-\lambda)f'(\bar{\lambda})+\tfrac{1}{2}(\bar{\lambda}-\lambda)^2f''(\bar{\lambda})+O(\bar{\lambda}-\lambda)^3\}F(\lambda)\,d\lambda}{\int \{g(\bar{\lambda})-(\bar{\lambda}-\lambda)g'(\bar{\lambda})+\tfrac{1}{2}(\bar{\lambda}-\lambda)^2g''(\bar{\lambda})+O(\bar{\lambda}-\lambda)^3\}F(\lambda)\,d\lambda} , \tag{26}$$

The integrals involving $(\bar{\lambda}-\lambda)$ vanish by definition of $\bar{\lambda}$, and using a binomial expansion for the denominator and neglecting powers of $(\bar{\lambda}-\lambda)$ higher than two, we obtain

$$\bar{\psi}_\varphi = \frac{\int \{f(\bar{\lambda})+\tfrac{1}{2}(\bar{\lambda}-\lambda)^2f''(\bar{\lambda})\}F(\lambda)\,d\lambda}{\int g(\bar{\lambda})F(\lambda)\,d\lambda} \times \left[1-\frac{\int \tfrac{1}{2}(\bar{\lambda}-\lambda)^2g''(\bar{\lambda})F(\lambda)\,d\lambda}{\int g(\bar{\lambda})F(\lambda)\,d\lambda}\right], \tag{27}$$

that is,

$$\bar{\psi}_\varphi = \frac{f(\bar{\lambda})}{g(\bar{\lambda})} + \frac{\int (\bar{\lambda}-\lambda)^2F(\lambda)\,d\lambda}{2g(\bar{\lambda})\int F(\lambda)\,d\lambda}\left[f''(\bar{\lambda})-f(\bar{\lambda})\frac{g''(\bar{\lambda})}{g(\bar{\lambda})}\right], \tag{28}$$

but from (24)

$$f''(\lambda) = \psi''(\lambda)g(\lambda)+2\psi'(\lambda)g'(\lambda)+\psi(\lambda)g''(\lambda) , \tag{29}$$

and hence (28) may be written

$$\bar{\psi}_\varphi = \bar{\psi}+V\left\{\tfrac{1}{2}\psi''(\bar{\lambda})+\psi'(\bar{\lambda})\frac{g'(\bar{\lambda})}{g(\bar{\lambda})}\right\}, \tag{30}$$

where $\bar{\psi}$ is $2 \arcsin (\bar{\lambda}/2d)$ and V is the variance of the spectral profile over the limits used.

The second term of equation (30) thus gives the correction to be made to the centroid determined by weighting the observed profile by $\varphi(\psi)$.

3·2. *Weighting function for the correction to vanish*

The requirement upon $g(\lambda)$ for the correction to vanish is

$$\tfrac{1}{2}\psi''(\lambda)+\psi'(\lambda)\frac{g'(\lambda)}{g(\lambda)} = 0 , \tag{31}$$

that is,

$$\frac{1}{2}\frac{\psi''(\lambda)}{\psi'(\lambda)} = -\frac{g'(\lambda)}{g(\lambda)} , \tag{32}$$

which may be integrated, giving

$$\tfrac{1}{2}\log [c\psi'(\lambda)] = -\log g(\lambda) , \tag{33}$$

where c is a constant of integration.

Thus,

$$g(\lambda) = \left(\frac{1}{c\,\psi'(\lambda)}\right)^{\frac{1}{2}} , \tag{34}$$

which, using equation (19), gives

$$g(\lambda) = (cd \cos\theta)^{\frac{1}{2}} = (\cos\theta)^{\frac{1}{2}} \tag{35}$$

choosing the value $c = 1/d$ for simplicity.

Using now equations (35), (23), and (16), we have

$$\varphi(\psi) = \frac{[\cos (\psi/2)]^{3/2}}{\sin (\psi/2)[1+\cos^2\psi]} , \tag{36}$$

which approaches

$$\varphi(\psi) \propto [\cos (\psi/2)]^{3/2} \tag{37}$$

at high Bragg angles.

3·3. *Correction to an unweighted centroid*

If the centroid $\bar{\psi}_0$ of the observed profile is determined in the normal manner, the correction for dispersion, Lorentz, and polarization factors is given by equation (30) with $\varphi(\psi) \equiv 1$.

In this case,

$$\bar{\psi}-\bar{\psi}_0 = -V\left\{\tfrac{1}{2}\psi''(\bar{\lambda})+\psi'(\bar{\lambda})\frac{B_1'(\bar{\lambda})}{B_1(\bar{\lambda})}\right\} = -V\left\{\tfrac{1}{2}\psi''(\bar{\lambda})+\psi'(\bar{\lambda})\left[\frac{d}{d\lambda}\log B_1(\lambda)\right]_{\bar{\lambda}}\right\}. \tag{38}$$

The first term is due to pure dispersion and the second due to the Lorentz and polarization factors.

Performing the differentiations,

$$\bar{\psi}-\bar{\psi}_0 = -\frac{V}{\bar{\lambda}^2}\tan^3\bar{\theta}\left\{3+\cot^2\bar{\theta}-\frac{8\cos^2\bar{\theta}\cos 2\bar{\theta}}{1+\cos^2 2\bar{\theta}}\right\}, \quad (39)$$

which approaches

$$\bar{\psi}-\bar{\psi}_0 = -(3V\tan^3\bar{\theta})/\bar{\lambda}^2 \quad (40)$$

at high Bragg angles.

This expression may be checked for the particular case of a single Gaussian profile, the correction for which has been derived by Lang in the paper quoted above.

It is to be remembered that V is the variance of the *spectral* profile, and not the *observed* one. The observed profile will be broadened symmetrically by the receiving slit width, for example, and it is clear that this cannot affect the displacement of its centroid, although it will increase its variance. Similarly the observed profile will be broadened by other factors, but the displacement of the centroid will be given by the sum of the separate shifts due to each factor, evaluated *before* folding all the weight functions together to obtain the observed profile.

It would appear therefore that Lang's use of the variable c, denoting the ratio of observed to natural half-widths, in the expression for the shift of the centroid, is in error. A similar argument holds against the techniques of replotting against sin θ or weighting by $(\cos\theta)^{3/2}$. These processes will only be accurate if the other aberrations of the line profile are negligible.

Dropping, therefore, the factor c in Lang's equation (7) his result is, in our notation,

$$\bar{\psi}-\bar{\psi}_0 \doteq -5\times10^{-6}\tan^3\bar{\theta}\text{ degrees}.$$

To check equation (40) against this expression we use the value of 0·0006 Å used by Lang for the half-width of the Cu $K\alpha_1$, singlet, which we assume to have a Gaussian profile. The variance will then be

$$V = \frac{(0{\cdot}0006)^2}{(2{\cdot}36)^2}\text{ Å}^2 = 6{\cdot}45\times10^{-8}\text{ Å}^2. \quad (41)$$

Equation (40) gives, therefore,

$$\bar{\psi}-\bar{\psi}_0 = -\frac{3}{(1{\cdot}54)^2}\cdot 6{\cdot}45\times10^{-8}\cdot\frac{180}{\pi}\tan^3\bar{\theta}\text{ degrees}$$
$$= -4{\cdot}7\times10^{-6}\tan^3\bar{\theta}\text{ degrees}, \quad (42)$$

which supplies the required confirmation.

4. Application of the correction

To apply the correction given by equations (39) or (40) the value of V must be known for the portion of the X-ray spectrum used. The assumption of Gaussian profiles for the characteristic lines will involve considerable error. The assumption of Cauchy profiles will be more accurate and this will be made in the present calculations, but the most acceptable method would make use of the variance calculated from spectroscopic data.

4·1. *Single Cauchy profile*

The variance of the single Cauchy profile

$$I = I_0/(1+k^2(\bar{\lambda}-\lambda)^2), \quad (43)$$

with mean value $\bar{\lambda}$ and half-width $2/k$ $(= H)$, over a range of $(+A, -A)$ about the mean, is given by

$$V = \int_{-A}^{+A}\frac{x^2dx}{1+k^2x^2}\Big/\int_{-A}^{+A}\frac{dx}{1+k^2x^2}, \quad (44)$$

which reduces to

$$V = \frac{H^2}{4}\left[\frac{2A'}{\text{arc tan } 2A'}-1\right], \quad (45)$$

where A' is A expressed in terms of the half-width. This expression depends quite critically on the range of integration, as distinct from a Gaussian profile where the 'tails' have a negligible effect.

Making the assumption of a Cauchy profile for the Cu $K\beta_{12}$ line, and using equations (45) and (40), the displacement of the centroid is plotted in Fig. 1, as

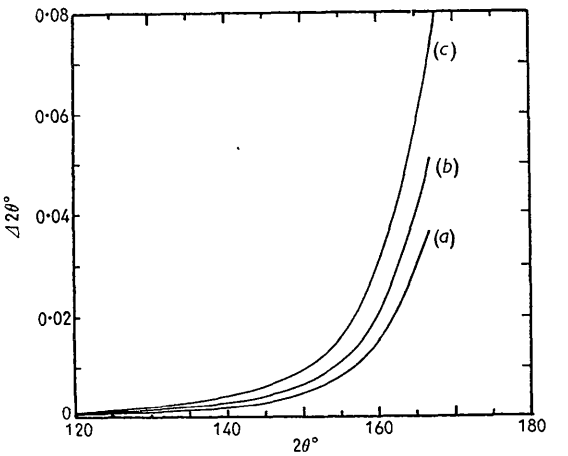

Fig. 1. Displacement towards high 2θ of the observed centroid of the Cu $K\beta_{12}$ line on the assumption of a Cauchy profile, for various ranges of integration. (*a*) $2A = 6\times$H.W. (*b*) $2A = 10\times$H.W. (*c*) $2A = 14\times$H.W.

a function of the Bragg angle, for various overall ranges of integration. The ranges, $2A$, are expressed in terms of the spectral half-width.

4·2. *Doublet*

Equations (39) and (40) hold independently of the form of the profile and all we require to be able to apply the correction to a doublet is, again, the variance of the spectral profile over the appropriate wavelength range.

If we assume the doublet to be composed of two

component profiles at a separation $\Delta\lambda$, we may find the total variance by adding the separate second moments about the new centroid, each weighted according to the relative magnitudes of the components. The second moment of each component about the centroid of the doublet may be found by using the parallel-axes theorem.

Thus if V_1 and V_2 are, respectively, the variances of two components whose integrated intensities are I_1 and I_2, the variance of the doublet is given by

$$V = \frac{1}{I_1+I_2}\left\{I_1\left[V_1+\left(\frac{I_2\Delta\lambda}{I_1+I_2}\right)^2\right]+I_2\left[V_2+\left(\frac{I_1\Delta\lambda}{I_1+I_2}\right)^2\right]\right\}. \tag{46}$$

For the Cu $K\alpha$ doublet we may take, reasonably accurately, $I_1 = 2I_2$, and $V_1 = V_2$. Equation (46) then reduces to

$$V = V_1+\tfrac{2}{9}(\Delta\lambda)^2 . \tag{47}$$

We again assume a Cauchy profile to determine V_1, which is therefore given by equation (45). Using a weighted mean value of the half-widths of the Cu $K\alpha_1$, and Cu $K\alpha_2$ profiles, namely $\frac{1}{3}(2.0{\cdot}60+0{\cdot}75)XU$, and setting $\Delta\lambda$ equal to $3{\cdot}82XU$, the correction for the doublet may be calculated from equation (39)

$$\bar{\psi}-\bar{\psi}_0 = -\frac{180}{\pi(1{\cdot}54)^2} \times\left\{\tfrac{1}{4}(0{\cdot}00065)^2\left[\frac{2A'}{\text{arc tan } 2A'}-1\right]+\tfrac{2}{9}(0{\cdot}00382)^2\right\} \times \tan^3\bar{\theta}\left\{3+\cot^2\bar{\theta}-\frac{8\cos^2\bar{\theta}\cos 2\bar{\theta}}{1+\cos^2 2\bar{\theta}}\right\}. \tag{48}$$

It will be noticed that we have used symmetrical limits for each component, whereas, of course, when we integrate over a range symmetrical about the centroid of the doublet the portions of the individual components included will be quite asymmetrical, and will even have a different asymmetry for each. We are, however, justified in this procedure by the fact that the term in the variance due to the separation of the doublet is much larger than the term due to the variances of the components; for the Cu $K\alpha$ doublet the ratio of the two terms is about 8 to 1. Thus the error introduced by neglecting portions of the tails of the components in calculating the latter term will normally be negligible. We will make this error as small as possible by using for A a weighted mean value of the distances between the centres of each component and their nearer limit. Fig. 2 shows the procedure for the Cu $K\alpha$ doublet.

Fig. 3 gives the displacement towards higher 2θ of the centroid of the Cu $K\alpha$ doublet, as a function of the Bragg angle, for various ranges of integration. The range is the distance between the limits used, converted to the wavelength scale, divided by the mean spectral half-width.

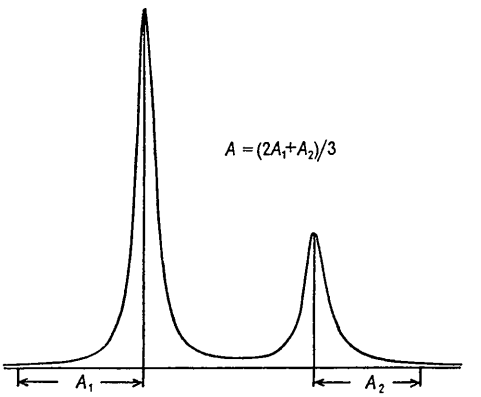

Fig. 2. The value of A to be used in calculating the displacements for a 2:1 doublet.

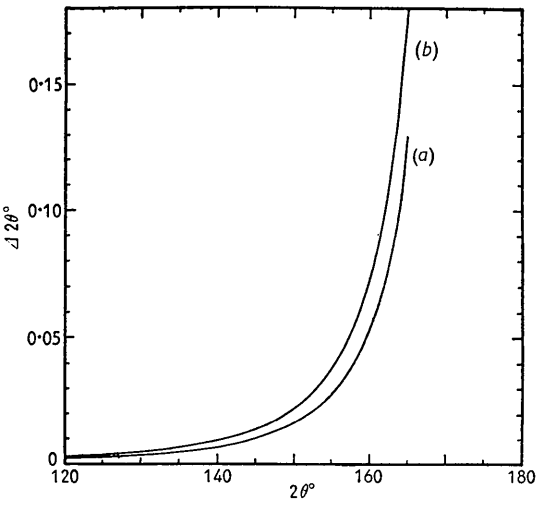

Fig. 3. Displacement towards high 2θ of the observed centroid of the Cu $K\alpha$ doublet assuming Cauchy profiles. (*a*) Range of integration $2A = 10\times$H.W. (*b*) $2A = 30\times$H.W.

5. Conclusions

The following conclusions may be put forward on the basis of the above analysis.

(i) The finite spread of wavelengths in the characteristic X-ray lines causes the observed centroid of a diffraction profile in the back-reflexion region to be displaced towards high 2θ.

(ii) The magnitude of the displacement is such that for precision measurements of lattice parameter with the Cu $K\alpha$ doublet a correction must be applied to all lines above $2\theta \simeq 110°$.

(iii) A correction may be applied most accurately by calculating the centroid of the observed profile in the normal manner and subtracting an amount, given by equation (39), which is a function of Bragg angle and the variance of the *spectral* profile.

(iv) The assumption of Cauchy profiles to calculate the variance of the spectral distribution will give reliable results for a doublet over normal limits, since a

large part of the variance in this case is due to the doublet separation only.

(v) At very high Bragg angles the correction is so large that unless values of the variance are known from empirical spectroscopic measurements, the methods of replotting against $\sin\theta$ or, alternatively, weighting by $(\cos\theta)^{3/2}$ may be comparable in accuracy to that suggested in 4. That they will be more accurate is unlikely, due to the increasing magnitude of vertical-divergence broadening at high angles.

(vi) For completeness, a warning given by Lang (1956) is repeated and extended here. If high accuracy is required, the various analytical or graphical methods proposed for separating the components of a doublet may not be performed on the profiles obtained in the back-reflexion region, due to the different degrees of dispersion in the two components. Such methods are sometimes used in order to find the peak positions of the components for lattice parameter measurement. In the opinion of the author such procedures will rarely, if ever, be worthwhile for this purpose for the following reasons.

If such accuracy is desired that it is thought worthwhile to contemplate such a separating process, then corrections for dispersion, vertical divergence, and other instrumental aberrations should also be applied. This however is almost impossible to effect for the peak position. To correct the doublet shape for dispersion it would be necessary to replot on a $\sin\theta$ scale before proceeding, and even then the result would not be accurate, due to the other aberrations present. For most of the other aberrations it would be necessary to 'unfold' the observed profile from their different weight functions, one by one, by Fourier methods to find the true peak position. Needless to say, this is not a practical course. Thus, the accuracy obtained in finding peak positions by resolving the doublet will be lost in the residual instrumental errors which cannot be eliminated.

Further, the labour involved in such a procedure will exceed that required to find the centroid of the complete doublet, and this latter point may be corrected fully for all the major errors (Wilson, 1950; Pike, 1957), including horizontal and vertical divergences, absorption, and dispersion. The lattice parameter may be found from the centroid of the doublet by using the corresponding value of wavelength from the spectral profile, in the Bragg equation. Until such time as reliable values of these points are determined spectroscopically, the weighted mean of the tabulated $K\alpha_1$, and $K\alpha_2$ components must be used.

It has been demonstrated that the centroid of a profile can be determined experimentally to a reproducibility of the order of $0{\cdot}001°\ 2\theta$, and it would seem that in all cases it will be more profitable to use this point than to try to separate the doublet components to find their peak positions (Pike, 1958).

A discussion of the subject of the determination of line positions for lattice-parameter measurement is in preparation by workers at Cardiff, in collaboration with a group at Philips Laboratories, Irvington, New York, and it is hoped that results will be published shortly.

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