THE REFRACTION OF X-RAYS IN IRON PYRITES

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Abstract

Refraction of x-rays in iron pyrites.—Preliminary values of $\delta = 1 - \mu$ were obtained by reflecting the first and fourth orders from a natural face of the crystal. Then, as suggested by Bergen Davis, by grinding the crystal so as to decrease the angle between the beam and the molecular planes to 15′, the angle of bending was increased from 15″ or less to as high as 210″. By calibration of the tangent worm and other precautions, lines were measured to 2″-5″. The values obtained for $\delta \times 10^6$ for MoKα_1, MoKβ_1, CuKα_1, and CuKβ_1 are $3.35 \pm .2$, $2.87 \pm .2$, $17.6 \pm .5$ and $13.2 \pm .4$. The corresponding values computed from the *Lorentz dispersion formula*, assuming 2 electrons in the K ring, are 3.34, 2.66, 17.7 and 13.6. The good agreement seems to indicate that the influence of the natural frequencies of the K electrons is not negligible. The *limits of total reflection* observed near grazing incidence, gave approximate values of the refraction; and the crowding together of MoKβ_1 and MoKγ_1, near grazing incidence also gave a value of δ for MoKβ_1.

Wave-lengths of MoKβ, CuKα, and CuKβ, are found to be .63102, 1.5372 and 1.3892 A.

Grating space of iron pyrites is found to be 2.7028 A.

EARLY experiments by various investigators soon after the discovery of x-rays detected no refraction of a beam passing through a prism. Later and more refined observations by Chapman,[1] Barkla,[2] and Webster and Clark[3] led to the same negative result. Barkla, using the prism method, believed that he had shown that the refractive index of potassium bromide and rock salt for λ .5 A differed from unity by less than 5×10^{-6}.

About 1920 Stenstrom,[4] Duane and Patterson,[5] and Siegbahn[6] began to notice continued discrepancies in the values they obtained for the wave-lengths of x-rays reflected from crystals at different orders, and pointed out that this could be explained by assuming an index of refraction slightly less than unity. Stenstrom from his observations calculated several values of $\delta = 1 - \mu$, which, however, could not be regarded as at all accurate. In 1922 Davis and Terrill[7] by this method obtained $\delta = 3 \times 10^{-6}$

[1] Chapman, Proc. Camb. Phil. Soc., p. 574, 1912
[2] Barkla, Phil. Mag. **31,** 257 (1916)
[3] Webster and Clark, Phys. Rev. **8,** 528 (1916)
[4] Stenstrom, Doctor's Dissertation, Lund, 1919
[5] Duane and Patterson, Phys. Rev. **16,** 532 (1920)
[6] Siegbahn, Comptes Rendues, **173,** 1350 (1921)
[7] Davis and Terrill, Proc. Nat. Acad. Sci. **8,** 537 (1922)

for Mo $K\alpha_1$ reflected from calcite, but the bending observed, about 4″ was hardly within the precision of their measurements.

Since the index of refraction is less than unity, total reflection should take place at sufficiently small grazing angles. This possibility was investigated by Compton,[8] who found the effect and determined the index of refraction of crown glass and silver for $L\beta_1$ of tungsten, obtaining 4.2 and 21.5×10^{-6}.

In the paper of Davis and Terrill[7] was contained the suggestion, due to Professor Davis, that the bending could be greatly increased by grinding the crystal at an angle ϕ to the molecular planes, slightly less than the angle θ_0 of reflection of the beam at these planes. The grazing angle of incidence would be nearly $(\theta_0-\phi)$, and as the bending is approximately inversely proportional to this, it could, by properly choosing ϕ, be made very large. This suggestion was embodied in several methods by Hatley,[9] who found for $MoK\alpha_1$ and calcite the value $\delta=2.03\pm.09\times10^{-6}$. The same idea is employed in the present investigation, of which some of the earlier results were presented before the American Physical Society.[10]

The direct current high potential set and the spectrometer employed have been previously described.[11] The tangent worm which rotated the crystal was found to have errors, and it was calibrated by an optical system. Light from an illuminated millimeter scale was reflected from an interferometer mirror to another mounted on the rotating crystal table, back from this to a third, and thence into a large transit telescope having a magnification of about 120. The optical path was 104 feet, and the rotation of the crystal table through 1″ caused the cross-wire of the telescope to move over the image about .15 mm. By means of this system the worm was calibrated and a curve constructed giving corrections as high as 18″ for some positions of the worm. In this investigation all positions of the crystal were read from the graduated hand wheel attached to the worm, the verniers being used merely to give the approximate values. Two x-ray tubes were employed, a water-cooled molybdenum tube and a water-cooled copper tube. In order to increase the amount of available radiation from the latter it was provided with a window consisting of a bubble of glass .006 cm thick blown on the end of a glass tube $\frac{1}{2}$ inch in diameter and 3 inches long which pointed in toward the target from the surface of the x-ray bulb.

[8] A. H. Compton, Phil. Mag. **45,** 1121 (1922)
[9] C. C. Hatley and Bergen Davis, Phys. Rev. **23,** 290 (1924)
[10] Bergen Davis and R. von Nardroff, Phys. Rev. **23,** 291 (1924)
[11] H. M. Terrill, Journ. Opt. Soc. **6,** 287 (1922)

The crystal used was an exceptionally fine sample of iron pyrites. Iron pyrites crystallizes in the cubic system, and the 100 planes were those used for reflection. Slit widths of .04 mm and .08 mm were used.

The procedure in obtaining reflection angles was to observe the crystal position at which a given line was reflected, then to turn the crystal until, in the optical system above described, a certain line in the millimeter scale was brought on the cross-wire of the telescope, when the position of the table was noted. The crystal table was then loosened, swung around through 180°, and clamped again, and the table was then rotated by the worm until the line in the millimeter scale was again brought on the cross-wire of the telescope, where the position was again noted. Then the crystal was turned until the x-ray line was again reflected, and this position observed. All these positions were corrected in terms of the worm wheel calibration. The values of θ_1 and α, which are the average of a number of observations, are believed to be accurate within 2″ in the case of the best lines and 5″ in the case of the wider and fainter lines.

In order to obtain a provisional value of $\delta = 1-\mu$, the lines MoKα_1 and MoKβ_1 were reflected from the natural surface of the pyrites crystal at the first and fourth orders, the second and third orders being absent. The results are given in Table I.

TABLE I

Radiation	*Order*	*Angle of reflection*
Mo Kα_1	1	7° 31′ 28.0″
Mo Kα_1	4	31° 34′ 42.4″
Mo Kβ_1	1	6° 42′ 18.5″
Mo Kβ_1	4	27° 50′ 3.4″

If θ_1 = angle of reflection at first order;
θ_n = angle of reflection at nth order;

then

$$\delta = 1-\mu = \frac{(n\sin\theta_1 - \sin\theta_n)(n\sin\theta_1 + \sin\theta_n)}{2(n^2-1)}. \qquad (1)$$

Using the angles above, approximate values of δ for these wave-lengths were found.

For Kα_1, $\delta = 4.6\times10^{-6}$;
Kβ_1, $\delta = 3.9\times10^{-6}$.

The crystal was then ground and polished at an angle ϕ with the molecular planes. This angle was determined by measuring on a spectrometer the angle between the reflecting surface and a reference surface of the crystal before and after grinding.

When x-rays are reflected at such a surface, a large amount of bending takes place at what, following Hatley, will be called acute incidence, and a small amount, 2″ to 5″, at obtuse incidence (see Fig. 1). Measurements were made of the angle turned through by the crystal between the two reflecting positions, first when the beam meets it coming as in the direction AB, and next as in the direction ED. It is evident that 180° minus

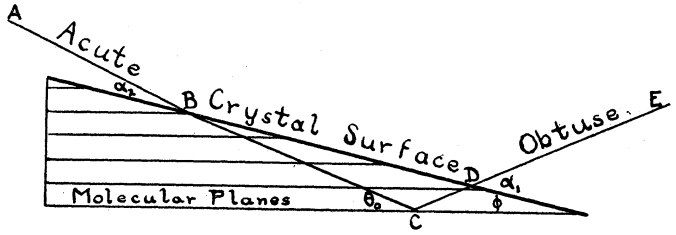

Fig. 1. Reflection of a beam from a crystal ground at an angle to the molecular planes.

this angle is equal to $(\alpha_1+\alpha_2)$. If θ_0 is the angle of reflection at the molecular planes inside the crystal, and $\alpha=(\alpha_1+\alpha_2)/2$, it may be shown that

$$\delta=\frac{(\sin\alpha-\sin\theta_0)(\sin\alpha-\sin\phi)(\sin\alpha+\sin\phi)}{(\sin\alpha-\sin^3\alpha)}. \tag{2}$$

For the unground crystal the relation holds that

$$\sin\theta_0=\sin\theta_1-\delta/\sin\theta_1+\delta\sin\theta_1. \tag{3}$$

In the work on the molybdenum radiation, the final values of δ were determined from Eq. (2) and (3) by a method of successive approximations, starting with the provisional values obtained above. The resulting values are shown in Table II, which gives the approximate calculated values of the bending at acute incidence.

TABLE II

Angle of grinding	α	Bending	$\delta\times10^6$
MoKα_1			
unground	7° 31′ 28.0″	5.4″	
6° 31′ 57.5″	7° 31′ 43.5″	39.1″	3.3 ±.9
7° 18′ 39.0″	7° 32′ 48.5″	169.2″	3.38±.24
MoKβ_1			
unground	6° 42′ 18.5″	5.1″	
6° 31′ 57.5″	6° 43′ 41.0″	172.7″	2.86±.20

The appearance of the radiation curves presented certain features of interest. The reflected radiation at acute incidence was more intense than that from the unground crystal, while at obtuse incidence it was much less. For example, in one case, if the maximum energy from the unground crystal be given as .83, the energy at acute incidence was 1.96, and at obtuse .22. This may be explained by assuming that the incident beam must on an average pass through a given number of molecular planes before reflection. Under these circumstances, as will be seen from Fig. 2, the total path inside the crystal traversed by the ray meeting it at obtuse incidence will be much greater than at acute, which in turn is considerably less than at the unground surface. This weakness at obtuse incidence, together with a certain broadening of the lines, which becomes marked at very small grazing angles, makes it impossible to diminish this angle indefinitely by increasing ϕ, and thus limits the bending obtainable.

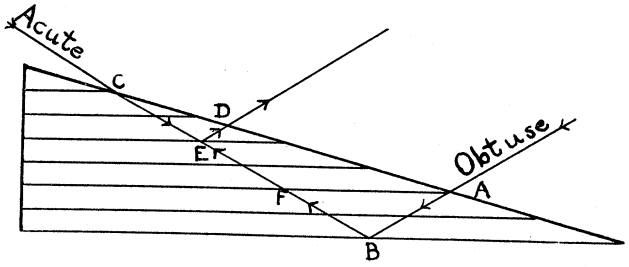

Fig. 2. Comparison of paths of two beams, one with acute incidence *CED*, the other with obtuse incidence *ABC* when both penetrate to two molecular planes beneath the surface before reflection.

If the general radiation curve is examined at small wave-lengths it is found that as the ray approaches grazing incidence, but some 6 to 20 minutes of arc before reaching it, the radiation curve drops off rather suddenly, showing that the incident ray can no longer penetrate the crystal, but is totally reflected. This should occur when the cosine of the grazing angle $=(1-\delta)$, and the wave-length will be given by $\lambda = 2d \sin \phi$ since, at the limit, the ray in the crystal will be parallel to its surface and hence meet the molecular planes at the angle ϕ. It may be shown that, at the critical angle, $\delta = \sin^2 \frac{1}{2} \theta_c$. The fact that the breaks in the general radiation curve were not very sharp made it impossible to use these angles for exact determinations of δ. Approximate values were obtained with total reflection beginning at a grazing angle of 7′ 34″ for $\lambda = 0.615$A, giving $\delta = 2.42 \times 10^{-6}$, and, with the crystal differently ground and using copper radiation, at an angle of 21′ 6″ for $\lambda = 1.451$ A, giving

$\delta = 18.8 \times 10^{-6}$. These values are in fair agreement with those found by other and more accurate methods.

In the case where $\phi = 6° \ 31' \ 57.5''$, it was noticed that MoKβ_1 and Kγ were but $4' \ 29''$ apart, whereas, with the unground crystal they were separated by $7' \ 16''$. This was to be expected, since the bending increases rapidly as grazing incidence is approached. A method was found, depending only roughly on the values of θ_0 and α, by which δ could be found from this crowding of the lines. This calculation, which is practically independent of the accuracy of the 180° rotation of the crystal table, gave $\delta = 2.88 \times 10^{-6}$ for Kβ_1, in close agreement with the values found above.

In the case of the copper radiation, the fourth order angles were too large to be reached by the ionization chamber. Therefore the preliminary value of δ, instead of being obtained by comparison of first and fourth order reflections, was simply assumed at a reasonable value. The method of successive approximation described above was then applied to the values of θ_1, and α obtained from the unground and ground crystals. The results are given in Table III, together with approximate calculated values of the bending at acute incidence.

TABLE III

Angle of grinding	α	Bending	$\delta \times 10^6$
CuKα_1			
unground	16° 31′ 31.5″	12.2″	
15° 33′ 37.5″	16° 33′ 6.7″	210.1″	17.6 ± .5
CuKβ_1			
unground	14° 53′ 39.0″	4.9″	
14° 12′ 29.5″	14° 55′ 20.3″	218.1″	13.2 ± .4

In Table IV are collected the sines of the angles of reflection at the molecular planes and the weighted means of the values of δ for the various lines measured, together with the values calculated from the Lorentz dispersion formula, which, in ordinary electrostatic units, may be written

$$\delta = \frac{e^2}{2\pi m}\left[\frac{n_1}{\nu^2 - \nu_1^2} + \frac{n_2}{\nu^2 - \nu_2^2} + \cdots\right]$$

where n_1, n_2, etc., are the number of electrons per unit volume having the natural frequencies of vibration ν_1, ν_2, etc., and ν is the frequency of the incident radiation. All the electrons except those of the K rings have frequencies so far below that of the radiation that their ν's may be omitted. The formula may thus be written

$$\delta=\frac{e^2N}{2\pi m}\left[\frac{K_{Fe}}{\nu^2-\nu_{Fe}{}^2}+\frac{Ks}{\nu^2-\nu s^2}+\frac{(Z_{Fe}-K_{Fe})+2(Zs-Ks)}{\nu^2}\right]$$

where N = number of FeS_2 molecules per cc,

Z = atomic number,

k = number of electrons in the K ring.

The natural frequencies were taken as those of the K absorption limit. For the Mo radiations the effect of changes in the values of k are not within the limits of experimental error, but for Cu radiation they are; and the table shows the theoretical values of δ obtained by assuming $k=0$, 1, 2, 3, the first of these corresponding to the assumption that the natural frequencies of the electrons play no part in the refraction. It will be observed that the experimental values are in close agreement with those predicted by the formula, and in the case of $CuK\alpha_1$ where the variations in δ introduced by different values of k are largest, distinctly favor the value of $k=2$. Just how the mechanism postulated in the derivation of the Lorentz formula is to be reconciled with quantum conceptions is a matter for speculation.

TABLE IV

Radiation	$\sin\theta_0$	λ_{air}	$\delta\times10^6$ (calc.) $(k=0)$	$(k=1)$	$(k=2)$	$(k=3)$	$\delta\times10^6$ (obs.)
$MoK\alpha_1$	.1309235	.707717 ±15	3.29		3.31		3.35 ±.20
$MoK\beta_1$	.1167353	.63102 ± 6	2.62		2.64		2.87 ±.20
$CuK\alpha_1$	.2843818	1.53722 ±15	15.58	16.58	17.60	18.61	17.6 ±.5
$CuK\beta_1$	.2569866	1.38915 ±15	12.69	13.12	13.53	13.95	13.2 ±.4

Ewald[12] has developed a theory of x-ray reflection according to which there is a certain "toleration angle" of deviation from Bragg's Law, that is, radiation is reflected not merely at the wave-length given by $\lambda=2d\sin\theta$ but also over a small range of angle extending to one side of this position. Since what is measured is the mean position of the range, all observed angles should differ from those expected from the Bragg relation by an amount equal to one-half the toleration angle. This toleration angle is a function of the grazing angle and also of the frequency of the incident radiation and the natural frequencies of the electrons in the crystal. The quantity which expresses the latter two relations is given by

$$\Omega=\frac{v}{2\pi}\frac{m}{e^2}(\omega_j{}^2-\omega_0{}^2)$$

[12] P. P. Ewald, Ann. der Phys. **46**, pp. 1 and 117 (1916), and **54**, 510 (1917)

where $1/v$ = number of electrons per cc,

ω_j = natural frequency of electrons,

ω_0 = frequency of radiation

It will be seen that Ω is identical with $-1/\delta$ as given by the Lorentz equation. For reflection at an unground surface, Ewald obtains the expression

$$\theta_0 = \theta_m + 2/(\Omega \sin \theta_0).$$

This may be transformed into

$$\sin \theta_0 = \sin \theta_m + 1/(\Omega \sin \theta_0) ,$$

which is identical with (3) except that it lacks the last term, which is small compared with the second, and except for the difference between $\sin \theta_m$ and $\sin \theta_0$ in the second term which, for an unground crystal, is negligible in comparison with $\sin \theta_0$. Hence any results which fit Ewald's formulas would also fit those of the refraction theory. Hjalmar,[13] using the photographic method, has made extremely careful observations of many wave-lengths reflected at orders up to the tenth. He compares his results with those to be expected from Ewald's theory and finds that the change in $\sin \theta_n/n$ for various orders is about as predicted. However, if the values of δ be calculated from his data they lead to results which are much too high. For example, using the first and eighth orders of reflection of $CuK\alpha_1$ from gypsum, δ comes out 18.4×10^{-6}, whereas the Lorentz equation gives 7.2×10^{-6}. Certain earlier and less accurate data of Hjalmar,[14] discussed by Ewald,[15] indicated that only about half of the electrons in the molecule were affected by the radiation, and thus entered into the equation; that is, this data would have given low values of δ. No explanation, however, could be made on such grounds of values which come out too high. They are perhaps due to the difficulty, inherent in the photographic method, of setting the crystal so that the axis of rotation lies in the plane of average penetration of the beam before reflection. It should be pointed out that apparently Ewald's theory would not predict total reflection.

Hatley[9] obtained from his measurements of $MoK\alpha_1$ reflected from calcite, corrected for refraction and also for the increase in wave-length in the ratio $1/(1-\delta)$ which must occur when the rays enter the crystal, the value $\lambda_0 = (.707717 \pm 15)$ A based on d for calcite $= 3.028 \times 10^{-8}$ cm. Correcting this for the change of wave-length in pyrites and using the

[13] E. Hjalmar, Zeit. f. Phys. **15,** 63 (1923)

[14] E. Hjalmar, Zeit. f. Phys. **1,** 439 (1920)

[15] P. P. Ewald, Zeit. f. Phys. **2,** 332 (1920)

value of sin θ_0 given for MoKα_1 in Table IV, the grating space of pyrites can be calculated, and is found to be (2.70280 ± 15)A. Using this value and the sin θ_0's for the other radiations, their wave-lengths in pyrites and thence in air may be obtained. The results of this calculation are given in Table IV.

In conclusion, the writer wishes to express his thanks to the various members of the Physics Department for their co-operation, and in particular to Professor Davis, who suggested the problem and whose advice and encouragement were an invaluable aid throughout the investigation.

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