Contribution to the X-Ray Diffraction Methods for Precision Determinations of Polycrystal Lattice Parameters

The purpose of our present study was to establish the effect of local film shrinkage on the accuracy of the lattice parameter determinations using the peak, line-width mid-point and centroid points of the X-ray diffraction line profile on the photometrical curve, and also to point out that it is advisable to employ, in the case of photographic recording too[1], the radiation wave-lengths corresponding to the line-width mid-point and centroid of the incident spectral distribution in the lattice parameter calculations from line-width mid-point and centroid of photometrical line profile, instead of commonly used in such calculations peak wave-lengths.

(1) Examination of X-ray film shrinkage. As is known, the non-uniform film shrinkage when processed yields an essential error in precision determinations of lattice parameters[3]. The use of the local shrinkage factor σ_i makes it possible to reduce considerably errors as compared to those obtained when using the mean film shrinkage factor $\sigma_{a\,v}$.

We examined the variations of the film shrinkage factor along the length of a film strip. For this purpose, the fiducial marks were scratched along the equatorial line of the film strip and also along the line parallel to it and 2 mm distant from the strip edge, using a special slitted pattern-rule. The spacings between the fiducial marks symmetrical about the central hole of the film were measured using comparator ISA-2 with accuracy of 0.005 mm, by the red light. Each film strip was measured 5 times. All the measurements before film processing were performed at a time, the temperature variations when measuring not exceeding 0.5 °C. All the films were processed simultaneously. A portion of the films was dried after 5 min water rinsing and the rest after 1 h rinsing. The films dried, the spacings between the fiducial marks were measured at the same temperature as before film processing.

The analysis of the experimental data obtained indicated the absence of any regularity in the film shrinkage variations along the strip. Also, the values of shrinkage factors determined along the film strip equatorial line are not the same as those determined along the strip near its edge for equal spacings between the fiducial marks. The rinsing time affects the film shrinkage factor as well.

The data obtained make it evident that any averaging in the film shrinkage factor determinations are inadmissible because the film shrinkage variations along the film strip are not regular and may be affected by many random factors, in particular by changes in the film processing conditions. Therefore, in precision determinations of the lattice parameters it is necessary to establish the local shrinkage factors, that is the shrinkage factors for each particular Debye ring and not for the given X-ray photograph as a whole, the measurements being made strictly along the film strip equatorial line. This last condition is not taken into account in[4].

(2) Determination of local shrinkage factors on X-ray diffraction photographs. A special device (Figure) was constructed for the determination of the local shrinkage factors on X-ray diffraction photographs. 2 films – one processed and the other unprocessed before the exposure – are placed together into the groove made in the cover[1]. Pinholes serving as fiducial marks are pierced by means of a pin (2) of 0.08 mm diameter near the Debye rings of substance under investigation in such a way that the spacing between one pair of marks (inside) be a little less and that between the second pair (outside) a little greater than the Debye ring diameter, the work being carried out by the dark-red light. The spacings between the marks are measured on a processed film using the comparator, at the temperature the film was exposed in the X-ray camera. The spacings between the corresponding marks on the second film after its exposure, processing and drying should be measured at the same temperature. The comparison is made in Table I of the aluminium lattice parameters calculated from X-ray diffraction photographs taken with CuK-radiation employing both the local and the average film shrinkage factors. The data show that in all the cases the standard deviations are greater for the parameters calculated with the average film shrinkage factor than for those calculated with the local one, the differences between parameters determined by the above 2 methods being greater at middle Θ angles than at high ones (see Table I, No. 1, 5, 9 for 422 α_1 and No. 4, 8, 12 for 333 α_2).

(3) Determination of the cristalline lattice parameters using the different points of the X-ray diffraction line profile on the photometrical curve. As mentioned above, 3 methods of lattice parameter estimations are compared: from the positions of the peak, line-width mid-point and centroid of the X-ray diffraction line profile on the photometrical curve using the wave-lengths corresponding to

[1] Wave-lengths corresponding to the incident spectral distribution centroid have been employed, for example, in [2] for the diffractometer method of X-ray diffraction pattern recording.
[2] J. Taylor, M. Mack and W. Garrish, Acta Cryst. *17*, 1229 (1964).
[3] M. E. Straumanis, Acta Cryst. *13*, 818 (1960).
[4] F. I. Bochkaev, Zav. Lab. *5*, 591 (1965).

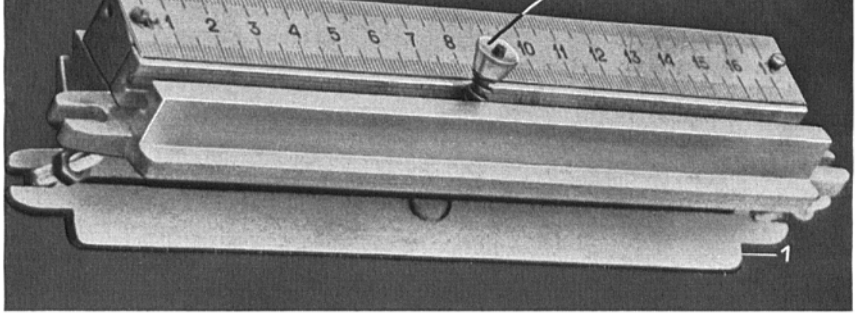

Table I.

No.	hkl	l	$l \cdot \sigma_{loc}$	$\theta°$	aÅ	Δa	l	$l \cdot \sigma_{av}$	$\theta°$	aÅ	Δa
1	422 α_1	127.590	127.721	68.760	4.04858	0.00001	127.590	127.682	68.766	4.04828	0.00018
2	422 α_2	125.402	125.532	69.124	4.04862	0.00003	125.402	125.492	69.131	4.04843	0.00003
3	333 α_1	52.073	52.123	81.332	4.04858	0.00001	52.073	52.110	81.334	4.04856	0.00010
4	333 α_2	46.108	46.164	82.323	4.04860	0.00001	46.108	46.141	82.327	4.04856	0.00010
		$a = 4.04859 \pm 0.00002$ $a_{corr} = 4.04862 \pm 0.00002$ $a_{red} = 4.04925 \pm 0.00002$					$a = 4.04846 \pm 0.00013$ $a_{corr} = 4.04849 \pm 0.00013$ $a_{red} = 4.04912 \pm 0.00013$				
5	422 α_1	127.601	127.733	68.753	4.04855	0.00007	127.601	127.693	68.765	4.04836	0.00014
6	422 α_2	125.372	125.502	69.129	4.04865	0.00003	125.372	125.462	69.136	4.04845	0.00005
7	333 α_1	52.091	52.141	81.329	4.04866	0.00004	52.091	52.128	81.331	4.04864	0.00014
8	333 α_2	46.011	46.067	82.339	4.04861	0.00001	46.011	46.044	82.343	4.04856	0.00006
		$a = 4.04863 \pm 0.00005$ $a_{corr} = 4.04865 \pm 0.00005$ $a_{red} = 4.04928 \pm 0.00005$					$a = 4.04850 \pm 0.00012$ $a_{corr} = 4.04853 \pm 0.00012$ $a_{red} = 4.04916 \pm 0.00012$				
9	422 α_1	127.673	127.805	68.746	4.04893	0.00011	127.673	127.765	68.753	4.04874	0.00003
10	422 α_2	125.384	125.514	69.127	4.04870	0.00012	125.384	125.474	69.134	4.04851	0.00020
11	333 α_1	52.163	52.213	81.317	4.04884	0.00002	52.163	52.201	81.319	4.04882	0.00011
12	333 α_2	46.132	46.188	82.319	4.04881	0.00001	46.132	46.165	82.323	4.04878	0.00007
		$a = 4.04882 \pm 0.00009$ $a_{corr} = 4.04885 \pm 0.00009$ $a_{red} = 4.04948 \pm 0.00009$					$a = 4.04871 \pm 0.00014$ $a_{corr} = 4.04874 \pm 0.00014$ $a_{red} = 4.04937 \pm 0.00014$				

$\sigma_{av} = 1.00072$, $\sigma_1 = 1.00103$, $\sigma_2 = 1.00104$, $\sigma_3 = 1.00096$, $\sigma_4 = 1.00122$, $t = 19$ °C

the equivalent points of the incident spectral distribution employed.

X-ray diffraction patterns were obtained from 99.99% purity aluminium powder. During preparation and exposure of the samples, precautions were taken to minimize the effect of the factors distorting the X-ray diffraction line profile such as the block size, the lattice parameter variations[6], instrumental factors etc. The aluminium powder was recristallization-annealed for 1 h at 350 °C with subsequent cooling in the furnace.

X-ray powder photographs were taken with CuK_α-radiation and a Preston-type powder camera RKF-86 of 86.15 mm diameter having the beam-limiting aperture 0.2 · 3 mm. The X-ray unit URS-70 with the tube BSV-2 was used operating at the 35 kV voltage and 18 mA current intensity. The tube focus-to-specimen distance was 160 mm. The specimens were prepared by coating a layer of aluminium powder on a strip of paper with a small amount of an adhesive and clamped in place so that they accurately fit the cylindrical surface of the X-ray camera (i.e. the focusing circumference).

Fiducial marks were pierced on the films before exposure in the way described in section (2).

X-ray powder photographs after film processing and drying were measured on the microdensitometer MPh-4 having logarithmical converter and automatic strip-chart recorder type EPP-30M2. The microdensitometer carriage motion rate was chosen minimal and that of the strip chart was 9600 mm/h. The density maxima corresponding to the X-ray diffraction lines were recorded on the diagram chart together with the fiducial marks density peaks.

The spacings between the pin-marks on the X-ray diffraction photograph were measured on the comparator immediately after microdensitometer photographic density measuring to avoid the possible film temperature variations. Each photograph was measured 5 times. The spacings on the diagram chart were measured with sliding calipers to an accuracy of 0.1 mm.

To determine the Debye ring diameters, to the spacings between inside pin-marks on the photograph were added the distances from a pin-mark to one or another point selected on the diffraction line profile peak, line-width mid-point or centroid, measured on the diagram chart and converted into the photograph distances by appropriate calculation[6]. Local conversion scale factors estimated from the spacings between the pin-marks located on either side of the doublet were used for both doublet positions (on each side of the central hole of the film).

As a peak-point of diffraction line profile, an intercept was taken of the diagram chart line profile with the straight line that passes through the mid-points of chords traced parallel to the background line. Tracing the background line, the amount of doublet separation was taken into account: with a sufficiently separated doublet, the background lines for each doublet component were traced and with a close doublet the common background line for both components was traced.

The diagram chart line profile centroid position was determined from the well-known formula

$$X_c = \frac{\sum_{i=1}^{n} I_i \, x_i}{\sum_{i=1}^{n} I_i},$$

where X_i is an abscissa of the elementary interval centroid and I_i is its ordinate. The number of intervals, n, was chosen between 30 and 35.

The CuK-radiation wave-lengths used in lattice parameter calculations from the line profile peak were taken from [7].

To obtain the wave-lengths corresponding to the mid-point and centroid of spectral distribution employed, the

[5] G. V. DAVYDOV, G. F. BELYAEVA and P. DZEKANOVSKAYA, Phys. Stat. Sol. *12*, K 29 (1965).

[6] JA. M. GOLOVCHINER, Zav. Lab. *6*, 710 (1964).

[7] L. I. MIRKIN, Spravotchnik po rentgenostrukturnomu analizu polikristallov, F.M.L. (1961).

Table II

No.	Line-peak				Line-width mid-point			Centroid		
	hkl	θ°[a]	*a*Å	Δa	θ°	*a*Å	Δa	θ°	*a*Å	Δa
1	422 α_1	68.752	4.04867	0.00003	68.748	4.04883	0.00003	68.747	4.048911	0.00010
2	422 α_2	69.122	4.04868	0.00004	69.122	4.04883	0.00003	69.127	4.04870	0.00009
3	333 α_1	81.331	4.04859	0.00005	81.324	4.04872	0.00008	81.316	4.04885	0.00004
4	333 α_2	82.323	4.04860	0.00004	82.318	4.04880	0.00000	82.320	4.04878	0.00003
		$a = 4.04864 \pm 0.00004$			$a = 4.04880 \pm 0.00005$			$a = 4.04881 \pm 0.00008$		
		$a_{corr} = 4.04867 \pm 0.00004$			$a_{corr} = 4.04883 \pm 0.00005$			$a_{corr} = 4.04884 \pm 0.00008$		
		$a_{red} = 4.04930 \pm 0.00004$[b]			$a_{red} = 4.04945 \pm 0.00005$			$a_{red} = 4.04947 \pm 0.00008$		

[a] The θ-angle values are the arithmetic means determined from 4 X-ray photographs. [b] Temperature during exposure $t = 19$ °C.

spectral distribution curve was approximated as a triangle having the altitude I_{max}. One obtains from the triangle the relations:

$$\lambda_{av} = \lambda_p + \frac{\Delta\lambda\,(\gamma - 1)}{2\,(\gamma + 1)},$$

$$\lambda_c = \lambda_p + \frac{2\,\Delta\lambda\,(\gamma - 1)}{3\,(\gamma + 1)},$$

where λ_{av} is the line-width mid-point wave-length, λ_c is the centroid wave-length of spectral distribution employed, $\Delta\lambda$ is spectral line breadth, and γ is asymmetry index[8].

The following wave-lengths were calculated from the above formulae:

$\lambda_{av\alpha_1} = 1.54053$Å, $\lambda_{av\alpha_2} = 1.54439$Å, $\lambda_{c\alpha_1} = 1.54054$Å,

$\lambda_{c\alpha_2} = 1.54441$Å.

The errors due to the oblique incidence of rays on the film and those due to specimen absorption were eliminated by the proper relative positions of the film and specimen in the camera[9].

The vertical and horizontal divergence corrections were not employed, believing that with the instrumental geometry chosen they can be neglected[10].

The correction of lattice parameters for refraction and their reduction to the temperature 25 °C were made by the formulae

$$a_{corr} = a\,(1 + \delta),$$

$$a_{red} = a_{corr}\,[1 + \alpha\,(25° - t)],$$

where $\delta = 1 - R$, R is the refractive index, t is the temperature of exposure; α is the coefficient of thermal expansion.

The lattice parameters calculated by use of the 3 above methods are given in Table II. The comparison of the data obtained by different methods show that the parameter values estimated from the X-ray line breadth mid-point precisely coincides with those estimated from line centroid, whereas the parameters estimated from the line peak differ considerably from the centroid parameters.

It should be noted that the aluminium lattice parameter calculated in the present work from the diagram chart line profile centroid with the use of corresponding wave-length and with due regard for local film shrinkage was consistent with the value obtained in [11] accurate to 0.00004.

The lattice parameter values estimated from centroid and line-width mid-point of diffraction line profile but with the use of the wave-length corresponding to the spectral distribution peak are listed in Table III. As is evident from these data, in this case as well, the parameters estimated by the above 2 methods coincide precisely. However the parameter values from Table III differ considerably from those from Table II. Moreover, the standard deviations for the lattice parameter values given in Table III are somewhat greater than those in Table II.

Table III.

No. *hkl*	Θ°	Line-width mid point		Centroid		
		*a*Å	Δa	Θ°	*a*Å	Δa
1. 422 α_1	68.748	4.04878	0.00009	68.747	4.04880	0.00012
2. 422 α_2	69.122	4.04868	0.00001	68.127	4.04854	0.00014
3. 333 α_1	81.324	4.04866	0.00003	81.316	4.04874	0.00006
4. 333 α_2	82.318	4.04864	0.00005	82.320	4.04863	0.00005
		$a = 4.04869 \pm 0.00006$			$a = 4.04868 \pm 0.00012$	
		$a_{corr} = 4.04872 \pm 0.00006$			$a_{corr} = 4.04871 \pm 0.00012$	
		$a_{red} = 4.04935 \pm 0.00006$			$a_{red} = 4.04934 \pm 0.00012$	

In conclusion, it should be noted that, with the use of the technique outlined in the present article, the X-ray diffraction method with photographic film records makes it possible to determine the lattice parameters of polycrystals to the sufficient accuracy employing relatively simple and not tedious calculations[12].

Выводы. Дан способ определения локального коэффициента усадки рентгеновской пленки. Экспериментально сопоставлены три способа определения параметров: по максимуму, по середине ширины и по центру тяжести фотометрической кривой. При этом для расчета параметров применялись вычисленные нами длины волн CuK_α-излучения, соответствующие середине ширины и центру тяжести кривой спектрального распределения.

G. V. Davydov, V. P. Dzekanovskaya and N. A. Erokhov

Chair of Solid State Physics, Pedagogical State Institute, Moscow (USSR), 8th September 1966.

[8] The values of $\Delta\lambda$ and γ for the line components α_1 and α_2 are taken from [7].

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[12] The authors wish to thank candidate of technical Science G. F. Belyaeva for her assistance.