REMARKS ON A PAPER[1] BY ARTHUR H. COMPTON ENTITLED: "NOTE ON THE GRATING SPACE OF CALCITE AND THE X-RAY SPECTRUM OF GALLIUM."

By H. S. Uhler.

IN the note by Compton the following sentence may be found on page 432, June, 1918: "The wave-lengths of the characteristic X-rays from gallium given by Uhler and Cooksey require revision because of this error in their determination of the grating space of calcite." Since this statement is made without any qualification, and as the general scientific reader may infer from Compton's criticisms that our data were carelessly treated, I feel obliged to say a few words to emphasize some points in our paper which have been completely ignored in the note under consideration. Even under these circumstances I should undertake the writing of a supplementary paper with great reluctance were it not for the fact that I hope to make a few comments and suggestions which may be helpful in the future study of X-ray wave-lengths.

The following sentences are quoted from our original paper.[2] "Since the problem which we had set for ourselves was to determine the glancing angles with respect to calcite, we considered the very accurate determination of the ratio of the grating space of calcite to that of rock salt to be an entirely independent question. In other words, the rock salt was employed because a sufficiently satisfactory reduction factor, if present in the literature of the subject, has escaped our notice, and it was desirable to obtain wave-lengths on the same basis as the tables of Siegbahn and others." These sentences were intended to convey the idea that we were not laying stress either on the absolute numerical values of the wave-lengths or on the grating space of calcite in terms of the centimeter as unit. The only object in calculating the wave-lengths in terms of 2.814×10^{-8} cm. for rock salt was to make possible a fair comparison with the surrounding data of Siegbahn's tables. Emphasis was laid only on the relative values of the wave-lengths as is shown by the fact that the word relative is printed in italics on page 651, line 6. Even then we began the next sentence with the words "Be this as it may, . . ." to imply that there may exist some unknown source of error which

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[1] Physical Review, *11*, p. 430, June, 1918.

[2] Physical Review, *10*, 649, 1917.

might invalidate the preceding optimistic remark. As far as I can see, no error of this kind is pointed out in Compton's note. That we were not claiming special accuracy for our value of the grating space of calcite (on the basis of 2.814×10^{-8} for rock salt) is made clear by the term "preliminary value" used in our summary.

The next topic for consideration is the ratio of the grating space of calcite to that of rock salt. In the first place, attention may be called to the fact that, although Compton seems to take exception to an isolated portion of our second sentence (quoted above), he does not give a numerical value for the ratio in question. He presents instead a well-known algebraic formula "(3)" for the reduction factor. If we could have obtained full information concerning the experimental history of both the numbers 3.028×10^{-8} and 2.814×10^{-8} (for calcite and rock salt, respectively) the problem of determining their ratio experimentally and independently of any earlier published work might not have arisen. It would have been sufficient to calculate the wave-lengths directly from 3.028×10^{-8} cm., as Compton has done in the last part of his note. Since, as will be pointed out in detail later, certain reasons occurred to us which seemed to throw doubt on the accuracy of one or both of the grating spaces given above, and as we were primarily interested in computing wave-lengths on the basis of 2.814×10^{-8} cm. (no matter whether this number is correct or incorrect) it seemed better to determine the relative grating space of calcite experimentally by using the same characteristic radiations with crystals of the two kinds and then employing the relation $d_1 = 2.814 \times 10^{-8} \sin \theta_2/\sin \theta_1$. The assumption that pure crystals of the same kind, from various sources and used by different investigators, have the same grating space (at the same pressure and temperature) underlies formula (3) [of Compton's note] as well as the experimental method just outlined.

In *Science Abstracts*[1] it is stated that E. Wagner has verified Moseley's value 2.814×10^{-8} cm. for rock salt. The reference given is "*Ann. d. Physik*, 49, 6, pp. 625–647, May 5, 1916." Since this Heft of the *Annalen* has never reached us, we were unable to read Wagner's original paper and thus to form an independent estimate of the trustworthiness of the datum 2.814×10^{-8} cm. Accordingly if this number happens to involve an appreciable error, the reduction of calcite glancing angles to wave-lengths by using $d_1 = 3.028 \times 10^{-8}$ cm. (assuming, for the time being, that this value is correct to three decimal places) would not enable satisfactory comparison with Siegbahn's tables to be made.

Attention will now be directed to Compton's value and direct calcula-

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[1] No. 225, Sept. 28, 1916, p. 392.

tion of the grating space of calcite. The last two sentences in his note are: "The probable error in the wave-length is estimated by Uhler and Cooksey on the basis of their probable error in measuring the angle. It should be noted that a much larger error in the wave-length is introduced by the uncertainty of the grating space." These statements pertain to absolute and not to relative wave-lengths, and they suggest that the same test be applied to the probable error $\pm 0.0010 \times 10^{-8}$ cm. given by Compton for his value of d_1. The theoretical formula

$$d_1 = \left[\frac{M_1}{2\rho_1 N\phi(\beta_1)}\right]^{1/3} \tag{1}$$

involves the errors pertaining to M_1, ρ_1, and $\phi(\beta_1)$ as well as the error in the value of N. The last named uncertainty is the only one that was taken into account in computing $\pm 0.0010 \times 10^{-8}$ cm. The molecular weight of calcium carbonate, M_1, has been decreased from 100.09 to 100.075 in the last few years. Since the probable error in M_1 is supposedly small and as I have no data at hand for estimating its value, I am forced to omit it from the numerical calculations. Nevertheless the existence of this error must not be overlooked.

In an earlier article[1] by Compton may be found: "The density of the crystal used was carefully determined, and was found to be $\rho = 2.7116 \pm 0.0004$ g. cm.$^{-3}$ (at 18°)." Apparently only one crystal was studied. Since the standard reference books on mineralogy and crystallography agree in giving the density as 2.714 gram/cm.^{3} (at about 18° C.) for pure native crystals and in stating that Iceland spar is sometimes (or even frequently) contaminated with impurities, affected by microscopic cavities, etc., the question arises as to whether the density obtained by ordinary hydrostatic weighing gives the exact value to be substituted for ρ_1 in equation (1). Furthermore, the following question also suggests itself: Does the lack of visible color afford a sufficient criterion for the purity of a given specimen of calcite? In other words, may there not be inclusions of material which would appreciably modify the density of a crystal but which would only show color in the ultraviolet region of the spectrum? Accordingly it seems to me that a special study of a fairly large number of apparently pure and perfect (free from local twinning) crystals needs to be made, using the same source of characteristic X-rays, in order to establish the *practical* validity of formula (1) and to show that there exists a one-to-one correspondence between the effective grating space and the mean density of the crystal.

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[1] Physical Review, 7, 655, 1916.

Equation (1) also involves the function

$$\phi(\beta_1) = \frac{(1 + \cos \beta_1)^2}{(1 + 2 \cos \beta_1) \sin \beta_1}.$$

The degree of precision of the angle β_1 may be readily overestimated. With the kind help of a colleague, who has made many investigations in crystallography and who has attained no little prominence in this subject, I have been able to ascertain the following facts. The value of the face angle β_1 is computed by spherical trigonometry from certain interior acute angles of the crystal. These interior angles are obtained by means of light "signals," a process which admits of an uncertainty of ± 5′ for a single determination. For this reason accepted values of angles have to be obtained from measurements made on a large number of selected specimens of the same kind. This matter is brought out very clearly by the table on page 381 of "Crystallography and Practical Crystal Measurement," by A. E. H. Tutton. The angular limits vary from 0′ to 16′. In two cases of 6 measurements each the range is 8′. It should also be noted that Tutton gives $\beta_1 = 101° 54'$ and ascribes the value 101° 55′ (which is apparently the accepted value) to von Groth. Accordingly a conservative estimate of the possible variations in the grating space d_1 may be obtained by allowing a range of ± 2′ in β_1 and of $\pm 0.006 \times 10^{23}$ in N, respectively. For $\beta_1 = 101° 57'$ and 101° 53′ I calculated the value of $\phi(\beta_1)$ to be 1.09695 and 1.09557, in the order named. [This assumes the correctness of the following numbers: $\sin (11° 53') = 0.2059195$, $\cos (11° 53') = 0.9785689$, $\sin (11° 57') = 0.2070580$, $\cos (11° 57') = 0.9783287$.] Using the first of these numbers in conjunction with $N = 6.068 \times 10^{23}$, the second with $N = 6.056 \times 10^{23}$, and employing the data $\rho_1 = 2.7116$ and $M_1 = 100.075$, given by Compton, I found $d_1 = 3.0265 \times 10^{-8}$ cm. and $d_1 = 3.0298 \times 10^{-8}$ cm., respectively. Consequently, the probable error $\pm 0.0010 \times 10^{-8}$ given in "$d_1 = 3.0281$[1] $\pm .0010 \times 10^{-8}$ cm." is appreciably smaller than the possible error $\pm 0.0016_3 \times 10^{-8}$, when four decimal places are taken into consideration. The range just given is decidedly conservative since $\pm 0.006 \times 10^{23}$ is a *probable* error (even wager), and the uncertainties of M_1 and ρ_1 have been treated as of value zero.

In the note in question it is also stated that: "Gorton has determined the grating space of calcite by a similar comparison method, using the same value of d_2, and obtains $d_1 = 3.028 \times 10^{-8}$ cm., which agrees absolutely with the theoretical value." I shall now attempt to show that

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[1] This is evidently a misprint since $\phi(101° 55') = 1.09626$, giving $d_1 = 3.02817$, *i. e.*, $d_1 = 3.0282$.

the concordance of these results is largely, if not entirely, accidental. In Table I. are collected the values of the grating space of calcite which I have computed from $d_2 = 2.814 \times 10^{-8}$ cm., for rock salt and the glancing angles given in Table I. of W. S. Gorton's paper.[1] For convenience in inspecting, the lines have been rearranged according to increasing values of d_2. With the single exception of the line a_1, which is characterized as "faint," there is a *systematic* difference between the values of d_2 obtained from weak lines on the one hand and from intense lines on the other. Although the unweighted mean is 3.028×10^{-8} cm., the extreme variation from 3.022×10^{-8} cm. to 3.035×10^{-8} cm. is too great to allow any conclusion to be drawn concerning the digit in the third decimal place. But this place must be taken into account in order to obtain the *absolute* agreement with the theoretical value mentioned by Compton. Since *ceteris paribus* it is more difficult to make settings on faint photographic impressions than on strong ones it is customary to assign weights to the experimental data and thus to form the general arithmetical mean. From the weights given in the fourth column of Table I. above I calculated the general mean and found it to be 3.030×10^{-8} cm. Accordingly, since the range of weights is not excessive, it may be argued just as well that the grating space of calcite given by D. L. Webster agrees absolutely with the value resulting from Gorton's experimental work.

Table I.

Name.	Strength.	$d_2 \times 10^8$ cm.$^{-1}$.	Weight.
k	faint	3.0224	2
b_2	very faint	3.0242	1
c	faint	3.0244	2
b_1	faint	3.0246	2
h	medium	3.0269	3
a	strong	3.0280	4
a_1	faint	3.0305	2
d	strong	3.0328	4
g	strong	3.0334	4
b	strong	3.0351	4

On the other hand, the following lines of evidence, derived from Gorton's paper, seem to me to show that a high degree of precision may not be attributed to his work on the X-ray spectrum of tungsten. (a) It is not stated that care was taken to adjust the crystals so as to cause their planes of reflecting atoms to be parallel to the axis of rotation of the spectrometer. Also nothing is said about diaphragming down

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[1] Physical Review, 7, 206, 1916.

the vertical dimensions of the slit and beam of rays. In a recent paper[1] I have shown that errors may arise from not taking into account the three-dimensional paths of the X-rays. (*b*) The slit width is given as 0.25 mm. This seems to me to be too wide an aperture, since Cooksey and I eventually found it necessary to employ a slit-width of only 0.02 mm. (*c*) Pairs of complementary exposures of the same line in the same spectral order, both on the right and on the left, were not taken. Instead, the shadow of an opaque pointed object was taken as the central or direct image. Hence, no attempt to eliminate errors arising from asymmetry in the apparatus seems to have been made. (*d*) Measurements made on Fig. 1 and on the first calcite reproduction of Plate 1 show that the negatives have been *reduced* in the ratio 5.0 to 3.3. With due allowance for the unflattering effects of the half-tone process, the lines still appear to me to be very unsatisfactory for accurate measurements. (Cooksey and I photographed the L series of tungsten, excited in a Coolidge tube, and found the lines to be sharp and satisfactory in all respects.) (*e*) Photographic *films* were used. Celluloid films are unreliable for absolute measurements because after fixing and drying they do not, in general, return to the same length which they had before developing. On the other hand, the fact that Gorton says nothing about the penetration of the X-rays into the crystals does not necessarily militate against his determination of the grating space of calcite in terms of that of rock salt, for, if the penetration of the same monochromatic radiation in the crystals of the two kinds is not markedly different, the error introduced in the ratio by applying no correction for penetration for fairly soft X-rays will be relatively small and probably negligible. This follows from the fact that the *ratio* of the sines occurring in the equation $d_1 = 2.814 \times 10^{-8} \sin \theta_2 / \sin \theta_1$ will not be greatly changed by algebraically adding small increments of the same sign to both the angles θ_1 and θ_2.

The following concrete examples of the undesirable behavior of gelatin may not be without interest. In the year 1905 I attempted, with the assistance of a professional photographer, to obtain a reduced negative of a wave-length scale by photographing down, with a large portrait camera, a specially prepared paper scale. It was necessary to use celluloid films in this work because the negative desired had to fulfil two conditions: (*i*) to register exactly with a series of spectrograms which had been obtained with a concave grating of about one meter radius of curvature, and (*ii*) to have the same thickness as the films used in the spectrograph. It was soon found that the method of trial and error was not applicable to the films, and this called attention to the

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[1] PHYSICAL REVIEW, *II*, I, 1918.

fact that successive spectrograms (cut from the same unexposed larger film but developed independently) of the same radiations were not, in general, superposable. A few years later, a friend of mine met with the same source of error in his preliminary work on the secondary standard wave-lengths of the iron arc, obtained with a Fabry and Perot interferometer and a concave grating of medium size. After losing much valuable time he traced the elusive cause of the inconsistencies of his data to the celluloid films which he was employing. As soon as the change was made from films, which coincided with the focal locus of the spectrographic system, to plates placed as mean chords to this curved surface, all the anomalous difficulties vanished. It may also be interesting to note, in this connection, that I once found a set of old glass spectrograms, that had been taken by the late Professor A. W. Wright, which exhibited the following phenomenon. The gelatin had partially separated from the glass backing and curled up. In so doing, the gelatin had carried with it thin sheets of glass of irregular thickness. In the long time which had elapsed, the cohesion of the glass had given way to the stresses in the gelatin and the adhesion of the gelatin to the glass.

In behalf of scientific progress the following remarks may not be inappropriate. In general, the study of wave-lengths has either one of two objects in view; (*i*) to find a connection between the wave-lengths or true frequencies and other physical quantities, and (*ii*) to obtain empirical relations between the reciprocals of the wave-lengths themselves. In case (*i*) it is necessary to express the wave-lengths in terms of a linear unit such as the centimeter. At the present time a limit of accuracy is set by the sources of error which are inherent in the methods of determining the grating spaces of crystals in terms of the centimeter. Fortunately the probable errors of the grating spaces of calcite, rock salt, and a few other crystals are small enough to admit of no ambiguity in testing any general relation which may be supposed to hold between X-rays and other physical quantities or phenomena. Case (*ii*) involves problems analogous to those presented by series and band spectra in ordinary spectroscopy. In the older subject the formulæ of Kayser and Runge, Rydberg, Ritz, Deslandres, Thiele, Birge, etc., were tested on the reciprocals of the wave-lengths and the velocity of light did not enter into the calculations. Since wave-lengths of fine lines, in the visible and ultra violet regions, can be determined to within three or four units in numbers involving seven significant figures it would be absolutely foolish to throw away several figures in the reciprocals of the wave-lengths merely because the number of permissible digits in true frequencies or numbers of vibrations per second is limited by the fact that the velocity of light has not been determined to anything like the precision that pertains to the wave-lengths in terms of the centimeter (Michelson, Fabry and Buisson.) The change from Rowland's tables to interferometer standards was not caused by the error (in terms of the cm.) in the number 5896.156, for the wave-length of the Fraunhofer line D_1 (computed by Rowland from the experimental data of Ångström, Müller and Kempf, Kurlbaum, Peirce, and Louis Bell) but rather by certain inconsistencies in the wave-lengths themselves due to combining auxiliary standards of solar and telluric origin. In the same general way, if glancing angles and relative wave-lengths of X-rays can be determined to a higher degree of accuracy than the absolute grating spaces of crystals it will not further the cause of pure science to sacrifice the more accurate data on account of the limitations now set by the less accurate.

Obviously the number of notes that might be published, if the champions of a certain value of a grating space were to correct all the X-ray wave-lengths given by investigators who had either intentionally or unwittingly used some other value for the same grating space, would be enormous. If a tentative value for the grating space of calcite were conventionally fixed (by a committee of the American Physical Society, or otherwise), then all X-ray wave-lengths could be given on a common basis and the probable error of the conventional number might be omitted in all problems involving primarily relative wave-lengths. Under this unifying condition the discrepancies between the wave-lengths of the same radiations obtained by different skilful observers would doubtless lead to greater knowledge of instrumental errors, of variations in crystals, and of possible changes in the wave-lengths themselves.

SLOANE PHYSICAL LABORATORY,
YALE UNIVERSITY,
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