0,4 XE. Die Schwänze der spektralen Verteilung sind völlig weggeschnitten. Durch Anschleifen der Kristalloberfläche kann das Profil der Linie so korrigiert werden, dass die Ausblendung eine Gauss-Verteilung erhält. Man braucht dann bei der Auswertung nur noch die Lage der Spitzen der Präparatreflexe und nicht mehr ihre Profile auszumessen.

2. Werden Messungen an stehenden Präparaten (nach Frohnmeyer & Glocker, 1953) mit Korngrössen zwischen 10μ und 40μ gemacht, so wird die spektrale Verteilung von Cu $K\alpha_1$ möglichst hoch monochromatisiert. Fig. 6 zeigt wieder die Registrierung der spektralen Verteilung von Cu $K\alpha_1$ und hineinregistriert eine hochmonochromatische Ausblendung im Maximum von Cu $K\alpha_1$. Die Halbwertbreite der Ausblendung ist etwa 0,03 XE. Mit dieser hohen Monochromasie können noch Unterschiede der Gitterkonstanten von Korn zu Korn bis zu 1/100 XE gemessen werden.

Diese Art der Monochromatisierung und ihre Anwendungsmöglichkeiten sind im Prinzip sehr einfach. Eine brauchbare technische Lösung ist dagegen schwierig. Obwohl die prozentuale Reflexion der $23\bar{5}4$ Quarznetzebene fast 60% beträgt, ist die Integralintensität der reflektierten hochmonochromatischen Strahlung wesentlich geringer als die Integralintensität einer emittierten Röntgen-Linie. Die Belichtungszeiten sind mit einem ebenen Rückstrahl-Monochromator um den Faktor 20 bis 50 höher als ohne Monochromator.

Eine technische Anwendung ist nur mit einer Hochstrom-Röntgen-Röhre und einem nach Johansson (1933) fokussierenden Rückstrahl-Monochromator möglich.

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The intensity distribution in the focus of curved-crystal monochromators and an estimate of its influence on precision measurements of lattice parameters.

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Introduction

Most of the geometrical factors which influence the precision measurements of lattice parameters have been investigated relatively thoroughly up to now (see for example, Parrish & Wilson, 1959). The influence of physical factors, particularly the spectral energy distribution of the direct beam, is not known so well. The effects of a distribution of lattice spacings and X-ray wavelengths on line position have been studied, for example by Lang (1956). Pike (1959) derived expressions for the shift of the centroid of a line due to dispersion, Lorentz and polarization factor with regard to the distribution of wavelengths, and Ladell, Parrish & Taylor (1959) have computed these factors for several common wavelength distributions using the classical formulae.

In estimating these effects on accurate measurements the non-monochromatized radiation has been considered thus far. Sometimes it appears necessary to monochromatize the radiation. The purpose of this paper is to investigate more closely the effect of accuracy of the Johansson monochromator alignment on the distribution of reflected X-ray wavelengths. (See also Čermák, 1960). The computations in a particular case will show the shift of the centroid and the variation of intensity of $K\alpha_1$ compared to $K\alpha_2$ due to the alignment and will make it possible to draw some conclusions concerning this type of monochromator.

Method of computation

The focus F of a tube (Fig. 1) is projected into F' as a part of focal circle k. F' will be considered henceforth to be the source of radiation. This approximation is sufficient if the aperture of crystal C is not great. The angle of incidence θ on reflecting planes of any ray

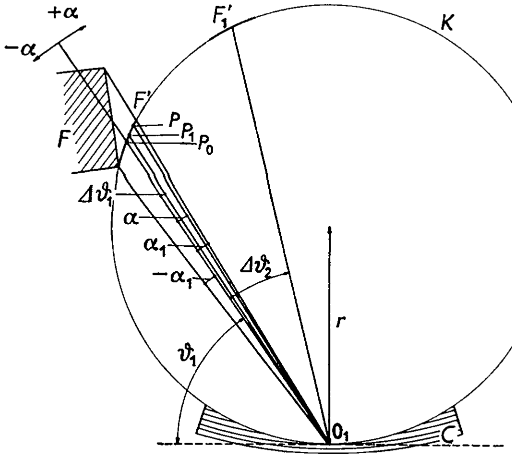

Fig. 1. Geometry of Johansson alignment.

emitted by a point in F' will be the same over the entire crystal. However this angle θ will be different for different points in F'.

Let us denote by λ_0 the wavelength corresponding to the maximum of $K\alpha_1$. Let $J(\lambda-\lambda_0)d\lambda$ be proportional to the energy output of the tube in the range λ to $\lambda+d\lambda$. $J(\lambda-\lambda_0)d\lambda$ then has appreciable values only near λ_0 (we neglect the continuous radiation). Let P_0O_1 make an angle θ_1 with the reflecting atomic planes of the crystal C and let this direction correspond to the maximum of the reflexion curve for λ_0 according to the Bragg law.

The direction P_1O_1 corresponding to λ makes then an angle $\theta_1+\Delta\theta_1$ with atomic planes, where

$$\Delta\theta_1=(\lambda-\lambda_0)(d\theta/d\lambda)\ .$$

We shall now consider the radiation of wavelength λ incident in the direction PO_1 making an angle $\theta_1+\alpha$ with the atomic planes. The argument of the reflexion function R will be in this case $\alpha-\Delta\theta_1$; for λ_0 it would be α only. The energy reflected by the crystal in the range of angles α to $\alpha+d\alpha$ and wavelengths λ to $\lambda+d\lambda$ will thus be

$$J(\alpha,\lambda)d\alpha d\lambda=G(\alpha)J(\lambda-\lambda_0)R(\alpha-\Delta\theta_1)d\alpha d\lambda\ ,$$

where $G(\alpha)$ is the distribution of tube-focus emissivity.

Two assumptions are made in this simple model:

(1) $G(\alpha)$ is the same throughout the whole aperture of the crystal; and

(2) the wavelength distribution $J(\lambda-\lambda_0)$ is the same at all points of the crystal.

Both of these are usually fulfilled to a reasonable degree.

If $G(\alpha)$, $R(\alpha)$, $J(\lambda-\lambda_0)$ are measured, we can easily find the wavelength distribution $J_1(\lambda)$ in the focus F'' of the monochromator

$$J_1(\lambda)d\lambda=J(\lambda-\lambda_0)d\lambda\int_{-\alpha_1}^{\alpha_1}G(\alpha)R(\alpha-\Delta\theta_1)d\alpha\ . \quad (1)$$

If we let the direction P_0O_1 intersect the centre of the source F', the integration limits $-\alpha_1$, α_1 are determined by the angular size of F'. If the source F' is shifted on the focal circle into a new position F_1', the line intersecting the centre of F_1' and O_1 will make an angle $\Delta\theta_2$ with the direction P_0O_1. After a simple transformation equation (1) can be rewritten in the form

$$J_1(\lambda,\Delta\theta_2)d\lambda$$
$$=J(\lambda-\lambda_0)d\lambda\int_{-\alpha_1}^{\alpha_1}G(\alpha)R(\alpha-(\lambda-\lambda_0)(d\theta/d\lambda)+\Delta\theta_2)d\alpha\ . \quad (2)$$

The shifting of F' on the focal circle by a small amount $\Delta\theta_2$ (several minutes or tens of minutes at most) has practically the same effect as the tilting of the crystal around an axis going through O_1 and perpendicular to the plane of incidence. This is just the case when the crystal is being aligned. Knowing $J_1(\lambda,\Delta\theta_2)$, we can easily determine the centroid of $K\alpha_1$ or of the doublet and the relative intensities of $K\alpha_1$ and $K\alpha_2$ for any value of $\Delta\theta_2$.

Computation of experimental data and results

In all these measurements a chromium-target tube with a line focus of dimensions 10 mm. × 1 mm. was used. The numerical values used for computation were: $\lambda_0=2{\cdot}28500$ kX.; $d=3{\cdot}336$ kX. ($(10\bar{1}1)$ planes of quartz); $r=250$ mm. The function $J(\lambda-\lambda_0)$ for the $K\alpha_1$ and $K\alpha_2$ lines was computed by means of a dispersion formula

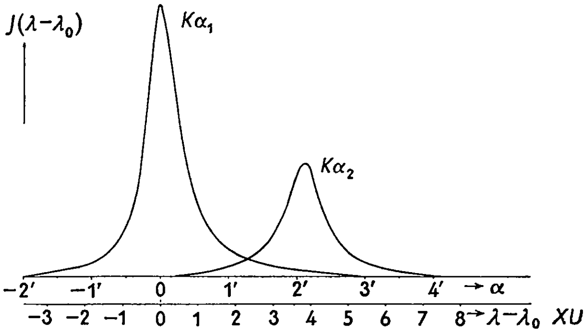

Fig. 2. Wavelength distribution of Cr $K\alpha_1$, $K\alpha_2$ used in computation.

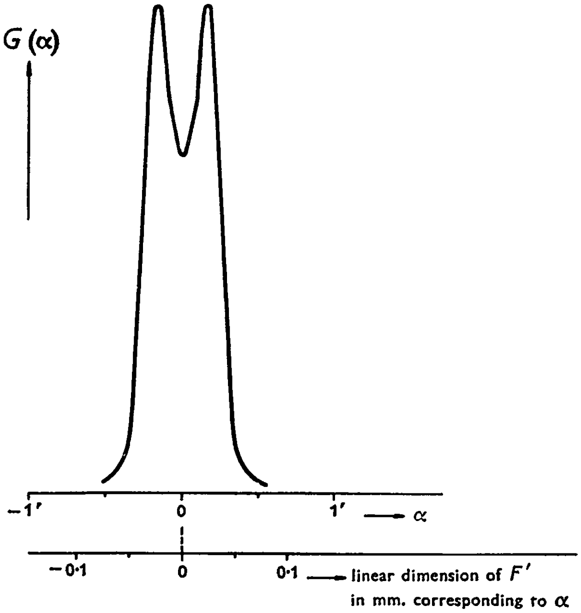

Fig. 3. Tube focus emissivity $G(\alpha)$; photometric record of a pinhole projection.

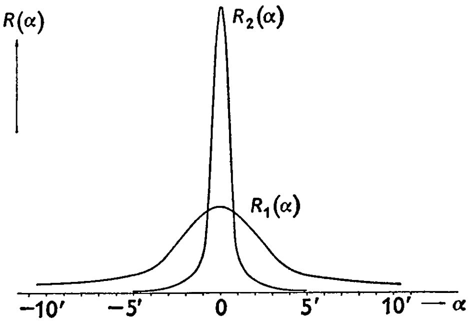

Fig. 4. Reflexion curves: $R_1(\alpha)$ (roughly ground crystals) and $R_2(\alpha)$ (polished crystals). The original curves measured with a two-crystal spectrometer were resolved by Stokes' method.

using the values of index of asymmetry and breadth of spectral lines quoted by Blochin (1957). The tails were truncated (Fig. 2).

The dispersion $d\theta/d\lambda = 0{\cdot}5484$ for $\Delta\theta$ in minutes, $\Delta\lambda$ in X-units. $G(\alpha)$ is shown in Fig. 3 as a microphotometer record of a pinhole pattern of the tube focus. The diameter of pinhole was 0·02 mm. The reflexion curves were measured using a double-crystal spectrometer with roughly ground crystals and with polished crystals. The reflexion curves $R_i(\alpha)$ for one crystal were obtained by Stokes' method, and serve only for illustration in two widely different cases (Fig. 4). Crystals with the curve $R_1(\alpha)$ were ground with an abrasive of average grain size 100–125μ, crystals with $R_2(\alpha)$ were polished.

Table 1. *Relative error of lattice parameter* $\Delta a/a$

$\Delta\theta_2$	$(\Delta\lambda_m - \Delta\lambda_s)/\lambda_0 . 10^4 = (\Delta a/a) . 10^4$	
−4′	1·41	crystal 1
−2′	0·79	reflexion
0′	−0·18	curve $R_1(\alpha)$
+2′	−0·97	
−3′	6·10	crystal 2
−1·5′	4·78	reflexion
−0·83′	1·99	curve $R_2(\alpha)$
0′	−0·79	
+0·83′	−3·13	
+1·5′	−4·40	

In Table 1 $\Delta\lambda_m$ and $\Delta\lambda_s$ are the centroid positions of the component $K\alpha_1$ monochromatized or non-monochromatized respectively, compared to the maximum of the original non-monochromatized $K\alpha_1$. Then

$$(\Delta\lambda_m - \Delta\lambda_s)/\lambda_0 = \Delta a/a \; .$$

We can thus see that the relative error in lattice constant determination depends to a great extent on $\Delta\theta_2$. The angle $\Delta\theta_2$ is in this case practically the measure of the tilting of the crystal from its exactly correct position. This tilting and consequently the error $\Delta a/a$ cannot be easily controlled. If $\Delta\theta_2$ is kept constant the shift of the centroid (and the error $\Delta a/a$) is much more significant if the reflexion-curve breadth is of the same order as the angular breadth of the source F'. If the reflexion curve $R(\alpha)$ is much broader than $G(\alpha)$ the distortion of the lines and the shift are smaller. There exists always one value of $\Delta\theta_2$ (definite position of crystal) for which $\Delta a/a = 0$, i.e. the centroid is not shifted. It is difficult to find this position and to maintain it. Moreover it has no practical meaning as it is simpler to make relative measurements.

Table 2. *Relative intensities of components* $K\alpha_1$, $K\alpha_2$

$\Delta\theta_2$	$I\alpha_1$	$I\alpha_2$	$I\alpha_1/I\alpha_2$	
−4′	0·130	0·142	0·916	crystal 1
−2′	0·302	0·194	1·56	reflexion
0	0·406	0·133	3·05	curve $R_1(\alpha)$
+2′	0·267	0·057	4·68	
−3′	0·041	0·217	0·191	crystal 2
−1·5′	0·214	0·316	0·678	reflexion
−0·83′	0·528	0·122	4·35	curve $R_2(\alpha)$
0′	1·00	0·039	25·8	
+0·83′	0·400	0·015	26·9	
+1·5′	0·140	0·0088	15·9	

It should be pointed out that there is always a certain amount of spectral-profile distortion.

Table 2 indicates the intensities of the monochromatized components $K\alpha_1$, $K\alpha_2$. The $K\alpha_1$ intensity for $\Delta\theta_2 = 0$ of crystal 2 is taken as unity. It may be seen that the intensities of the components as well as their ratio $I\alpha_1/I\alpha_2$ depend considerably on $\Delta\theta_2$. Variations of these values are greater the smaller the breadth of $R(\alpha)$. The ratio $I\alpha_1/I\alpha_2$ does not have its correct spectral value for $\Delta\theta_2 = 0$. The $K\alpha_1$ integrated intensity of crystal 2 attains its maximum, taken as unity, approximately in the position $\Delta\theta_2 = 0$. Crystal 1 has its $K\alpha_1$ integrated intensity maximum only about 0·4 of the maximum integrated intensity of crystal 2 in the same position. This could not have been expected, as the integrated reflexion of crystal 1 is 2·15 times greater than the integrated reflexion of crystal 2 as measured with the double-crystal spectrometer. It may be explained by the ratio of breadths of reflexion curves $R_1(\alpha)$ or $R_2(\alpha)$ to the angular breadth of F'.

Conclusions

(1) Monochromators of the Johansson type always distort the wavelength distribution of the incident beam. The distortion depends to a great extent on the alignment of crystals and increases with the decreasing breadth of $R(\alpha)$ and $G(\alpha)$. It does not seem advisable to use these monochromators in absolute measurements of lattice parameters, as the distortion cannot be simply controlled. A good agreement between the measurements with monochromatized and non-monochromatized radiation cannot be expected as a rule. However these monochromators may be used for relative measurements of lattice parameters.

(2) The monochromatization will be the better, the sharper the peak of the function $\psi(\lambda)$ in (2):

$$\psi(\lambda) = \int_{-\alpha_1}^{\alpha_1} G(\alpha) R(\alpha - (\lambda - \lambda_0)(d\theta/d\lambda) + \Delta\theta_2) d\alpha \; .$$

This requires simultaneously a narrow $G(\alpha)$ (sharp focus) and a narrow $R(\alpha)$ (relatively perfect crystal). It is not sufficient if only one of these curves has a sharp maximum. If these requirements are fulfilled, a suitable spectral range may be chosen by an appropriate tilting of the crystal.

(3) If an intense monochromatized beam is required, the crystal must have not only a large integrated reflexion, but also a reflexion curve of suitable breadth, comparable with the angular breadth of the source. It appears to be desirable that these breadths should not differ greatly. If $R(\alpha)$ is too broad, the whole reflexion range of the crystal cannot be fully used. If $R(\alpha)$ is too narrow, only a small area of the source contributes to the diffracted radiation. The criterion of a large integrated reflexion only is not sufficient.

(4) All values were computed separately for $K\alpha_1$ and $K\alpha_2$. It is hardly possible to apply usual methods for doublet resolution because of the *a priori* unknown ratio $I\alpha_1/I\alpha_2$ in the reflected beam in F''.

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Diffractometer measurement of low-order powder reflexions.

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1. Introduction

A precise determination of low-order lines is necessary when the high-angle region is too crowded, or too weak, to be of any use for:

(i) indexing of patterns when the unit cell is unknown;
(ii) measuring lattice parameters;
(iii) measuring differences in line position between various specimens, caused e.g. by solid solution or by structure defects.

A vast number of research problems falls into the above categories if the angular region is specified as $2\theta = 0°–45°$, with special emphasis on the region 5°–30°, though of course no fixed limits can be given.

As to precision, present diffractometer as well as focusing-camera techniques allow measurements of 2θ to within $\pm 0{\cdot}01°$ in routine determination. Such an accuracy is usually sufficient to make indexing possible (de Wolff, 1957). There can be no doubt, however, that improved accuracy greatly simplifies the indexing problem (Pike, 1959) and that it would be very useful for applications (ii) and (iii) as well. Accordingly, the present paper deals with attempts to reduce the error to a few thousandths of a degree.

2. Existing methods

One way of dealing with the problem is to use an internal standard with known cell constants. This solution is, in principle, capable of yielding a precision limited by the instrumental accuracy and the precision of the lattice parameter of the standard. However, its application is often tiresome, because the necessary sequence of standard lines in the low-angle region is likely to cause frequent overlappings with lines of the unknown. Also the proportion of the mixture is not easily matched to give satisfactory conditions of intensity, and the background is higher than it is for the pure sample. Finally, a suitable standard is sometimes difficult to find because of physical or chemical requirements.

The internal-standard method therefore cannot be regarded as universal. In looking for other methods, one cannot escape an investigation of line profiles, shifts and breadth as caused by various instrumental effects. It then turns out that photographic methods are ruled out because the strongly asymmetric profiles caused by vertical divergence cannot be measured with the required precision; essentially these methods have too many non-linear properties. To reduce the asymmetry very long exposure times are needed. Moreover, photographic methods suffer essentially from the same difficulty in eliminating the 'specimen-displacement error' as other existing methods, as described below.

The normal 'reflexion-type' diffractometer has been investigated thoroughly. A diffraction line can be measured by determining its centre of gravity and applying a few simple corrections (see for example, Parrish & Wilson, 1959). The basic difficulty appears to be the uncertainty of the spectral line profile. This is not very important for our problem, since the ensuing angular error does not exceed $0{\cdot}001°\ \theta$ in the low-angle region.

One correction, however, the 'specimen-displacement error' cannot be made in the usual way by extrapolation, since it is assumed no high-angle lines are available. Once the low-angle lines have been indexed, this correction could of course be found as an extra parameter. For low-symmetry compounds this is by no means easy, and it is of no help in the cases (i) and (iii) mentioned above. The error is likely to be important; it is equal to $114{\cdot}6\ (t/R) \cos \theta$ (in degrees 2θ) where t = displacement and R = goniometer radius (Wilson, 1951).

3. Advantages of 'transmission-type' diffractometer

A much more favourable situation exists for the diffractometer combined with a focusing monochromator as shown in Fig. 1. This instrument is closely related to

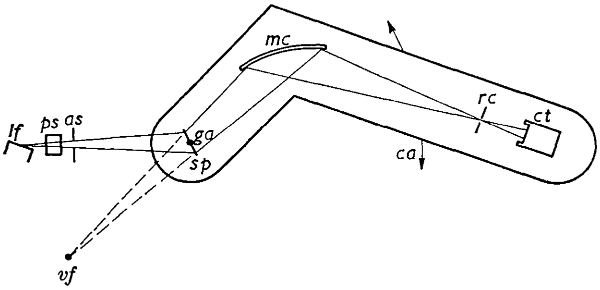

Fig. 1. Geometry of the transmission-type diffractometer.

lf: tube line focus.
ps: parallel (Soller) slits.
as: aperture slit.
sp: specimen, rotating at half the speed of the counter arm.
vf: virtual focal line of monochromator.
ga: goniometer axis.
mc: bent monochromator crystal, mounted on counter arm.
ca: counter arm.
rs: receiving slit.
ct: counter tube.