Non-Laue Maxima in the Diffraction of X-Rays from Rocksalt—Equatorial Maxima

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The existence of non-Laue maxima in the diffraction of x-rays was first recognized in 1938 by Wadlund for a continuous spectrum of x-rays and by Laval for monochromatic x-rays. A brief description of Laval's exhaustive work is given. The main points of the theories of Zachariasen, of Raman, Nilakantan and Nath, and of Preston, Bragg and Jauncey are also described. In the authors' experiments Cu$K\alpha$, Cu$K\beta$, or Mo$K\alpha$ x-rays with a weak background of continuous radiation were diffracted from an etched cleavage face of a thick rocksalt crystal. With the crystal face set to give the 200 reflection of Cu$K\alpha_1$ a total divergence of 1.6′ was found in the reflected beam, indicating very little warping in the layers near the crystal surface. With the crystal face turned by steps of 1° from a glancing angle of 45°07′ to 28°07′ the positions of the non-Laue maxima associated with the 400 and 620 Bragg reflections were found. The non-Laue spots are called associated Bragg spots. All photographs showed a shift of the maximum intensity of the associated Bragg spot from the position of the corresponding Bragg spectrum line which is greater than zero. This result differs from that of Raman and Nilakantan, who report zero shift with rocksalt. The observed shift is always less than Zachariasen's theoretical value for a given Δ, the angle by which the crystal is set away from the position for a Bragg reflection. Possibly for $\Delta<1°$ the Zachariasen formula holds. From the value of Δ at which the associated Bragg spots disappear the shortest effective wave-lengths of the elastic waves concerned are about 13A to 17A. These are between 2 and 3 times the minimum wave-length in Debye's specific heat theory. On the Preston-Bragg-Jauncey view a shift less than the Zachariasen value implies that the groups of atoms which give rise to the associate Bragg spots are considerably larger than an atom plus its 12 nearest neighbors as supposed by Preston.

1. INTRODUCTION

THE first realization that at least some of the diffuse spots and streaks which sometimes appear on a Laue photograph and which do not belong to the Laue pattern may not be accidental in the sense of depending upon the particular crystal sample under test seems to have occurred in 1938. In that year Wadlund[1] using the continuous spectrum from a tungsten target tube found that a Laue photograph of rocksalt taken with a longer exposure than usual showed diffuse radial streaks in addition to the customary Laue spots. He obtained the same pattern of streaks with different samples of rocksalt. Similar streaks appeared with different samples of sylvine (KCl). In the same year Laval[2] began a systematic experimental study of the x-rays diffracted from the front face of a crystal when it is turned away from the Bragg position for reflection of monochromatic Cu$K\alpha$ or Mo$K\alpha$ x-rays. The results of further experimental study were reported during the first half of 1939 in the *Comptes rendus*[3] and a full and exhaustive report of the study of the effect with monochromatic x-rays was published during the first half of 1939 in the Bulletin de la Société Française de Minéralogie.[4] Lonsdale[5] has called attention to this excellent and exhaustive paper by Laval. We believe that the effect we are discussing was first established by Wadlund for continuous x-radiation and by Laval for monochromatic x-rays.

Laval's work[4] was done with Mo$K\alpha$ and Cu$K\alpha$ x-rays reflected from a bent crystal of quartz. The rays were then scattered by crystals of sylvine, rocksalt, diamond, calcite, and aluminum into an ionization chamber which could detect the arrival of one photon every two seconds. Most of Laval's work was done with the non-Laue diffraction maxima for sylvine associated with the 200, 400, 600, 220 and 440 reflections of monochromatic Mo$K\alpha$ x-rays at room temperature (290°K). He also investigated the non-Laue maxima for sylvine associated with the 200 and 400 reflections at 550° and 665°. Laval describes his results in terms of the reciprocal lattice. Consider the vectors $\mathbf{k}_0$ and $\mathbf{k}$, each of whose magnitudes is $1/\lambda$ and whose directions are, respectively, those of the incident

[1] A. P. R. Wadlund, Phys. Rev. **53**, 843 (1938).
[2] J. Laval, Comptes rendus **207**, 169 (1938).
[3] J. Laval, Comptes rendus **208**, 1512 (1939).
[4] J. Laval, Bull. Soc. Franc. Mineral. **62**, 137 (1939).
[5] K. Lonsdale, Nature **146**, 806 (1940).

and scattered beams of x-rays. Laval calls the vector $\mathbf{k}-\mathbf{k}_0$ (see Zachariasen's paper[6]) the *vecteur de diffusion*. Drawing this vector from the origin of the reciprocal lattice, Laval calls the point at the other end of the vector the *pole de diffusion*. We shall translate this by "diffraction pole." The magnitude of $\mathbf{k}-\mathbf{k}_0$ is $(2/\lambda)\sin\frac{1}{2}\phi$, where ϕ is the angle of scattering. When the diffraction pole falls on the *hkl* reciprocal lattice point, the *hkl* Bragg reflection occurs. According to Laval, each reciprocal lattice point is surrounded by a region of strong scattering. If the diffraction pole falls within this region, the intensity of scattering is large but of smaller order of magnitude than that of Bragg reflection. Between the regions of strong scattering surrounding each reciprocal lattice point there exists the region of weak scattering. If the diffraction pole falls within this region, the intensity of scattering is of the order of magnitude of Jauncey, Harvey and Woo's diffuse scattering.[7] Laval states that each region of strong scattering is divided into subregions by equi-scattering (*isodiffusion*) surfaces. If the diffraction pole is moved along an equi-scattering surface, the intensity of the scattered rays remains constant. Laval experimentally determines these surfaces to be surfaces of revolution about the line joining O, the origin of the reciprocal lattice, to M, the *hkl* point of the reciprocal lattice. An equi-scattering surface is not spherical. Its dimension is greater in the direction perpendicular to OM than its dimension along OM. Further, the distance from M to an equi-scattering surface in the direction from M to O is less than that in the opposite direction. The maximum intensity of a non-Laue diffraction spot will be determined by the position of the point of tangency between the sphere of reflection and an equi-scattering surface surrounding the *hkl* reciprocal lattice point for a given Δ, the angle by which the *hkl* planes[8] are turned from the Bragg angle θ for the *hkl* reflection. As a result of the shape of Laval's equi-scattering surfaces, the shift $\phi_{aB}-2\theta$ is less than that given by Zachariasen's theoretical formula[6]

$$\tan\phi_{aB}=\frac{2\sin\theta\cos j}{1-2\sin\theta\sin j} \tag{1}$$

or Zachariasen's approximate theoretical formula

$$\phi_{aB}-2\theta=2\Delta\sin^2\theta, \tag{2}$$

where ϕ_{aB} is the angle of scattering for the rays arriving at the position of maximum intensity of the non-Laue diffraction maximum associated with the *hkl* Bragg reflection, j is the angle of incidence on the *hkl* planes, and $\Delta=j-\theta$. Equation (1) was derived independently by Raman, Nilakantan and Nath.[9] Both derivations, however, depend on the assumption of spherical equi-scattering surfaces surrounding the *hkl* reciprocal lattice point.

The experimental work of Laval with monochromatic rays has been confirmed by Preston,[10] Siegel and Zachariasen,[11] Raman and Nilakantan,[12–14] Lonsdale, Knaggs and Smith,[15] Jauncey and Baltzer,[16] and Siegel.[17] Raman and Nilakantan's results have been discussed by Zachariasen.[18,19]

2. Discussion of Theory

Zachariasen[6] and Raman and Nath[7] give the vector relation

$$\mathbf{k}-\mathbf{k}_0+\boldsymbol{\tau}=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3, \tag{3}$$

where the vectors $\mathbf{b}_i$ $(i=1, 2, 3)$ are reciprocal to $\mathbf{a}_i$ $(i=1, 2, 3)$, the edges of the unit cell of the crystal. The magnitude of $\boldsymbol{\tau}$ is $1/\Lambda$, where Λ is the wave-length of elastic waves of frequency ν

[6] W. H. Zachariasen, Phys. Rev. **57**, 66A (1940); *ibid.* **57**, 597 (1940).
[7] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931); Y. H. Woo, Phys. Rev. **38**, 1 (1931) and **41**, 21 (1932); G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).
[8] For brevity we shall speak of the *hkl* planes even though we are dealing with, say, the 622 reflection which is a second-order reflection from the 311 planes.

[9] C. V. Raman and P. Nilakantan, Proc. Ind. Acad. Sci. **11A**, 379 (1940); C. V. Raman and N. Nath, Proc. Ind. Acad. Sci. **12A**, 83 (1940).
[10] G. D. Preston, Proc. Roy. Soc. **A172**, 116 (1939).
[11] S. Siegel and W. H. Zachariasen, Phys. Rev. **57**, 66A (1940); *ibid.* **57**, 795 (1940).
[12] C. V. Raman and P. Nilakantan, Proc. Ind. Acad. Sci. **11A**, 389 (1940); Curr. Sci. **9**, 165 (1940).
[13] C. V. Raman and P. Nilakantan, Proc. Ind. Acad. Sci. **11A**, 398 (1940).
[14] C. V. Raman and P. Nilakantan, Proc. Ind. Acad. Sci. **12A**, 141 (1940).
[15] K. Lonsdale, I. Knaggs and H. Smith, Nature **146**, 332 (1940).
[16] G. E. M. Jauncey and O. J. Baltzer, Phys. Rev. **58**, 1116 (1940).
[17] S. Siegel, Phys. Rev. **59**, 371 (1941).
[18] W. H. Zachariasen, Nature **145**, 1019 (1940).
[19] W. H. Zachariasen, Phys. Rev. **59**, 207 (1941).

in the crystal. Raman and Nath[7] write (3) in the form

$$(n/d)+(1/\Lambda)=n/d_m, \tag{4}$$

where $1/d$, $1/\Lambda$, and $1/d_m$ are treated as vectors and d is the grating space for the hkl planes, and where n is the order of reflection for the hkl planes. The effect of the elastic waves of the crystal is to modify ("modulate" according to Laval) the grating space d so that it assumes the value d_m for a small fraction of the time that the x-rays are incident on the crystal. According to Zachariasen the elastic waves are a consequence of the thermal agitation of the atoms of the crystal as in Debye's theory of specific heats of solids.[20] According to Raman and Nath the elastic waves are excited by the incident x-rays by means of a quantum process. Zachariasen's theory gives $\boldsymbol{\tau}$ parallel or antiparallel to $\mathbf{k}$. Raman and Nath make two tentative assumptions concerning $\boldsymbol{\tau}$. Their first assumption corresponds to the result of Zachariasen's theory just mentioned and so they arrive at Eqs. (1) and (2). In their second assumption $\boldsymbol{\tau}$ is taken perpendicular to the line joining the origin and the hkl point of the reciprocal lattice and in the plane of incidence for the hkl planes. This second assumption leads to

$$\sin\tfrac{1}{2}\phi_{aB}\cos(j-\tfrac{1}{2}\phi_{aB})=\sin\theta \tag{5}$$

and the approximate relation

$$\phi_{aB}-2\theta=0, \tag{6}$$

even though $j\neq\theta$. Laval's experimental results give the shift $(\phi_{aB}-2\theta)$ as being between the value given by (1) or (2) and that given by (5) or (6), with perhaps the experimental shift closer to (6) than to (2).

Discussing Wadlund's results with rocksalt and sylvine, Zachariasen[21] suggested that the diffuse streaks might be due to a two-dimensional lattice appearing on the surfaces of the mosaic blocks which constitute these crystals. Preston[10] concludes that his results with aluminum do not support this idea. Instead, Preston suggests that the crystal is broken up into groups of atoms by the thermal vibrations of the lattice. The groups form three- but not two-dimensional lattices. Bragg[22] has examined Preston's idea for the case of scattering by a group of eight point-atoms arranged at the corners of a cube of edge a. Jauncey[23] has further examined the scattering of a simple cubic array of point-atoms with N atoms on an edge and with a distance a between adjacent atoms. Jauncey has found that the theory gives rise to (2) for small values of $\Delta=(j-\theta)$ and for values of $N=2$, 3, 4, 5. This is an astonishing result.

Equation (2) fairly well fits the results obtained for rocksalt by Siegel and Zachariasen,[11] for diamond by Raman and Nilakantan,[12] and for sylvine by Lonsdale, Knaggs, and Smith.[22] Since Eq. (2) can be obtained by at least two—if not three—different theories, experimental agreement with (2) does not support any one of these theories above any other. It will be necessary to study the intensity as well as the law of position in order to choose between the theories. However, the experimental law of position is in some doubt. In addition to Laval's finding of a shift $(\phi_{aB}-2\theta)$ less than given by (2), Raman and Nilakantan report results with sodium nitrate[13] and rocksalt[14] which fit (6) rather than (2). We have therefore undertaken an experimental study of the law of position of non-Laue maxima for rocksalt.

3. Experimental Method

Instead of the method of penetration through a crystal plate used by Raman and Nilakantan,[14] we have, following Laval[2–4] and Siegel and Zachariasen,[11] used the method of scattering from the 100 cleavage face of a thick rocksalt crystal. Raman and Nilakantan using the penetration method for rocksalt were forced to use Mo$K\alpha$ and Mo$K\beta$ rays in order to obtain sufficient intensity. The optimum thickness in the penetration method equals $1/\mu$ for scattering in the forward direction, where μ is the linear absorption coefficient. For Mo$K\alpha$ rays in rocksalt, $\mu=18.0$ cm^{-1} and the optimum thickness is 0.55 mm, while, for Cu$K\alpha$ rays in rocksalt, $\mu=165$ cm^{-1} and the optimum thickness is 0.06 mm. It is impractical to use Cu$K\alpha$ rays in the penetration method because of the great loss of

[20] P. Debye, Ann. d. Physik **39**, 789 (1912).
[21] W. H. Zachariasen, Phys. Rev. **53**, 844 (1938).
[22] W. H. Bragg, Nature **146**, 509 (1940).
[23] G. E. M. Jauncey, Phys. Rev. **59**, 456 (1941); Nature **147**, 146 (1941).

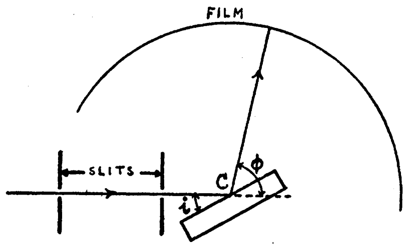

FIG. 1. Diagram of apparatus.

intensity if a reasonably thick plate is used. On the other hand, when Mo$K\alpha$ rays are used, the shift $\phi_{aB}-2\theta$ becomes small if Eq. (2) represents the experimental law. For instance, $\sin\theta$ for B_{620} (the 620 Bragg reflection) is 0.4 and $\phi_{aB}-2\theta=1.6°$ for $j-\theta=5°$. But if Cu$K\alpha$ rays are used, $\sin\theta=0.863$ and $\phi_{aB}-2\theta=7.45°$. If it is desired to show that $\phi_{aB}-2\theta\neq 0$, this can be shown more convincingly with Cu$K\alpha$ rays than with Mo$K\alpha$ rays but in the case of Cu$K\alpha$ rays the front face method should be used.

The experimental arrangement is shown in Fig. 1. The primary beam of x-rays makes a glancing angle of incidence i on a 100 cleavage face of rocksalt. Scattering occurs in various directions ϕ. The circle represents the photographic film which is bent into a cylinder about a vertical axis through C. The radius of the cylinder is 9.64 cm. Each slit is rectangular, being 0.275 mm wide and 1.45 mm high. The slits are 10 cm apart. From the values of i at which various Laue spots disappear, $\lambda_{\min}$ was estimated to be 0.58A when the copper target tube was used so that the tube was operated at 21 kv peak. A molybdenum target tube operated at about 35 kv peak was used for a few pictures.

All crystal surfaces have been etched with a twenty-percent solution of alcohol in distilled water in order to remove any warped surface layers which might be present. The 200 Bragg reflection of Cu$K\alpha_1$ gave a line 0.7 mm wide on a film placed 150 cm from the axis about which the crystal may be turned. The width of 1.6′ calculated from this data compares well with that corresponding to the half-width of 87″ at half-maximum found by Kirkpatrick and Ross[24] for rocksalt with a double crystal spectrometer. The surfaces of our crystals were thus reasonably free of warping.

It may be objected that Cu$K\alpha$ x-rays are so highly absorbed that in the front face method the rays only penetrate a few atomic layers and that therefore in this method a surface phenomenon is observed. This might explain such difference as occurs between any results we may obtain and those of Raman and Nilakantan. In the arrangement of Fig. 1 the intensity which is scattered from a layer of the crystal next to the surface is proportional to

$$1-\exp[-\mu t\{(1/\sin i)+1/\sin(\phi-i)\}], \quad (7)$$

where t is the thickness of the layer. The thickness which gives rise to one-half the intensity in an aB (associated Bragg) spot is therefore

$$0.693/\mu\{(1/\sin i)+1/\sin(\phi-i)\}. \quad (8)$$

An aB_{620} spot occurs at $i=44°\,40'$ and $\phi_{aB}=124°\,06'$ with Cu$K\alpha$ rays. The half-value thickness is therefore 1.6×10^{-3} cm. A linear dimension of the mosaic blocks of which rocksalt is believed to be composed is of the order of 10^{-4} cm. Hence the layer which contributes one-half of the intensity of the aB_{620} spot is about 16 mosaic blocks thick. Had the thickness been a fraction of that of a mosaic block, we would have abandoned this method but, as it is, we feel some justification in assuming that the layer is thick enough for the crystal surface effect to be relatively small.

In this paper we have limited ourselves to a study of the equatorial ($hk0$) associated Bragg spots. In each photograph a Bragg line is placed on the film by rocking the crystal through a small angle about $i=i_B$, where i_B is the glancing angle of incidence on the 100 cleavage face which gives rise to an $hk0$ Bragg reflection. The exposure is for an interval of a few seconds up to a minute depending on the particular Bragg line. For the higher orders of reflection the Bragg line is a doublet due to the presence of Cu$K\alpha_1$ and Cu$K\alpha_2$. The crystal is then turned away from the Bragg position to another value of i. With this new value of i the film is exposed for some 10 to 20 hours. For equatorial spots, the L_{hk0} spot ($hk0$ Laue spot) is displaced from the position of the B_{hk0} line ($hk0$ Bragg reflection) by $2(i-i_B)$. All angular measurements are made from the original films or from microphotometer traces of these films. For equatorial spots $(i-i_B)=(j-\theta)$.

[24] P. Kirkpatrick and P. A. Ross, Phys. Rev. **43**, 596 (1933).

4. Experimental Results

A sample photograph is shown in Fig. 2. The various Laue spots are indicated on the figure. In addition the B_{400}, B_{600}, and B_{620} lines for Cu$K\alpha_1$ and Cu$K\alpha_2$ are shown and these are used as fiducial marks for standardizing the photograph. We note the three strong associated Bragg spots, $aB_{400\alpha}$, $aB_{400\beta}$ and $aB_{640\beta}$, and a faint diffuse spot $aB_{620\beta}$. The subscripts α and β refer to the Cu$K\alpha$ and Cu$K\beta$ spectrum lines, respectively. The angle of glancing incidence on the 100 cleavage face for this photograph was $i=30°\ 50'$. In Fig. 3 is shown the reciprocal lattice construction for $i=30°\ 50'$. Two circles α and β with centers, respectively, at P_α and P_β are drawn. These represent the spheres of reflection for the Cu$K\alpha$ and Cu$K\beta$ spectrum lines, respectively. It is to be noted that the α circle passes close to the 400 point. Therefore an $aB_{400\alpha}$ spot should appear on the corresponding photograph. As seen in Fig. 2 this spot does appear. Further, the β circle of Fig. 3 passes close to the 400, 620 and 640 points. In Fig. 2, the corresponding $aB_{400\beta}$ and $aB_{640\beta}$ spots appear. If Fig. 3 is carefully drawn, the point 620, though close to the β circle, is further from the circle than either of the points 400 or 640. It is a rule that the further a reciprocal lattice point is from the sphere of reflection the fainter, but more diffuse, the corresponding aB spot is. We should then expect the $aB_{620\beta}$ spot to be faint and as seen from Fig. 2 it is faint (it may not show on the reproduction).

In Fig. 4 are shown strips cut from 18 photographs similar to Fig. 2. The first or top strip gives the equatorial spots for $i=45°\ 07'$. The i for successive strips decreases by 1° until the 18th or bottom strip is reached when $i=28°\ 07'$. The Bragg reflection lines for Cu$K\alpha$ rays fall in the vertical lines headed by $B_{400\alpha}$, $B_{600\alpha}$, $B_{620\alpha}$ in Fig. 4. These lines are used as fiducial marks for the respective strips. The 400 and 620 Laue spots fall into the slant lines headed by L_{400} and L_{620} in Fig. 4. It is seen that as the L_{400} spot approaches the $B_{400\alpha}$ line, an associated Bragg spot ($aB_{400\alpha}$) first appears in the 6th strip (this is so on the original negative but may not be evident in the reproduction). The aB spot is always between the B line and the L spot. Experimentally the aB_{hkl} spot is associated with the B_{hkl} line. If an $L_{h'k'l'}$ spot is made to approach a B_{hkl} line, no aB spot appears unless $h'k'l'=hkl$. When the L_{400} spot falls on the B_{400} line, photographic reversal and halation appears as shown in the 13th strip. Following the progress of the L_{620} spot down from the first strip, we note that the $aB_{620\alpha}$ spot disappears in the 11th strip (on the original negative). A slight indication of photographic reversal is shown for L_{620} in the 5th strip. The center of the Laue spot is not quite in the position of the $B_{620\alpha}$ line but the Laue spot has a width due to divergence of the incident beam as determined by the slit system. The divergence is sufficient to cause some Bragg reflection.

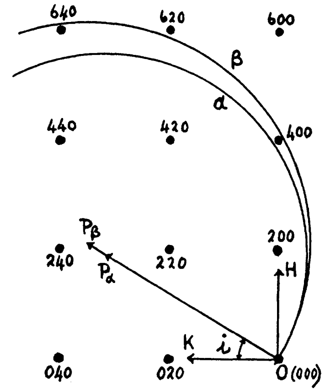

Fig. 3. Reciprocal lattice construction for the experimental conditions of Fig. 2. Geometric construction shows that the diffuse spots $aB400\alpha$, $aB400\beta$, $aB620\beta$, and $aB640\beta$ are likely to occur for $i=30°\ 50'$.

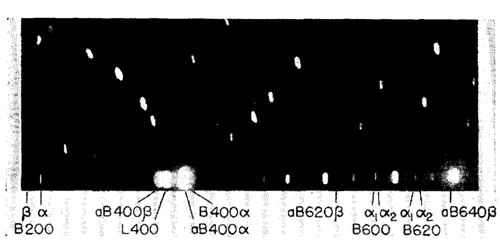

Fig. 2. Sample of photograph showing the associated Bragg reflections of Cu$K\alpha$ and Cu$K\beta$ x-rays for a glancing angle of incidence of $i=30°\ 50'$ on the 100 cleavage face of rocksalt. The figure is reduced to about one-third of the size of the original photograph.

The experimental values of the shift $(\phi_{aB}-2\theta)$ are given in Table I. The value of $i_{B400\alpha}=\theta_{400\alpha}$ is 33° 07′ and that for $i_{B620\alpha}$ is 41° 15′.

From Table I we conclude that the shift $(\phi_{aB}-2\theta)$ is less than that given by Zachariasen's Eq. (2). The shift, however, is not zero as reported by Raman and Nilakantan.[14] Possibly at small values of Δ (1° or less), the shift is given by (2). Our result is in general agreement

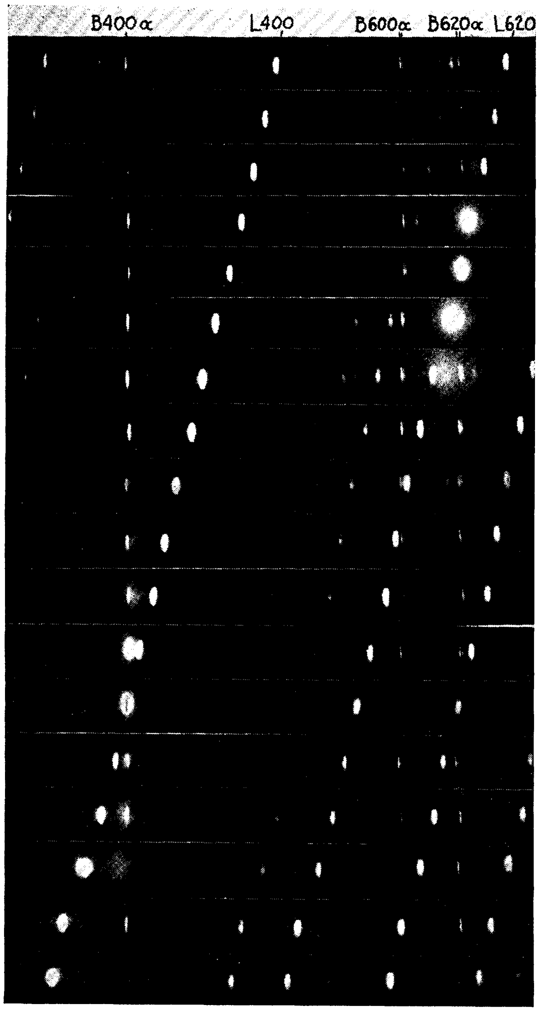

FIG. 4. Equatorial reflections of copper x-rays from cleavage face of rocksalt. Glancing angle of incidence is $i=45°\,07'$ for top strip with i decreasing by 1° for each successive strip. The lines $B400\alpha$, $B600\alpha$, and $B620\alpha$ are placed as fiducial marks on the strips. An associated Bragg spot $aB620\alpha$ is visible on the upper strips. The associated Bragg spot $aB400\alpha$ is first apparent (on the original negative) for the 6th strip, becomes more intense and less diffuse approaching the 13th strip, and then gradually decreases in intensity. A diffuse reflection $aB400\beta$ appears on the last four strips.

with Laval's results. The equi-scattering surfaces surrounding the 400 and 620 reciprocal lattice points are not spherical but are shaped in a way similar to that found by Laval.

We have obtained a few films with a molybdenum target tube. The microphotometer trace for the $aB_{600\alpha}$ spot obtained with $\Delta=3°\,00'$ shows a shift of $0°\,22'\pm 0°\,11'$. This is greater than zero but is less than $0°\,51'$ as given by (2). From (8) and $\mu=18.0$ cm^{-1} the half-value layer for the $aB_{600\alpha}$ spot is 6.5×10^{-3} cm or about 65 mosaic blocks thick when Mo$K\alpha$ rays are used. Since our result with Mo$K\alpha$ rays qualitatively supports our results with Cu$K\alpha$ rays, we feel that our conclusion is not a consequence of the effective layer of rocksalt being too thin.

5. Discussion of Results

From Fig. 1 of Zachariasen's paper[6] it can be shown that the magnitude of $\boldsymbol{\tau}$ which gives rise to strong scattering in the scattering direction ϕ is

$$|\boldsymbol{\tau}|=1/\Lambda=(2/\lambda)\{\sin^2\theta+\sin^2\tfrac{1}{2}\phi-2\sin\theta\sin\tfrac{1}{2}\phi\cos(\tfrac{1}{2}\phi-j)\}^{\frac{1}{2}}. \quad (9)$$

This reduces to the approximate relation

$$\Lambda=\lambda/\{\delta^2+4\Delta(\Delta-\delta)\sin^2\theta\}^{\frac{1}{2}}, \quad (10)$$

where $\delta=\phi-2\theta$. If we wish to find the Λ which gives rise to the maximum intensity of an associated Bragg spot, we replace ϕ by ϕ_{aB} in the formula for δ. The values of $\delta=(\phi_{aB}-2\theta)$ and Δ for the least visible $aB_{400\alpha}$ spot are 2.4° and 7.0°, respectively, so that from (10) $\Lambda=13.3$A. The respective values for the least visible $aB_{620\alpha}$ spot are $-5.4°$ and $-5.13°$, so that $\Lambda=17.5$A. In the Debye[20] theory of specific heats, the minimum value of Λ for a simple cubic crystal is twice the grating space, so that, treating rocksalt as a simple cubic crystal at least for the equatorial associated Bragg spots, we find $\Lambda_{\min}=5.628$A. As Fine[25] points out the solid is treated as a continuum in the Debye theory until $\Lambda_{\min}$ is approached. At this place in the theory it is suddenly remembered that the solid consists of atoms separated by pretty definite distances. In the case of tungsten crystals Fine finds that the vibration spectrum, instead of having a maximum at a frequency equal to Debye's $\nu_{\max}$, has two sharp maxima at frequencies 0.82 and 0.55 times the Debye $\nu_{\max}$. Though rocksalt is a polar and tungsten a nonpolar crystal, it may well be that the Λ spectrum exhibits a maximum in the neighborhood of $\Lambda=12$A. With such a maximum one could not expect a 400 reciprocal lattice point of rocksalt or sylvine to be sur-

[25] P. C. Fine, Phys. Rev. 56, 355 (1939).

rounded by a spherical equi-scattering surface which would be tangent to the sphere of reflection when $\Delta=7°$. Zachariasen's theory as at present stated must break down for rocksalt at $\Lambda=2$ or 3 times 5.628A. Furthermore, Brillouin[26] points out that the instantaneous distribution of density in an elastic wave can no longer be treated as sinusoidal when Debye's $\Lambda_{\min}$ is approached. Reflection of x-rays from elastic waves is limited to first-order reflection only when the waves may be treated as sinusoidal. If Λ approaches $\Lambda_{\min}$, the reflection takes place according to

$$n\lambda=2\Lambda\sin\theta. \tag{11}$$

One may expect that in (4) the term $1/\Lambda$ should be multiplied by an integer n' when Λ approaches $\Lambda_{\min}$.

From Table I it may be concluded that the Zachariasen formula for the shift holds for the $aB_{400\alpha}$ spot when $\Delta=1°$. The value of Λ for this case is 96A, which is 17 times $\Lambda_{\min}$. In the region $0°\leq\Delta\leq1°$ the corresponding elastic waves may be treated as sinusoidal and in this region Zachariasen's theory may hold. However, there is the question of the alignment of the mosaic blocks. Compton and Allison[27] in discussing the work of others with the double crystal spectrometer quote half-widths at half-maximum of 7 seconds, 87 seconds, and 30 minutes with different samples of rocksalt. On account of these facts there is great uncertainty in the value of Δ when $\Delta\lesssim1°$. For this reason Laval completely avoided the region of $\Delta\lesssim1°$. We believe that the experimental field separates into three regions to be studied—the region of $\Delta\lesssim1°$, the region of strong scattering for $\Delta>1°$, and the region of weak scattering. It would be very interesting to study the effect of temperature in the first region. It is well established that the effect of a rise in temperature is to increase the intensity of the scattering in the second and third regions.

So far in this section the discussion has been in terms of Zachariasen's theory. However, there is the Preston-Bragg-Jauncey theoretical viewpoint. In Jauncey's paper[23] curves are shown for the scattering from a simple cubic lattice with N atoms on an edge. For $\Delta=5°$ and the 620 associated Bragg reflection of Cu$K\alpha$ x-rays from rocksalt (treated as a simple cubic crystal), the curves show a maximum at $(\phi_{aB}-2\theta)$ given by Zachariasen's Eq. (2) for $N=2$, 3, 4. There is a definite breakdown at $N=6$ and the shift becomes less than Zachariasen's shift. From our experimental results we would in terms of this theory conclude that $N>6$. It is hoped to discuss this matter further in a later paper.

TABLE I. *Shift* $(\phi_{aB}-2\theta)$*:* Cu$K\alpha$ *x-rays.*

aB_{400}			aB_{620}		
Δ	$\phi_{aB}-2\theta$ Exp.	Eq. (2)	Δ	$\phi_{aB}-2\theta$ Exp.	Eq. (2)
7.0°	2.4°	4.17°	3.87°	4.5°	5.76°
6.0	2.4	3.58	2.87	3.2	4.27
5.0	2.1	2.98	1.87	1.8	2.78
4.0	1.6	2.38	0.87	0.9	1.30
3.0	1.3	1.79	−0.13	0.0	−0.19
2.0	0.8	1.19	−1.13	−1.2	−1.68
1.0	0.6	0.60	−2.13	−2.3	−3.17
0.0	0.0	0.00	−3.13	−3.6	−4.66
−1.0	−0.4	−0.60	−4.13	−4.5	−6.15
−2.0	−0.6	−1.19	−5.13	−5.4	−7.64
−3.0	−1.2	−1.79			
−4.0	−1.8	−2.38			
−5.0	−1.8	−2.98			

Note added in proof.—In references 16 and 23 the term "modified Bragg reflection" was used. In the present article this term has been replaced by the term "associated Bragg reflection" and the symbol *mB* by the symbol *aB*. The reflection indices in the references should be doubled.

[26] L. Brillouin, Ann. de physique **17**, 88 (1922).
[27] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, 1935), pp. 401, 729.

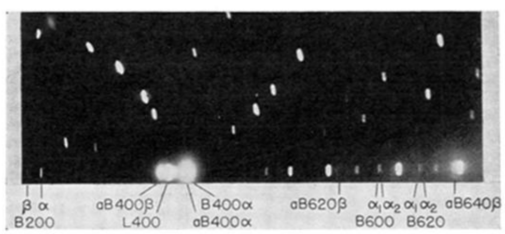

FIG. 2. Sample of photograph showing the associated Bragg reflections of Cu$K\alpha$ and Cu$K\beta$ x-rays for a glancing angle of incidence of $i=30°\ 50'$ on the 100 cleavage face of rocksalt. The figure is reduced to about one-third of the size of the original photograph.

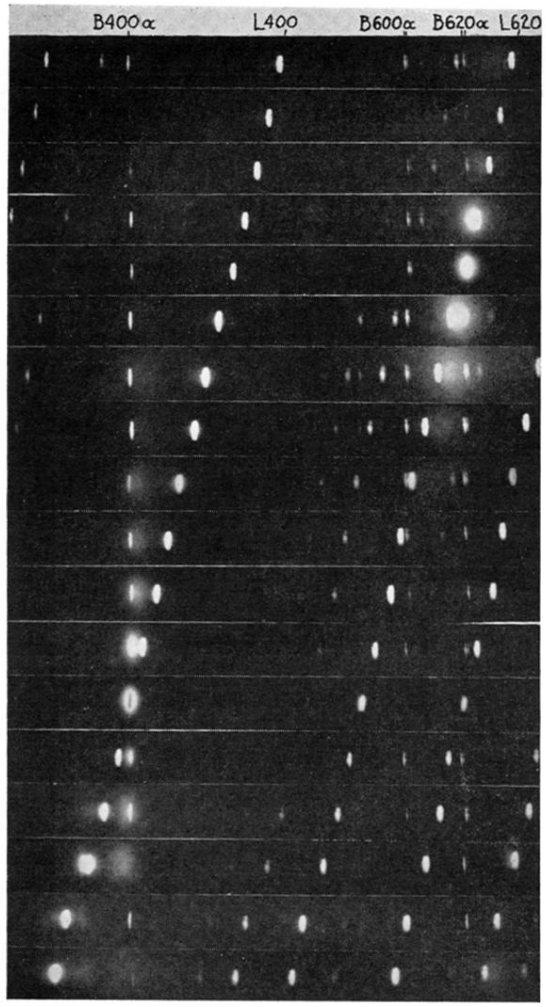

FIG. 4. Equatorial reflections of copper x-rays from cleavage face of rocksalt. Glancing angle of incidence is $i=45°\,07'$ for top strip with i decreasing by 1° for each successive strip. The lines $B400\alpha$, $B600\alpha$, and $B620\alpha$ are placed as fiducial marks on the strips. An associated Bragg spot $aB620\alpha$ is visible on the upper strips. The associated Bragg spot $aB400\alpha$ is first apparent (on the original negative) for the 6th strip, becomes more intense and less diffuse approaching the 13th strip, and then gradually decreases in intensity. A diffuse reflection $aB400\beta$ appears on the last four strips.