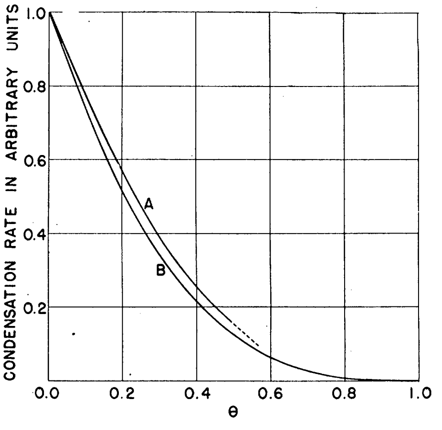

FIG. 2. Condensation rate as a function of fraction of surface covered. Curve B is experimental, curve A theoretical.

tion. This has been pointed out by Roberts.[8] It appears, therefore, that mobility should be the important factor governing the motion of the phase boundaries. In that case, Langmuir's calculations show[9] that, for large values of θ,

$$2t/\tau_K = 0.26/(1-\theta)^2, \tag{4}$$

where τ_K is the average time that elapses before an adsorbed molecule, located at an external corner of one phase, hops into an available site in the other phase. From Eq. (4) we obtain

$$d\theta/dt = (1-\theta)^3/0.26\tau_K. \tag{5}$$

Comparing this with Eq. (3), and using the value of 0.25 min.$^{-1}$ for a (Fig. 1), we find that $\tau_K = 31$ minutes.

For smaller values of θ, the condensation rate will be approximately the same as for an immobile film. Curve A (Fig. 2), showing how the rate varies with θ, was obtained by using a model described by Roberts[10] and by assuming that each adsorbed molecule prevents adsorption on the four neighboring sites. The curve is to be compared with the experimental curve B, representing the expression $(1-\theta)^3$. The fact that curve B lies below curve A may be due indirectly to the mobility of the adsorbed molecules. Since τ_K is fairly small, the potential hills between sites must be of the order of kT in height. Thus the molecules will describe quite large oscillations about their mean positions. This could cause partial screening of the four *next* nearest sites and therefore produce a lowering of the condensation rate.

---

[8] Reference 4, p. 23, footnote.

[9] Reference 7, Eqs. (65) and (66).

[10] Reference 4, p. 35.

SEPTEMBER 15, 1941 PHYSICAL REVIEW VOLUME 60

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

O. J. BALTZER
Wayman Crow Hall of Physics, Washington University, St. Louis, Missouri

(Received July 3, 1941)

No previous quantitative measurements have been made of the temperature dependence of the non-Laue diffraction maxima at lowered temperatures, although it has been known that the non-Laue diffraction pattern of many crystals nearly disappears at liquid-air temperature. In the present experiment, an ionization chamber and electrometer tube circuit have been used in determining the intensity of the non-Laue maxima observed when copper $K\alpha$ x-rays are diffracted from a rocksalt crystal. Measurements have been made at room temperature and at liquid-air temperature for the 200, 400, and 600 regions of scattering. It is found that the experimental decrease in intensity at liquid-air temperature is in fair agreement with an expression of the form $(1-e^{-2M})$, where e^{-2M} is the well-known Debye-Waller temperature factor.

1. INTRODUCTION

IT has been established that the intensity of the non-Laue diffraction maxima is dependent upon the temperature of the crystal specimen. Preston[1] showed that the intensity of these dif-

---

[1] G. D. Preston, Proc. Roy. Soc. **A172**, 116 (1939).

fuse spots was greatly enhanced at elevated temperatures for crystals of sodium chloride, aluminum, and magnesium, but that the temperature effect was less with diamond. Laval,[2] using an ionization chamber method, measured the scattered intensity at room temperature and at 500°C for potassium chloride and found a marked increase at the higher temperature. Raman and Nilakantan[3] have reported a definite increase with temperature for sodium nitrate. Lonsdale and collaborators[4] have observed that for many crystals, including KCl and $NaNO_3$, the diffuse spots almost completely disappear at liquid-air temperatures, and that this temperature effect is completely reversible.

Although there is sufficient qualitative evidence that the intensity increases with temperature, there have been no published quantitative data, with the exception of Laval's work in 1939, regarding the temperature dependence of the non-Laue diffraction maxima. If, as the Faxen-Waller-Zachariasen theory[5–7] supposes, the non-Laue diffraction maxima are a result of a thermal diffuse scattering, then we would expect to find a large decrease in intensity at liquid-air temperature. According to the theory proposed by Raman and his associates,[8] however, the phenomenon is not primarily thermal in origin so that the temperature effect would be less pronounced in this theory. It is, therefore, worth while to attempt a quantitative measurement of the intensity at lowered temperatures and to obtain the numerical ratio of the diffracted intensity at room temperature to the intensity at liquid-air temperature. The present research has been restricted to a study of the effect of low temperature upon the intensity of the non-Laue maxima observed when Cu $K\alpha$ x-rays are diffracted from rocksalt.

2. Apparatus and Experiment

A demountable, copper target x-ray tube was operated at a potential of approximately 25 kilovolts peak and at a current of 20 milliamperes. A constant voltage double motor-generator set in parallel with a bank of storage batteries was used to decrease fluctuations in line voltage. A gradual deposition of evaporated tungsten and of decomposed carbon from the diffusion pump oil was found to cause a detectable decrease in the intensity of the Cu $K\alpha$ radiation. The target was, therefore, cleaned at frequent intervals, and, as a further precaution, a liquid-air trap was used to secure improved vacuum conditions. A nickel filter, 0.0082 gram/cm², gave an intense beam of Cu $K\alpha$ x-rays together with a weak background of continuous radiation that did not interfere in the scattering measurements. The primary beam was defined by fixed collimating slits of lead. The dimensions of the slit closer to the x-ray tube were 0.030 cm wide by 0.100 cm high, and of the further slit were 0.024 cm wide by 0.088 cm high, with a separation of 5.0 cm between the slits. The rocksalt crystal was separated by a distance of 2.0 cm from the second slit. All measurements were made with the crystal displaced by more than 2° from a Bragg angle of strong reflection. Under this condition, no Bragg reflection can possibly occur, so that the relatively large divergence of the primary beam is not only permissible but also serves to minimize the statistical fluctuations in the measurements.

In order that the crystal be cooled down to

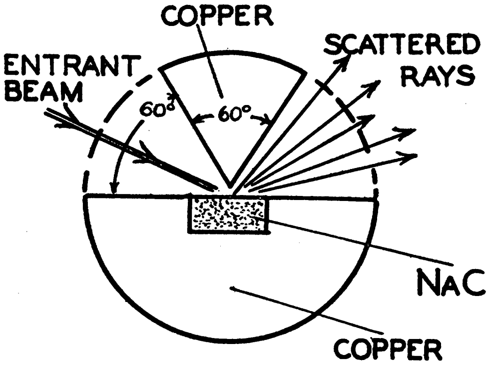

FIG. 1. Horizontal section through copper crystal holder for use at low temperature. Vertical dimension of slot for entrant beam was 3 mm. Opening for scattered rays had a vertical angular width of 15°.

---

[2] J. Laval, Bull. Soc. Franc. de Mineralogie **62**, 137 (1939).

[3] C. V. Raman and P. Nilakantan, Proc. Ind. Acad. Sci. **11**, 398 (1940).

[4] K. Lonsdale, Nature **146**, 806 (1940); K. Lonsdale, I. Knaggs, and H. Smith, Nature **146**, 332 (1940).

[5] H. Faxen, Zeits. f. Physik **17**, 266, 277 (1923).

[6] I. Waller, Zeits. f. Physik **17**, 398 (1923).

[7] W. H. Zachariasen, Phys. Rev. **57**, 597 (1940); W. H. Zachariasen, Phys. Rev. **59**, 207 (1941).

[8] C. V. Raman and P. Nilakantan, Proc. Inc. Acad. Sci. **11**, 379, 389 (1940).

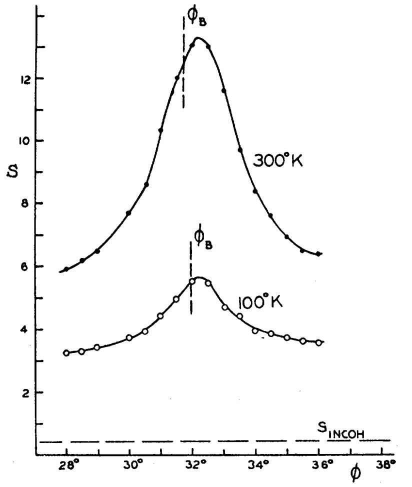

FIG. 2. Intensity of non-Laue diffraction maximum of Cu $K\alpha$ x-rays from rocksalt. Crystal displaced by 3° from 200 Bragg position of selective reflection.

liquid-air temperature without condensation of water vapor on the face of the crystal, it is necessary that the crystal be kept within a leak-free, evacuated spectrometer chamber. A vacuum chamber of radius 2¾″, mounted on a goniometer head, was constructed for this reason and also to prevent spurious intensity measurements resulting from scattering from air, and to lessen any decrease in x-ray intensity due to absorption in air. The exit for x-rays diffracted from the rocksalt was through a slot in the vacuum chamber extending from the primary beam position of $\phi = 0°$ to a scattering angle of $\phi = 115°$, so that all reflections of Cu $K\alpha$ rays from rocksalt out to the 600 reflection could be studied. The slot was covered by Cellophane, 0.008 cm thick, which withstood the atmospheric pressure outside the evacuated chamber.

The crystal and crystal holder could be rotated within the vacuum chamber by means of a vacuum-tight shaft, and the angular position of the crystal could be read with a precision of 1′. The ionization chamber could also be rotated about the axis of the goniometer, and its angular position could be determined with a similar accuracy. The crystal holder was constructed from a solid cylindrical copper block with slots cut in the block for the entrant beam upon the crystal and for the scattered x-rays, as indicated in Fig. 1. The front, cleavage face of the rocksalt crystal rested upon a vertical plane passing through the axis of rotation of the spectrometer. Because of the geometrical design of the holder which shielded and almost completely surrounded the crystal, it was assumed that the temperature of the crystal face was within a few degrees of the temperature of the crystal holder. On top of the copper block containing the crystal was a sylphon bellows which served as a liquid-air reservoir. Liquid air could be poured into the reservoir from outside the spectrometer by means of a vacuum-tight connecting shaft.

Measurements of the scattered x-ray intensity and of the intense primary beam were made with an argon-filled ionization chamber coupled to a Western Electric D-96475 low grid current tube in the Barth type of balanced amplifier circuit.[9] The ionization chamber had an effective length of 7.5 cm and a diameter of 3 cm and contained argon at a pressure of 1.5 atmospheres. The ionization chamber window measured 2.46 mm wide by 15.0 mm high and was at a distance of 8.25 cm from the axis of rotation of the crystal.

The rocksalt specimen was cleaved from an artificially grown parent crystal. A series of photographs taken at increasing distances from the specimen indicated that the divergence of the 200 Bragg reflection line from the cleavage face was less than 2′. This indicates that the rocksalt was reasonably perfect and that there was little warping or distortion of the surface layer.

Measurements of the scattered intensity were made using both the steady deflection and the more sensitive rate-of-drift methods. It is desirable that the observed galvanometer deflec-

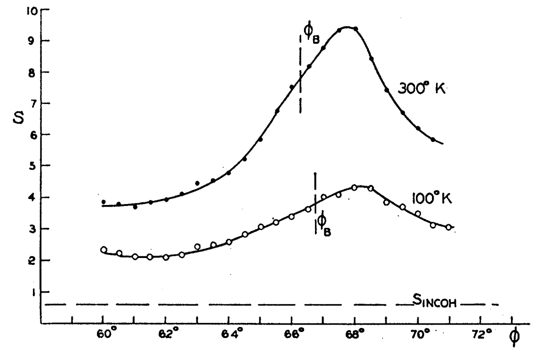

FIG. 3. Intensity of non-Laue diffraction maximum of Cu $K\alpha$ x-rays from rocksalt. Crystal displaced by 3° from 400 Bragg position of selective reflection.

---

[9] D. B. Penick, Rev. Sci. Inst. 6, 115 (1935).

tions be reduced to some form giving an absolute intensity of scattering which is independent of any particular experimental arrangement. This was done by transforming all readings to S values, where S is the ratio of the observed scattering per electron to the scattering from one electron as given by the J. J. Thomson theory.[10] Experimentally, we have

$$S=\frac{4\mu}{\rho}\,\frac{W}{NZ}\,\frac{m^2c^4}{e^4}\,\frac{R^2}{A(1+\cos^2\phi)u(\phi,i)}\cdot\frac{D_{\phi,i}}{D_0},\tag{1}$$

where $D_{\phi,i}$ and D_0 are the observed deflections due to the scattered rays and to the primary x-ray beam, respectively; R is the crystal-ionization chamber distance; A is the area of the ionization chamber window;

$$u(\phi,i)=\frac{2\sin(\phi-i)}{\sin(\phi-i)+\sin i}\tag{2}$$

is a geometrical factor to correct for the absorption effects within the crystal at a glancing angle of incidence i upon the crystal face;[11] W and Z are the average atomic weight and the average atomic number of (Na+Cl); N is Avogadro's number; and $\mu/\rho=74.8$ is the mass absorption coefficient of Cu $K\alpha$ x-rays in (Na+Cl).

The intensity of scattering of the non-Laue diffraction maxima associated with the 200, 400, and 600 reflections of Cu $K\alpha$ x-rays was determined for various scattering angles and for various values of $\Delta\equiv j-\theta$, where j is the glancing angle of incidence on the reflecting planes, and θ is the Bragg angle for reflection. For $\Delta>7°$, especially at a temperature of 100°K, the non-Laue diffraction maxima are extremely broad and barely distinguishable above the background of weak diffuse scattering; for $\Delta<1°$, the divergent primary beam permitted some ordinary Bragg reflection to occur. Measurements were, therefore, restricted to the region $2°<\Delta<7°$ in this investigation.

It is important that allowance be made for the contraction of the grating space as the temperature of the crystal is reduced. Due to this contraction, it was experimentally observed that the Bragg angle for the 600 reflection of Cu $K\alpha$ x-rays at 100°K was 35′ greater than the corresponding Bragg angle at 300°K. This agrees, within the limits of the experimental error, with the value 37′ calculated from the temperature coefficient of linear expansion, $\alpha=3.8\times10^{-5}$, for rocksalt.[12]

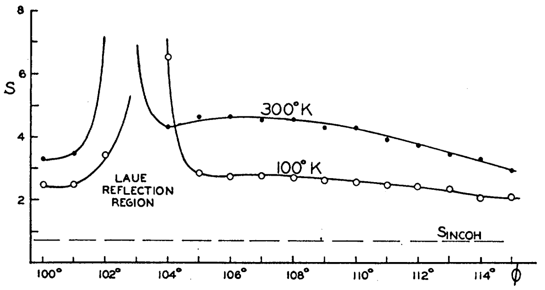

FIG. 4. Intensity of non-Laue diffraction maximum of Cu $K\alpha$ x-rays from rocksalt. Crystal displaced by −4° from 600 Bragg position of selective reflection.

The temperature contraction was always taken into account by making all measurements with respect to the Bragg angles of reflection at each particular temperature. Thus, a value of $\Delta=3°$ at liquid-air temperature implies that the crystal was displaced by 3° with respect to a Bragg angle at liquid-air temperature and not with respect to the corresponding Bragg angle at room temperature.

3. Experimental Results

Figure 2 is a typical result illustrating the diminution in scattered intensity at 100°K for the non-Laue diffraction maximum associated with the 200 region of reflection. The experimental points represent the scattered intensity in S units as the ionization chamber is moved, at small angular intervals, across the region of strong diffuse reflection. For this particular example, the crystal was displaced by 3° with respect to the 200 Bragg angle. Other distribution curves for $2°<\Delta<7°$ showed a similar relative decrease in intensity as the temperature is reduced, and it is concluded that there is no large change in the temperature effect for these different values of Δ.

The observed scattering is made up of two parts—one due to coherent scattering, the other

---

[10] G. E. M. Jauncey and W. D. Claus, Phys. Rev. **46**, 941 (1934).

[11] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 414 (1936).

[12] *International Critical Tables* (McGraw-Hill, 1928) **3**, p. 43.

TABLE I. *Comparison of the experimental ratio of intensity scattered at a temperature of 300°K to that scattered at 100°K with the ratio calculated from the expression* $(1-e^{-2M})$. *The values of the crystal setting in each reflection are those shown in Figs. 2–4.*

REGION OF REFLECTION	TEMPERATURE EFFECT EXPERIMENTAL	TEMPERATURE EFFECT CALCULATED
200	2.25	2.43
400	2.18	2.18
600	1.91	1.89

due to incoherent scattering. The incoherent scattering does not depend upon the temperature or upon the orientation of the crystal and is not connected with the non-Laue diffraction maxima. The incoherent scattering must, therefore, be subtracted from all observed S values if we wish to know the resultant S_{coh}. The magnitude of the incoherent scattering, which is indicated on the graphs by the horizontal dashed line, S_{incoh}, may be calculated from the relation,[13]

$$S_{\text{incoh}}=\frac{1-\dfrac{(\sum E_r{}^2)_{\text{Na}^+}+(\sum E_r{}^2)_{\text{Cl}^-}}{Z_{\text{Na}}+Z_{\text{Cl}}}}{\left(1+\dfrac{h}{mc\lambda}\operatorname{vers}\phi\right)^3}, \tag{3}$$

where $(\Sigma E_r{}^2)$ is the incoherent scattering function tabulated by Compton and Allison.[14]

After subtracting the incoherent scattering from all observed measurements, it is found that the intensity of the non-Laue diffraction maximum associated with the 200 reflection from rocksalt is, at 300°K, approximately 2.25 times greater than the intensity at 100°K. This ratio is obtained by averaging over the entire diffuse reflection region contained within the scattering angles $\phi=29°$ to $\phi=36°$; if we consider the peak intensity alone, the ratio of the relative scattering at 300°K to that at 100°K becomes more nearly 2.5. Possibly this indicates that the peak intensity may fall off somewhat more rapidly than the intensity diffracted at neighboring scattering angles.

From the large decrease in scattered intensity at 100°K, it is apparent that photographs taken at liquid-air temperature would reveal almost complete disappearance of the diffuse reflection pattern as has already been noted by Lonsdale.[4] The exposure time at 100°K must be more than doubled in order that the same photographic blackening be obtained.

In Fig. 3, the crystal was displaced by 3° from the 400 Bragg angle. The coherent scattering within the strong scattering region $\phi=62°$ to $\phi=71°$, is 2.18 times more intense at room temperature than at liquid-air temperature. The peak intensity is reduced by a factor of 2.35 at liquid-air temperature.

The position of maximum intensity of the diffuse reflection is clearly displaced from the position (marked by the vertical lines ϕ_B), at which the Bragg spectrum line may be observed. The divergence of the primary beam limits the accuracy of the measured value of $90'\pm15'$, although this is in reasonably good agreement with the displacement observed in the photographic method.[15]

The non-Laue diffraction maxima become more diffuse at larger scattering angles. Figure 4 gives the scattering intensity distribution in the region of the 600 reflection for $\Delta=-4°$. The shift in the position of the intense Laue spots is due to the temperature contraction of the crystal. The non-Laue diffraction pattern is shifted by a similar amount. If we take into account this shift and also correct for the incoherent scattering, we find that the non-Laue diffraction intensity is reduced by a factor of 1.91 at liquid-air temperature.

4. CONCLUSION

According to the Debye-Jauncey-Harvey-Woo[16–18] theory of diffuse scattering from crystals, the intensity of the coherent portion of the scattering is proportional to the factor $(1-e^{-2M})$ where e^{-2M}, the well-known Debye-Waller[6] temperature factor, is a function of the scattering angle and of the absolute temperature. If, for the characteristic temperature of rocksalt, the

---

[13] G. G. Harvey, P. S. Williams, and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).

[14] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), p. 782.

[15] G. E. M. Jauncey and O. J. Baltzer, Phys. Rev. **59**, 699 (1941).

[16] P. Debye, Ann. d. Physik **43**, 49 (1914).

[17] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **37**, 1203 (1931); G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).

[18] Y. H. Woo, Phys. Rev. **38**, 1 (1931); Y. H. Woo, Phys. Rev. **41**, 21 (1932).

value $\Theta = 281°C$ is chosen and if NaCl is treated as a simple cubic crystal, the calculated ratio for the temperature effect according to the factor $(1-e^{-2M})$ is found as shown in the last column of Table I. The experimental value for the decrease in scattered intensity at 100°K relative to the intensity at 300°K for the non-Laue diffraction maxima associated with the 200, 400, and 600 orders of reflection is given in the second column. It is seen that the agreement between the second and third columns is fairly good. No quantitative comparison of the experimental results with the predictions of the Faxen-Waller-Zachariasen theory have been made because an exact evaluation of the theoretically scattered intensity is rather difficult. However, a temperature dependence of the form $(1-e^{-2M})$ will be approximately valid so that it can be stated that the present experimental evidence does not disagree radically with conclusions based upon the Faxen-Waller-Zachariasen theory.

The author is greatly indebted to Dr. G. E. M. Jauncey for his interesting and helpful discussions concerning this investigation.

SEPTEMBER 15, 1941 PHYSICAL REVIEW VOLUME 60

Positive and Negative Thermionic Emission from Molybdenum

R. W. Wright
University of Wisconsin, Madison, Wisconsin

(Received July 31, 1941)

The positive and negative thermionic emission from molybdenum has been studied. The electron work function was found to be 4.20 volts and the positive ion work function was 8.6 volts. The positive ion constant term was in good agreement with Smith's equation.

The positive ion emission from molybdenum has been studied by several investigators with discordant results. These studies have been attempts to determine the positive ion work function and the constant term in Smith's[1] equation which, for molybdenum, has the following form:

$$\ln I + 0.453 \ln T + 6.22 \times 10^{-4} T = -(\varphi_{0+}e/kT) + 28.39. \quad (1)$$

Smith also considered the energy cycle:

$$\varphi_{0-} + \varphi_{0+} = H_0 + V, \quad (2)$$

where φ_{0-} is the electron work function, φ_{0+} the positive ion work function, H_0 is the heat of evaporation of a neutral atom and V is the ionization potential of the atom.

Moon[2] has obtained from the Langmuir-Kingdom-Saha theory of positive ion emission, the following relation:

$$\frac{n_p}{n_a} = \frac{\sigma_p}{\sigma_a} \exp\left[-\frac{11{,}600(V-\varphi_{0-})}{T}\right], \quad (3)$$

where n_p and n_a are the rates of evaporation of positive ions and neutral atoms, σ_p and σ_a the statistical weights of the two, V is the ionization potential and φ_{0-} is the electron work function.

Smith[1] found that his data fit Eq. (1) with $\varphi_{0+} = 6.1$ volts and a constant term of 15.9. Barnes[3] obtained $\varphi_{0+} = 8.2$ volts and a constant term equal to 26.5; values which are in better agreement with the theory. Barnes also noted that his data failed to give a straight line, the low temperature points falling above the line drawn through the high temperature points. Wahlin and Reynolds[4] found $\varphi_{0+} = 8.3$ volts for well outgassed molybdenum. They used the value of H_0 equal to 5.75 volts taken from the unpublished work of Dr. E. R. Piore. Grover,[5] using a modified Dempster mass spectrograph, to be certain that the ions measured were from the molybdenum and not from some alkali impurity, found $\varphi_{0+} = 8.9$ volts and a constant term of 25.3. He

---

[1] L. P. Smith, Phys. Rev. **35**, 381 (1930).

[2] P. B. Moon, Proc. Camb. Phil. Soc. **28**, 490 (1932).

[3] L. L. Barnes, Phys. Rev. **42**, 491 (1932).

[4] H. B. Wahlin and J. A. Reynolds, Phys. Rev. **48**, 751 (1935).

[5] Horace Grover, Phys. Rev. **52**, 982 (1937).