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Absolute X-Ray Wave-Lengths by Refraction in Quartz

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The refractive index of quartz for Cu $K\alpha_1$ radiation was measured by means of the double crystal spectrometer. The quartz prism was placed between the two crystals of the spectrometer and the deviation measured. Measurements were made with the x-rays incident both internally and externally on the prism. Accuracy was such that the refractive index could be determined as $1-\mu=\delta=(8.553\pm0.005)\times10^{-6}$. The absolute wave-length of the x-rays was calculated from the quantum theory of dispersion and was found to agree with wave-lengths as measured by ruled gratings. With the newer data on fundamental constants, positions of the critical absorption limits of Si and O and the resonating strengths of bound electrons the previous photographic results were recalculated and found to likewise substantiate the ruled grating value.

MEASUREMENTS on the refractive index of quartz for x-rays have been made by photographic means using the prism method.[1–3] However, there is an inherent difficulty with this method as used heretofore. It is necessary to measure to the edges of certain of the lines and there is, of course, an uncertainty in such a measurement. On the other hand, if the prism is placed between the crystals of a double crystal spectrometer[4] this difficulty is eliminated by the fact that directions are measured directly and not by linear displacements on a photographic plate.

The determination of the refractive index for a given wave-length involves the measurement of two angles, the first being the angle between the direct beam and the refracted beam and the second one being the angle between the direct beam and the prism face. Calling these angles β and α, respectively (Fig. 1) the expression for $\delta=1-\mu$ becomes, for small angles[3] $\delta=\beta(\alpha-\beta/2)$ in the case of externally incident radiation and $\delta=\beta(\alpha+\beta/2)$ for internally incident radiation.

Thus to determine β by the use of a double crystal spectrometer it is only necessary to set the second crystal for the peak of the direct beam and then rotate the second crystal to the peak of the refracted beam. An auxiliary means, however, must be employed to measure the angle α, since the prism must be rotated beyond the critical angle for reflection in order to get a refracted beam. In the present case light from a slit S was reflected from the surface of the quartz prism and focused on the eyepiece of a calibrated travelling microscope M. The angle α was then determined by rotating the prism until the angle of incidence for the x-rays was less than the critical angle and taking two positions of the reflected beam.

The absorption in quartz is such that for the Cu $K\alpha$ lines the effective depth of prism used is not more than 0.001 mm. Thus for any particular position of the second crystal only the radiation in a very narrow beam is measured in the refracted line. In Fig. 2 it is seen that the angle of incidence for the α_1 line is less than that for the α_2 line. Thus even though the refractive index of α_2 is greater than that of α_1 the α_2 line will appear between the α_1 line and the direct beam. Fig. 3 shows the case for internal incidence and it may be seen that the α_2 line will fall outside of the α_1. Since these two refracted beams lie too close together to be completely resolved it is necessary to make a correction for the presence of the α_2 line. The refracted beam will be wider for each α line than the parent beam due to the difference in the angles of incidence on the prism of the two sides of the line. The character of the beams reflected from the prism is likewise changed. In the direct beam there is one position of the second crystal for which both α_1 and α_2 lines are reflected. But since the longest wave-length is reflected from the prism at the greatest angle the relative positions of α_1 and α_2 are reversed. Thus while α_1 is reflected at one position of the second crystal, α_2 is reflected at another and larger angle. This essentially puts the reflected beams in the $(1, +1)$ position so far as shape and width are concerned.

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[1] H. E. Stauss, Phys. Rev. **36**, 1101 (1930).

[2] A. Larsson, Dissertation, Uppsala (1929).

[3] J. A. Bearden, Phys. Rev. **39**, 1 (1932).

[4] B. Davis and C. M. Slack, Phys. Rev. **27**, 18 (1926).

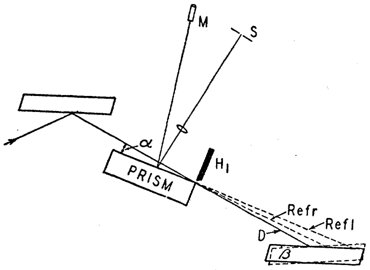

FIG. 1. Diagram showing the position of the quartz prism and the half slit H_1. The reflected beam is used in the determination of the glancing angle α.

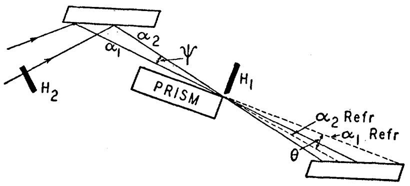

FIG. 2. Case for external incidence. Because of different angles of incidence the angles ψ for θ are not equal. ($\theta>\psi$.) Thus the α_2 refracted beam appears between the α_1 refracted beam and the direct beam.

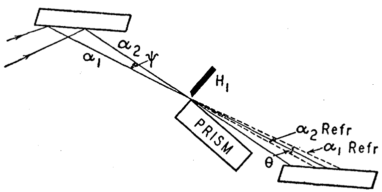

FIG. 3. Case for internal incidence. Here $\theta<\psi$ and the α_2 position lies beyond the α_1 position.

Thus the effective widths of the various lines may be summarized as follows: The direct beam has the $(1-1)$ width; the reflected beam has the $(1+1)$ width and the refracted beam has a width intermediate between $(1-1)$ and $(1+1)$. If the second crystal is rotated to the normal $(1, +1)$ position the conditions are changed. Then the reflected beams are in the $(1, -1)$ and the direct in the $(1, +1)$. It is true that in this position the α_1 and α_2 lines are not confused but on the other hand the intensity in the refracted beam drops to about one-third of that in corresponding positions in the $(1, -1)$.

Since the intensity of the refracted beam becomes too low to measure accurately for refracted angles greater than four minutes it is necessary to provide some means of blocking out the direct beam, which still has an appreciable intensity at these angles. This was easily accomplished by a half slit H_1 as shown in Fig. 1. The half slit was mounted on a slide so it could be removed from the path of the beam for the determination of the direct and reflected beams.

At first an attempt was made to eliminate the α_2 line from the refracted beam by using a half slit H_2 in the position shown in Fig. 2. However, the separation of the α_1 and α_2 beams at this point was only 0.1 mm, so it was not certain when only the α_2 line was eliminated. This method was abandoned when erratic results were obtained in favor of a direct correction for the presence of the α_2 line.

APPARATUS AND ALIGNMENT

The primary voltage was regulated by the control described heretofore.[5] The high voltage was rectified by four oil immersed kenotrons and filtered by a 0.5 mfd. condenser. The fine focus copper tube was operated on a balanced circuit. The electron beam was drawn out into a line focus by means of two Helmholz coils fed with 60 cycle a.c. in order to allow sufficient current and hence x-ray intensity for the measurements. The calcite crystals used showed theoretical resolving power since the rocking curve width for Cu $K\alpha_1$ was 9.8″. The ionization currents were measured by an FP-54 pliotron in a circuit described by DuBridge and Brown.[6] The ionization chamber was made of iron and was so free of contamination that the effects of the latter could be eliminated from measurements. The tube was operated at a sensitivity of 230,000 div./volt with a leakage resistance of 10^{11} ohms. The ionization current at the peak of the refracted line was about 2×10^{-14} ampere and could be measured to about 1 percent.

A Societe Genevoise double crystal spectrometer was used. The graduated circle on which the second crystal was mounted was read by four carefully calibrated microscopes. The accuracy of setting on the peak of a line and of reading the circle was such that on repeated measurements the position of the peak could be reproduced to within 0.2″ of arc.

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[5] Bearden and Shaw, Rev. Sci. Inst. **5**, 292 (1934).

[6] L. A. DuBridge and H. Brown, Rev. Sci. Inst. **4**, 532 (1933).

In the present case it is not necessary to align the prism as accurately as in the photographic experiments because no fine slits are involved. The prism face was within 0.25 mm of its axis of rotation; the axis and the prism face were made parallel to within three minutes of arc of the second crystal axis and the prism edge was within 5 minutes of being parallel to the axis of the prism.

The width of the direct beam was 9.8″. The width in the (1+1) position was 40.0″ and the width of the reflected beam was about 42″. Thus it is seen that the prism face was quite flat. The refracted beam was about 2″ wider than one would expect from the different angles of incidence of the two sides of the line and probably represents the inhomogeneity of the prism edge. The prism edge was prepared by the method previously described.[3] When the edge was examined with a microscope of magnification 300 it appeared quite sharp.

The only significant correction is that due to the displacement of the peak of the refracted line produced by the α_2 line. This correction was made in the following manner. Knowing the approximate indices for the α_1 and α_2 lines one can then calculate their separation for any particular value of angle α. It is also known that their intensities are in the ratio of 2 : 1. Knowing the shape of the sum of the two from the observed line shape it is only necessary to assume various line widths and by means of the Hoyt equation[7] plot curves until the observed shape is obtained. Then the displacement of the peak of the curve representing the sum from the peak of the α_1 component gives the correction to be applied to the angle β.

Fig. 4 shows a sample of the refracted beams obtained. In this case angle α was about 25 minutes. The ionization current at the peak was about 10^{-14} ampere. The two Hoyt curves assumed are also shown and the resulting correction to β.

Twenty-one determinations of δ were made in all—fourteen with the x-rays incident externally and seven internally. The results are listed in Table I with their various weights.

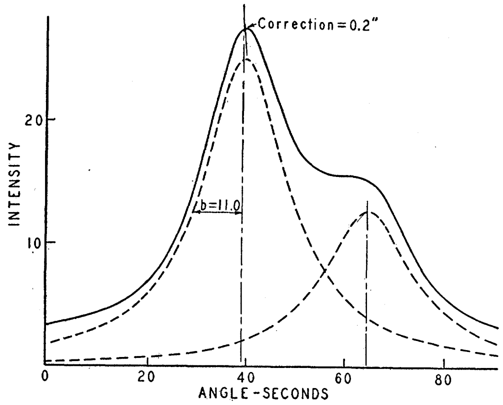

FIG. 4. Sample of refracted beam (external incidence). In this case $\beta=4'\ 20''$. The two Hoyt curves are shown and the resulting correction to β.

TABLE I.

Method	α	β	$\delta\times10^6$	Weight
Internal incidence.	29′ 40.3″	3′ 14.0″	8.560	3
	28′ 57.0″	3′ 18.4″	8.563	3
	30′ 36.5″	3′ 8.6″	8.560	3
	36′ 38.5″	2′ 39.7″	8.552	2
	36′ 44.8″	2′ 39.0″	8.536	2
	23′ 26.0″	3′ 58.5″	8.551	4
	36′ 46.0″	2′ 39.0″	8.541	2
External incidence.	32′ 39.7″	3′ 15.8″	8.568	0.5
	30′ 18.6″	3′ 32.4″	8.566	0.5
	25′ 46.9″	4′ 15.7″	8.528	0.5
	26′ 8.6″	4′ 12.7″	8.548	0.5
	31′ 49.7″	3′ 21.3″	8.557	3
	31′ 46.8″	3′ 21.5″	8.551	3
	31′ 49.0″	3′ 21.3″	8.556	3
	37′ 14.4″	2′ 47.6″	8.550	2
	38′ 41.0″	2′ 42.2″	8.540	2
	38′ 40.3″	2′ 42.2″	8.537	2
	24′ 59.0″	4′ 26.0″	8.543	4
	24′ 50.0″	4′ 27.7″	8.534	4
	31′ 18.2″	3′ 25.4″	8.584	4
	31′ 1.5″	3′ 27.1″	8.557	10

The first four determinations in the externally incident method were given small weights because of the fact that temperature variations of the first crystal holder due to the heat from the x-ray tube and the Helmholz coils were producing erratic results. Water cooling of the x-ray tube box eliminated this difficulty. The remaining results were weighted according to the angle β—large angles of β having the greatest weight. In the last result the second crystal was turned to the (1+1) position and β measured there as well as in the (1−1). Thus this value was given considerable weight.

The average deviation from the mean is about 0.010×10^{-6} and the probable error is 0.003

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[7] A. Hoyt, Phys. Rev. 40, 477 (1932).

$\times 10^{-6}$. Since the calibration of the microscopes is the only appreciable source of consistent error it is reasonably certain that the error is not more than $\pm 0.005 \times 10^{-6}$.

The results of this experiment then indicate that the refractive index for $\lambda = \mathrm{Cu}\ K\alpha_1$ is given by

$$1-\mu=\delta=(8.553\pm 0.005)\times 10^{-6}.$$

The absolute wave-length of the x-rays used may be calculated from the quantum theory of dispersion. In the derivation of the formula it is necessary to assume a law for the variation of absorption coefficient with wave-length. For all practical purposes a law of the form of λ^n is sufficiently accurate. However, it is very difficult to derive the formula unless n is an integer or half integer. Grosskurth[8] has shown that $n=2.75$ (approximately). Therefore in the following calculations the wave-length was calculated on the assumptions of a λ^3 and $\lambda^{2.5}$ law and the $\lambda^{2.75}$ law value interpolated. The formulae are:

$$\lambda(\text{absolute})=\delta^{\frac{1}{2}}\left[\frac{\rho}{W}\cdot\frac{e}{m}\cdot\frac{F}{2\pi}\sum_1^s N_s \times\left\{1+\frac{1}{x_s^2}\ln\,(x_s^2-1)\right\}\right]^{-\frac{1}{2}}$$

on the assumption of a λ^3 law and

$$\lambda\ (\text{absolute})=\delta^{\frac{1}{2}}\left[\frac{\rho}{W}\cdot\frac{e}{m}\cdot\frac{F}{2\pi}\sum_1^s N_s\left\{1+\frac{3}{2x_s^{\frac{3}{2}}} \times\left(\frac{\pi}{2}-\operatorname{ctn}^{-1}x_s^{\frac{1}{2}}-\tfrac{1}{2}\ln\frac{x_s^{\frac{1}{2}}+1}{|x_s^{\frac{1}{2}}-1|}\right)\right\}\right]^{-\frac{1}{2}}$$

on the assumption of a $\lambda^{2.5}$ law,[9] where $\delta=1-\mu$; ρ = density, W = molecular weight; F = Faraday constant; N_s = effective number of electrons in shell s; and $x=\lambda_0/\lambda$, where λ_0 = critical absorption limit for shell s.

The binding corrections were made for electrons in the K shells of silicon and oxygen and the L shell of silicon. The remaining electrons were assumed free.

The data used for the $K\alpha_1$ line of copper were:

$F=9648.9$ e.m.u./mol,
$\delta=8.553\times 10^{-6}$,
$\rho=2.6484$ g/cc at 28°C[3],
$W=60.06$
$e/m=1.7574\times 10^7$ e.m.u./g,
$\lambda=1.538$ for use in corrective terms,
Si K absorption[10] = 6.731A,
Si L absorption[10] = 127A,
O K absorption[10] = 23.0A,
N_K for Si[11] = 1.6,
N_L for Si[9] = 5.4,
N_K for O[11] = 1.78.

Williams gives N_L for Cu, Ag and Pb as being about 5.0. In the present case it was assumed that the value for Si would be very little different. Adding the fraction of an electron left over from the K shell then gives Si $N_L=5.4$. However, the use of either $N_L=5$ or 8 makes a difference of only one part in 15,000 in λ. Since the O L limits are at an even greater wave-length than those for Si no correction for their binding is necessary.

Substitutions in the formulae then give:

λ^3 law: $\lambda=1.5393$A,
$\lambda^{2.5}$ law: $\lambda=1.5407$A,

and on interpolation for the $\lambda^{2.75}$ law there results

$$\lambda=1.5400\text{A}$$

for the Cu $K\alpha_1$ line.

This wave-length value may be compared with those yielded by use of crystals and gratings. Measurements of grating wave-lengths by Bearden[12] have indicated that the value obtained is about 0.25 percent higher than the crystal result, while Siegbahn[13] gets 0.17 percent. The value chosen in the present work is 0.23 percent. Thus for the copper $K\alpha_1$ line

crystal	grating	refraction
1.5367A	1.5403A	1.5400A

Not a single value of the refractive index was obtained low enough to give the crystal wave-

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[8] K. Grosskurth, Ann. d. Physik **20**, 197 (1934).

[9] See e.g., E. J. Williams, Proc. Roy. Soc. **A143**, 358 (1934).

[10] Siegbahn, *Spect. der Röntgenstrahlung*, 2nd Ed., pp. 267, 350, 411.

[11] J. A. Wheeler and J. A. Bearden, preceding paper.

[12] J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

[13] M. Siegbahn, Zeits. f. Physik **87**, 291 (1933–34).

length. In view of the accuracy obtained there appears to be little doubt that the wave-length as indicated by refraction agrees with the grating value.

It was thought worth while to recalculate the wave-length from photographic results of Bearden and Stauss[1] using the newer data now available on the fundamental constants, the wave-lengths of the critical absorption edges of Si L and O K and the effective number of electrons in the K and L shells. Larsson's values appear to be too high, so no attempt was made to include them. Table II gives the various wave-lengths computed for a $\lambda^{2.75}$ absorption law.

TABLE II.

	Crystal	Grating	Refraction
	Bearden		
Cu $K\alpha_1\alpha_2$	1.5380	1.5416	1.5404
Cu $K\beta$	1.3888	1.3921	1.3916
Mo $K\alpha_1\alpha_2$	0.7089	0.7105	0.7098
Mo $K\beta$	.6307	.6322	.6324
	Stauss		
Mo $K\alpha_1$	.7075	.7091	.7096
Mo $K\beta$	.6307	.6322	.6333

Consistent errors in the photographic experiments may easily explain the failure of exact agreement with the grating results. On adding the percent deviation from the grating value one finds the values to agree to within 0.03 percent. Thus contrary to previous conclusions it now appears that the previous as well as the present experimental results substantiate the grating values of x-ray wave-lengths instead of the crystal wave-lengths.

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The Vapor Pressure of Calcium between 500 and 625°C

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The vapor pressure of solid calcium has been measured between 500 and 625°C, by the method of molecular effusion. The amount evaporated was determined by microtitration to better than 10^{-6} g. The results are well represented by the empirical equation: $\log p$ (in mm) $= 8.15 - 9670/T$. The present values for the pressure are about ten times smaller than those previously reported by Pilling for the same temperatures. Since the specific heat of solid calcium is known as a function of T, the "vapor pressure constant," or "chemical constant," can be computed. The new pressure data lead to the correct value for this constant, but the old ones do not. For the heat of evaporation at $T=0$ the value 4.53×10^4 cal./mole is obtained.

INTRODUCTION

IN experiments on thin metal films the material is often deposited by evaporation in vacuum from a hot source of controlled temperature. The amount deposited in a given time can then be calculated from the geometry of the apparatus, if the vapor pressure of the metal is known for the temperature in question. Except for the alkali metals, mercury and a few others, vapor pressure data in the range usually involved in evaporation work are very meager. The following is a report on some new pressure determinations for calcium, which were undertaken in connection with electron scattering experiments with thin calcium films.

METHOD

Consider an enclosure of absolute temperature T, containing ideal gas particles of mass m at a pressure p. From kinetic theory it is known, that the number of particles escaping in unit time through a small opening δs in the wall into a solid angle element δo in a direction making an angle θ with the normal to δs, is given by:

$$dn/dt = p(2\pi mkT)^{-\frac{1}{2}}\delta s(\delta o/\pi)\cos\theta,$$

where k is Boltzmann's constant. Introducing instead the gas constant pro mole R, the molecular weight M and the number of moles N, one obtains:

$$p = (dN/dt)(2\pi MRT)^{\frac{1}{2}}\pi/\delta s\delta o\cos\theta. \qquad (1)$$