THE ABSORPTION AND REFRACTION CORRECTIONS AND THE LATTICE CONSTANT OF CHROMIUM*

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ABSTRACT

It has been shown by using x-radiations from a Cu and a Cr target that the absorption correction can be neglected at Bragg angles larger than 76°, if the powder mounts are thin enough (0.12 to 0.2 mm. in diameter), using a Lindemann glass hair as a core. However, refraction corrections are necessary to balance the constants obtained with x-radiations of different wavelengths. Adequate correction equations were derived by Ewald, and by A. J. C. Wilson.

The lattice constants of high purity electrolytic chromium and of chromium obtained by the decomposition of chromium iodide were determined with chromium radiation (see Table 3). A refraction correction of +0.00015 kX was added to the results. In contrast to the results obtained with Cu-radiation, no breaks could be detected in the expansivity curves between +10 and 50° C. because of the lower precision of determination (1:40,000 to 1:60,000 with Cr radiation). (Precision with Cu-radiation: about 1:400,000, taking the probable errors in consideration). The average expansion coefficients of the samples agreed with those obtained by Hidnert.

INTRODUCTION

It was shown previously that *no* absorption correction is necessary for lattice constants computed from the last strong line of Debye-Scherrer patterns, if thin Lindemann glass hairs of a diameter 0.08 to 0.1 mm., covered with the powder under study, are used as powder samples.[1,2] It also was shown that the application of the refraction correction *is necessary* in order to balance the lattice constants of the same substance obtained with different x-radiations.[3] However, the introduction of the refraction correction in the case of precision lattice constant determinations from powder patterns has been questioned again recently.[4] Therefore, it seemed advisable to check experimentally once more the question of refraction correction and simultaneously that of the absorption correction.

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[1] Straumanis, M., and Ievinš, A., Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode, J. Springer Berlin 1940, p. 36; reprinted by Edwards Brothers, Inc., Ann Arbor, Michigan (1948). See also *J. Appl. Phys.*, **20**, 726, 728 (1949).

[2] Klug, H. P., and Alexander, L. E., X-Ray Diffraction Procedures, J. Wiley, New York (1954), pp. 455 and 98.

[3] Straumanis, M., Ievinš, A., and Karlsons, K., *Z. physik. Chemie*, **B42**, 143 (1939).

[4] Barrett, C. S., Structure of Metals, McGraw-Hill, New York (1952) p. 150.

A good opportunity was afforded by the determination of the lattice parameters of four high purity chromium samples, using the radiations obtained from a copper and from a chromium target. The starting material was a sintered electrolytic chromium sample (see Table 1), which produced with Cu-radiation very sharp lines even in the highest back reflection region, so that the last line No. 14 (indices 321)[5] at a Bragg angle of 87.36° (at 30° C.) could be measured very well.[6] The line 321, as shown on Fig. 1, has the appearance of a small circle. The difference in diameter of the circle could be clearly seen with the naked eye when the temperature of the sample was changed by 10° C. Fig. 1 shows the diffraction rings at greater temperature differences.
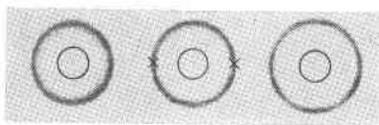
FIG. 1. Back reflection 321α_1 line ($\theta = 87.474°$ to 87.106°) of chromium produced by copper radiation. Temperatures of the sample: 10°, 30° and 60° C. (from left to right). The hole for the collimator is 2 mm. wide. The crosses indicate the points of measurement of the lines. Magnification: 2$\times$

Because of the large back reflection angle and the sharpness of the line the reproducibility of the lattice constant measurements was very high, better than 1:400,000 (considering the probable error), so that a slight break in the expansivity curve of chromium at 32.5° C. could be detected.[6] This point could not be found by other x-ray methods because of their lower precision.[7]

The result of the direct measurement of the a constant of the chromium sample (see below) with copper radiation was

$$2.879123 \pm 0.000007 \text{kX at } 20.0° \text{ C.}$$

not corrected for refraction. As the diameter of the sample was around 0.12 mm. and the reflection angle was above 87°, no absorption correction was applied, because for such a sample at such high angles the absorption correction vanishes. So, the constant above was regarded as a correct one within the given error limits and was used as a standard for comparison with lattice parameters obtained with the same and similar samples but with chromium radiation, yielding the last line No. 6 at a comparatively low Bragg angle of 76.4°. The question of shifting the lines due to absorption by very thin samples (0.1 to 0.2 mm. in diameter) was

[5] Straumanis, M. E., *Am. Mineral.*, **37**, 48 (1952).

[6] Straumanis, M. E., and Weng, C. C., *Acta Crystallogr.*, **8**, 367 (1955).

[7] Fine, M. E., Greiner, E. S., and Ellis, W. C., *J. Metals*, **3**, 56, 189 (1951).

then attacked by: (1) construction of an a-θ (Bragg angle) diagram, and (2) by comparing the lattice parameters as obtained by chromium and copper radiations.

I. The Chromium Used and the Experimental Procedure

Four high purity chromium samples were used, two of them produced by electrolytic methods and the other two by the iodide method.[8] The two latter samples (from the Battelle Memorial Institute) consisted of shiny crystals and were of two different compositions: one sample being

TABLE 1. Composition of 3 High Purity Chromium Samples

Impurity	Sintered electrol. Cr. in % by weight	Iodide Cr. (low in metalics) in % b.w.	Iodide Cr. (low in nonmetallics) in % b.w.
H	0.0001	0.0009	0.0001
O	0.0088	0.014	0.001
N	0.019	0.013	0.001
C	0.005		0.001
S			0.003
Sb	0.01		
Si		<0.001	0.001
Fe		<0.001	0.005–0.1
Cu		<0.001	<0.001
Mn		<0.001	0.001–0.01
Mg		<0.001	<0.001
Co		<0.001	—
Ni		—	<0.005
Ca		<0.001	<0.001
Re		<0.001	0.0001–0.001
W		<0.1*	0.001–0.01

* Tungsten probably not present but standard used was only this sensitive.

low in metallic admixtures, and the other low in non-metallics, such as hydrogen, nitrogen, carbon and sulfur.[8] The chemical analyses of the three samples, as given by the manufacturers, differ somewhat and are listed in Table 1. The purity of the fourth sample, an electrolytic, degassed chromium (from C. Hardy Inc.) was probably of the same grade as that of the sintered sample (it was treated in hydrogen at an elevated temperature) because of the close agreement of the lattice constants of the two samples (see Table 3).

[8] Goodwin, H. B., Gilbert, R. A., Schwartz, C. M., and Greenidge, C. T., *J. Electrochem. Soc.*, **100**, 152 (1953). Metallurgical evaluation of iodide chromium; see Maykuth, D. J., Klopp, W. D., Jaffee, R. J., and Goodwin, H. B., *ibidem* **102**, 316 (1955).

Small quantitites of each of the samples were ground in agate mortars. Because of plastic deformation, the metal, after being ground for several hours, was in the form of fine leaflets. The powder was then carefully sieved through a 325 mesh screen. Only the fine powder that passed the sieve was placed in a silica glass bulb, which was evacuated while being heated, then sealed off. Next, the bulb was heated at 850° C. for $2\frac{1}{2}$ hours to expel the remainder of the dissolved gasses in the chromium powder, and to recrystallize the highly deformed metal leaflets. A longer time for heating or a higher temperature could not be applied, because otherwise the grain size would become so coarse that spots would be formed on the x-ray powder diagrams.

The exact values of the lattice constants of the 4 chromium samples were calculated from powder diagrams obtained in precision cameras of 64 mm. diameter, the sample and the camera having a constant temperature. The constancy of the temperature was maintained within limits of $\pm 0.05°$ C. by placing the camera in a special thermostat for a few hours previous to the exposure. The temperature was controlled by circulating water of a thermostatic bath, as previously described.[1,9,10] The exposures were made at ten-degree intervals between 10 and 50° C. For measuring the films, which were 18 cm. in length, a comparator accurate to 0.001 mm. was used. The bare films were inserted into the camera in the asymmetric position so that no correction for film shrinkage nor comparison with a standard substance was necessary. The values of the lattice constants were computed directly from the Bragg angles obtained from the measurement of the films[10] without application of any analytical or graphical extrapolation method. The powder mount was as thin as possible, 0.12 to 0.2 mm. in diameter,[1,9,10] and was rotated during the exposure. In contrast with copper radiation, chromium radiation could be used without complications; the films were clear and the lines sharp and uniform, even without scanning the sample.[11] The collimator bore was 0.8 mm. However the low Bragg angle of 76.4°, of the last doublet No. 6 (211 α_1 and α_2 of Cr radiation) appreciably decreased the precision of the calculated lattice constants. The doublet was clearly resolved, though only α_1 could be used for the lattice constant calculations because the constants calculated from α_2 lines were too low. Evidently the readings of the α_2 lines (according to Bradley and Jay) were influenced by the strong lines which were in close proximity.[12] The wavelength of CrKα_1 used was 2.28503kX, and the exposure time was one hour.

[9] Straumanis, M. E., and Aka, E. Z., *J. Appl. Phys.*, **23**, 330 (1952).

[10] Straumanis, M. E., *Analyt. Chem.*, **25**, 700 (1953).

[11] Straumanis, M. E., and Aka, E. Z., *Rev. Scient. Instr.*, **22**, 843 (1951).

[12] Bradley, A. J., and Jay, A. H., *Proc. Physic. Soc.*, **44**, 563, 574 (1932).

II. THE ABSORPTION CORRECTION

For the construction of the θ-a curve the four strongest interferences in the powder patterns of chromium (chromium radiation) were used: 110β, 110α, 200α and $211\alpha_1$. However the respective Bragg angles, as determined from only *one* film would very seldom give the true a-θ curve, because of the great fluctuation of the constants calculated from lines at lower angles, due to the presence of $\sin\theta$ in the Bragg equation. The only possibility of obtaining the true average statistical curve is to measure the mentioned lines on several films and then to plot the average results.
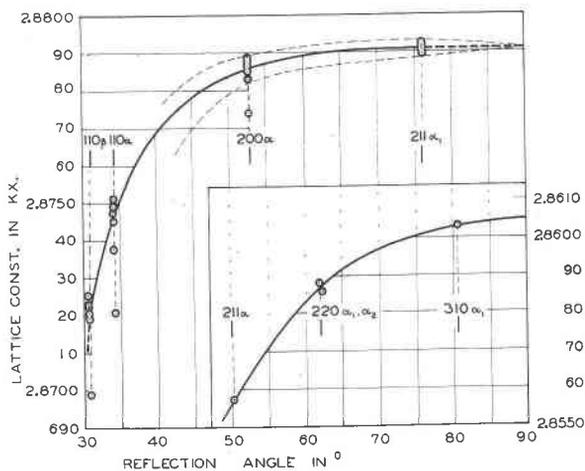
FIG. 2. Lattice constant of Cr (powder mount 0.12 to 0.2 mm. in diameter) versus θ (Cr radiation); 64 mm. camera; 30.0° C. Inset: Lattice constant of Armco Fe (the powder mount was thicker) versus θ (Co radiation) according to Bradley and Jay; 90 mm. camera.

Six films were used for this purpose, these were of electrolytic chromium at a sample temperature of 30.0° C.

As the lattice constants of both electrolytic chromium and the sintered sample (Table 1) agreed closely (Fig. 3), three powder patterns of each sample were used. From the four mentioned lines the lattice parameters were computed and plotted against the Bragg angle θ. Of course, the scattering of the computed lattice parameter values (because of $\sin \theta$) increased with a decreasing angle of reflection. To show the a-θ relation the Kettmann extrapolation curve[13] was drawn through the estimated peaks of the accumulations of the computed points and a smooth curve (Fig. 2) which seemed to terminate in a line parallel to the abscissa, was obtained. This may mean that the average constant as computed

[13] Kettmann, G., *Z. f. Physik.*, **53**, 198 (1929).

from $211\alpha_1$ ($\theta = 76.4$) is the final value and *does not have to be corrected* for absorption, providing powder mounts as previously described are used.[1,9,10] The downwards tendency of the curve at lower angles is the result of the increased absorption (and refraction) effect at these angles. In the inset of Fig. 2 a curve, obtained from the data compiled by Bradley and Jay,[14] is shown. Here a correction of the constant calculated from the highest reflection angle is necessary. The thin broken lines on Fig. 2 indicate the increase of the accidental error in the lattice constant measurement with decreasing angle θ. To be sure that the position of the last 211 lines is not affected by absorption within the error limits, the a-constant calculated from this line was compared with that obtained with copper radiation, being free of any influence, as mentioned in the introduction. For this purpose the precise value of the a-constant of sintered electrolytic chromium, determined with chromium radiation, and the linear expansion coefficient to reduce the obtained values to 20° C., was necessary.

The exposures were made at three different sample temperatures, the $211\alpha_1$ lines were measured and the constants were calculated. From the latter the expansion coefficient was determined, and then the constants were reduced to 20.0° C., as previously shown[1,2,9,10] The results are summarized in Table 2. As the precision of the determinations when com-

TABLE 2. LATTICE CONSTANT OF SINTERED ELECTROLYTIC CHROMIUM COMPUTED FROM THE 211 α_1 LINE (CrK α_1 RADIATION). AVERAGE VALUES OF TWO FILMS AT EACH TEMPERATURE

t in ° C.	Lattice constant in kX		Expans. coeff. in deg.$^{-1}$
	a_t	a_{20}	
10.0	2.87885	2.87902	
30.0	2.87905	2.87889	5.73×10^{-6}
50.0	2.87951	2.87902	
	Average	2.87898 ± 0.00005 kX	

pared with the measurements made with copper radiation, was lower (probable error ± 0.00005 kX), the break in the a–t curve could not be detected and a straight line was drawn through the middle of the experimental points (Fig. 3). Nevertheless, the average linear expansion coefficient of $\alpha = 5.73 \times 10^{-6}$ was close to the value of 5.93×10^{-6}, the mean obtained with copper radiation. Hence, the two lattice constants of the

[14] Bradley, A. J., and Jay, A. H., *Proc. Physik. Soc.*, **44**, 563, 574 (1932).

sintered sample, obtained with the two different radiations and reduced to 20° can now be compared:

$$CuK\alpha_1; \qquad \theta = 87.420° \quad a_{20} = 2.87912 \text{ kX (rounded off)}$$
$$CrK\alpha_1; \qquad \theta = 76.429° \quad a_{20} = 2.87898 \text{ kX}$$

The considerable difference of 0.00014 kX between these two values, which is completely outside of the experimental error limits given above, indicates that a correction is still necessary. As there is no plausible reason for another correction, *except the refraction correction* to balance out the results obtained with various wavelength radiations, this was applied.

III. THE REFRACTION CORRECTION

The correction for refraction was introduced by the use of the equation as derived by Ewald:[15]

$$a_{corr.} = a_n \left(1 + \frac{5.4 a^2 d}{h^2} 10^{-6} \right) \qquad (1)$$

a_n being the constant calculated from the angle θ, λ, and hkl; d is the density of the substance, and Σh^2 the sum of the squares of x-ray indices. This equation was derived from

$$a = a_n \left(1 + \frac{\delta}{\sin^2 \theta} \right) \qquad (2)$$

δ being 1-μ, where μ is the refraction index. The equations are valid only for the case of symmetrical reflection from the plane hkl, and the correction increases with increasing density and with decreasing hkl. Consequently, constants determined with soft radiations (Cr, Fe) will need larger corrections than those obtained with short waves (Cu, Mo).

The fact that the application of a refraction correction to the measurements of x-ray wave lengths, as calculated from different orders of reflection of the rays from a plane of a single crystal, is necessary, was shown by Stenström, Hjalmar and Larsson in Siegbahn's laboratory.[16] The same correction was also applied in the case of the determination of precise lattice parameters using a single crystal plane, for example by DuMond and Bollman,[17] and recently by Ericsson.[17a]

There is no agreement as to whether the refraction correction should

[15] See e.g. Lindh, A. E., in Wien-Harms, Handb. d. Experimentalphysik, XXIV/2, pp. 94, 116, Akad. Verlagsges., Leipzig (1930).

[16] Siegbahn, M., Spektroskopie der Röntgenstrahlen, 2nd ed., p. 21, Berlin, J. Springer (1931).

[17] DuMond, J. W. M., and Bollman, V. L., *Phys. Rev.*, **50**, 524 (1936).

[17a] Ericsson, G., *Ark. Fysik*, **7**, 415, 420 (1954); See also Brogren, G., *ibidem*, **7**, 47, 53 (1953).

be applied to lattice parameters calculated from powder patterns. Many authors used,[18] and still are using it in the form as indicated by eq. (1) or a similar one,[19] but some authors recommend neglecting this correction.[4]

The reason for this uncertainty is, without doubt, the difficulty of making the decision by direct measurements because of the minuteness of the correction and because of the somewhat lower accuracy of the powder method as compared with the spectroscopic method. The uncertainty still remains even if the very last lines were used for computation but no precautions concerning constancy of the temperature of the sample, which frequently happens, were made.[1,9,10] However the precision of the method used in this work is high enough[1,6,10] to establish the difference in lattice constants obtained with various x-radiations.

The theoretical considerations of Wilson showed that the refraction correction also has to be applied to lattice spacings calculated from *powder patterns* to obtain the true lattice spacing. In the case of a cubic crystal the extrapolated lattice spacing has simply to be increased by a fraction $(1-\mu)$ of itself.[20] According to Klug and Alexander this conclusion of Wilson can be written in a form:[2]

$$a_{corr.} = a_{obs} \times (1 + \delta) \tag{3}$$

where $\delta = 1 - \mu$, and can be calculated for a certain substance from the dispersion equation,[2,15,21] which gives values close to the experimentally determined indexed of refraction.[15,16] In comparing equation (2) with (3) it is easily seen that the latter can be derived from the former if θ approaches $\pi/2$.[22] Hence, using equations (1) or (3), nearly the same corrections should be obtained for constants computed from high Bragg angles.

Consequently for the refraction correction of chromium ($d = 7.2$) with copper and chromium radiations, values 6.1×10^{-5}, and 13.6×10^{-5} kX respectively were obtained with the simple Wilson formula (3). These corrections agree very well with those calculated by eq. (1). The final value of the corrected lattice constant of sintered electrolytic chromium at 20° C., obtained with $CuK\alpha_1$ and $CrK\alpha_1$ radiations, is then as follows:

$CuK\alpha_1$:	2.87912	$CrK\alpha_1$:	2.87898 kX
Refr. corr (eq. 1):	0.000064 (Wilson 0.000061)		0.00015 (Wilson 0.000136)
a_{20} =	2.87918 ± 0.00001 kX		2.87913 ± 0.00005 kX
	or 2.88500 Å		

[18] Miller, P. H., Jr., and DuMond, J. W. M., *Phys. Rev.*, **57**, 198, 203 (1940).

[19] Jette, E. R., and Foote, F., *J. Chem. Phys.*, **3**, 605, 611 (1935).

[20] Wilson, A. J. C., *Proc. Cambr. Phil. Soc.*, **36**, 485 (1940).

[21] See also v. Laue, M., Röntgenstrahl-Interferenzen, Akad. Verlagsges. Leipzig (1948), p. 294, equat. (27.4).

[22] Straumanis, M. E., *Acta Crystallogr.*, **8**, 654 (1955).

As the two results agree now within the error limits (probable error ± 0.00005 kX) of the less precise determination, there might be, or might not be at all, any difference in the two determinations. Some doubt in discarding the absorption correction in the case of chromium radiation may arise, because the constant was calculated from $211\alpha_1$, at a relatively low angle of only $76.4°$, and because the extrapolation operation used might be too rough (it also could terminate in a line not quite parallel to the abscissa). So the absorption correction was computed,[23] and found to be $+0.00003$ kX for an opaque sample. As this value is smaller than the precision of determination ± 0.00005 kX, it is quite unimportant. However, the absorption correction can definitely be omitted at angles of reflection around and above $80°$, because the correction decreases with increasing angle of reflection, and because of the nearly transparent sample used.[1,2,10] In any case, this example with chromium shows that the absorption correction is *negligible*, while the *refraction correction is necessary* because the latter diminishes the differences in the lattice constant values as obtained by the x-radiations of different wavelenghts.

IV. Lattice Constants and Expansion Coefficients of Four High Purity Chromium Samples

Finally, lattice constant and expansion coefficient determinations of 3 more chromium samples of high purity (see Table 1) were made for purposes of comparison. Chromium radiation was used because these 3 samples did not produce the last interference with a sufficient sharpness with copper radiation.

As before, no breaks in the expansivity curves could be found with these samples, because of the lower precision of measurements. All of the constants at $20°$ and corrected for refraction are summarized in Table 3.

Table 3. Lattice Constants (Corrected for Refraction) and Expansion Coefficients of Four Kinds of Chromium at 20.0° C.

Chromium	Radiation	Lattice constant in		Aver. exp. coeff. in deg.$^{-1}$ betw. 10 and 50° C.
		kX	Å	
Sintered Electrol.	Cu	2.87918 ± 0.00001	2.88500	5.93×10^{-6}
Sintered Electrol.	Cr	2.87913 ± 0.00005	2.88495	5.73
Electrolytic	Cr	2.87915 ± 0.00004	2.88497	5.56
Iodide (low metallic)	Cr	2.87909 ± 0.00006	2.88491	4.92
Iodide (low nonmetallic)	Cr	2.87907 ± 0.00007	2.88489	6.14

[23] Eq. 18A, p. 404, of M. J. Buerger's X-ray Crystallography, J. Wiley, New York (1942).

The error limits given in the Table are (the rounded off) probable errors, and they do not include the systematic errors.

The variation of the lattice parameter of the four chromium samples with temperature is shown in Fig. 3.

Table 3 shows finally that the lattice parameter of the two electrolytic chromium samples agrees within the error limits with that obtained with
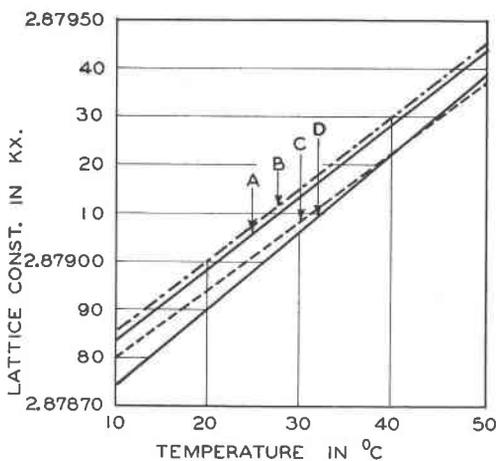
FIG. 3. Lattice parameter of Cr (Cr radiation) versus temperature. The constants are not corrected for refraction. A—sintered electrolytic Cr. B—electrolytic Cr. C—iodide Cr low in metallics. D—iodide Cr low in nonmetallics.

copper radiation, while the parameter of the two high purity chromium samples obtained by the thermal decomposition of chromium iodide is only slightly smaller, if the error limits given are considered. The expansion coefficients of all four samples are similar.

V. Discussion and Conclusions

It follows from theoretical consideration and from the measurements that a smooth θ-a curve can only be obtained if several (at least 4 or 6) precision films are measured and the computation results are plotted. Hence, the probability that a good curve, as shown on Fig. 2, will be obtained from the measurement of only one film is low. Consequently, the analytical and graphical extrapolation methods, using for the extrapolation the lines above 60° from only one film, may give a much larger mistake than anticipated even when the sample was kept at constant temperatures. Correct results will be obtained by determining the angles

of reflection from several films, and then using the average values of all or of the closest results for each line for the further operations. In this respect the methods using a larger number of interferences on one film starting for instance from 30°, are more reliable.[24] In all cases the largest weight should be and is given to the last back reflection line,[25] because the constant calculated from this line is affected by the smallest random error. In the present article it is shown again that the lattice parameter of cubic substances can be calculated with high precision from one single last line, and, if the powder mount is thin enough (0.1–0.2 mm. in diameter), without application of the absorption correction. Thus the time-consuming extrapolation procedures can be avoided. Nevertheless, the precision of the method (with the film in the asymmetric position to exclude film shrinkage) is higher than that of the extrapolation methods, as demonstrated with Table 3. Even with chromium radiation producing the last line at a comparatively low Bragg angle, the precision concerning accidental errors is 1 part in 40,000 to 60,000, but in the case of copper radiation it is 1 part in about 400,000 and better.

The films used for lattice constant determination (Table 2) also make it possible to calculate the expansion coefficient. Although only one last line on each film was utilized, the agreement with the measurements of others, working with extrapolation methods, is within the error limits found by them. Constants between 2.8784 to 2.8790 kX at temperatures 18 to 20° have been reported in recent years,[7,26,27] which agree very well with our values: 2.8792 and 2.8791 kX at 20° C. The slightly larger constants obtained in our work may be due to the high purity of the chromium used.

From the agreement of these measurements with the best results of other authors it follows that working with a thin powder mount, with a film in the asymmetric position, and with a precise camera, any correction can be neglected for constants computed from lines above 77°, except the refraction correction which has to be added to the constant directly calculated from the Bragg angle of the respective line.

For the calculation of the refraction correction, equations (1) and (3), giving nearly identical results, can be used. However, for constants obtained from lines at a reflection angle below 80°, equation (1) is preferred. There are no sufficient reasons for omitting this correction;[22]

[24] Taylor, A., and Sinclair, H., *Proc. Phys. Soc.* (London), **57**, 126 (1945); Nelson, J. B., and Riley, D. P., *Proc. Phys. Soc.* (London) **57**, 160 (1945).

[25] Hess, J. B., *Acta. Cryst.*, **4**, 209 (1951).

[26] Taylor, A., and Floyd, R. W., *J. Inst. Metals*, **80**, 577 (1952).

[27] Pearsons, W. B., and Hume-Rothery, W., *J. Inst. Metals*, **81**, 311 (1953).

moreover, it has been shown that the correction helps in balancing out the constants calculated from films obtained with different wavelengths radiations.

The average expansion coefficients (Table 3) of 4.92 to 6.14×10^{-6} deg.$^{-1}$ of chromium between 10 and 50° C. agree fairly well with those established by Hidnert[28] (5.7 to 6.6 or 7.5×10^{-6} up to 100° C.).

[28] Hidnert, P., *J. Res. Nat. B. St.*, **26**, 81 (1941); *Phys. Rev.*, **39**, 186 (1932).

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