SEPTEMBER 1, 1931 PHYSICAL REVIEW VOLUME 38

REFLECTION OF MERCURY FROM ALKALI HALIDE CRYSTALS

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(Received July 24, 1931)

Abstract

The distribution of mercury atoms scattered from NaCl, KCl, KBr and KI has been studied by means of an ionization gauge as a function of the angle of incidence and temperatures of scatterer and incident beam. The following facts are observed for the first three crystals: (1) There is a directed beam whose deviation from a specular position increases at smaller glancing angles. (2) The angle between the crystal surface and the direction of maximum intensity in the directed beam becomes less for lower crystal temperature and higher beam temperatures. (3) The relative number of atoms scattered at random increases with decrease in crystal temperature. (4) The directed beam becomes more sharply defined at lower crystal temperatures. Within the limits of error of the present experiments no discernible change is produced by rotation of the scattering crystal about an axis perpendicular to the plane of its face. The above facts are shown to be, qualitatively at least, consistent with a space-grating theory of reflection. In the case of KI the scattering was entirely random, i.e., according to the cosine law. This is also true for scattering by glass.

Introduction

LITTLE is known about the details of the processes by which energy is transferred from a solid to a gas. Previous studies of the scattering of atoms striking the surfaces of solids have shown that the following processes occur.

First, atoms striking the surface of a solid may be adsorbed and subsequently re-evaporated,[1,2] so that all directions of motion of the atoms leaving the surface are equally probable, leading to the familiar cosine distribution. The velocity of the re-evaporated atoms is determined by the temperature of the surface on which they were adsorbed.

Second, the superposition characteristics of the quantum mechanics which find their intuitive expression in the wave concept lead us to expect phenomena analogous to space and surface grating diffraction in optics. The experiments of Knauer and Stern[3] and Estermann and Stern[4] establish clearly the existence of phenomena of the latter type and the experiments of Johnson[5,12] on scattering of atomic hydrogen could scarcely be otherwise interpreted. The existence of specularly reflected beams of atoms[6] together with an apparent velocity selection[7] suggested by the results of double reflection

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[1] R. W. Wood, Phil. Mag. **30**, 300 (1915).
[2] I. Langmuir, Phys. Rev. **8**, 149 (1916).
[3] F. Knauer and O. Stern, Zeits. f. Physik **53**, 779 (1929).
[4] I. Estermann and O. Stern, Zeits. f. Physik **61**, 95 (1930).
[5] T. H. Johnson, Phys. Rev. **36**, 381 (1930).
[6] A. Ellett and H. Olson, Phys. Rev. **31**, 643 (1928).
[7] A. Ellett, H. Olson and H. Zahl, Phys. Rev. **34**, 493 (1929).

experiments and of experiments in which the velocities were measured directly has been interpreted by H. F. Olson and the present writers as evidence of a process analogous to Bragg reflection of x-rays.

Any process which is to result in thermal equilibrium between a solid and a gas in contact must provide for the transfer of energy and for the dependence of this energy transfer upon relative temperatures of solid and gas. Obviously the first mechanism discussed, that of condensation and subsequent re-evaporation, is satisfactory from this point of view.

It may be asked whether the two latter mechanisms, surface or space-grating reflection, provide a means for the attainment of thermal equilibrium. Where the effective mass of the crystal is large, i.e., where a large number of atoms scatters coherently so that the resolving power is large, the amount of energy transferred will be very small. The experiments of Stern, Knauer and Estermann show that in those cases of surface-grating diffraction which they have studied the velocity distribution of the scattered atoms is just that characteristic of the gas from which they came. These atoms in rebounding from the crystal have exchanged momentum and consequently energy with the crystal, but the large effective mass of the crystal renders the energy transfer negligible.

That the distribution of intensity in an optical spectrum is determined by the nature of the source rather than by the temperature of the diffraction grating is of course due in the same way to the fact that the effective mass of the grating is large compared to that of a photon. If we could experiment with gratings sufficiently light or photons sufficiently massive we might expect to detect in the spectrum of the grating the influence of the temperature of the grating as well as that of the source.

Similarly with heavy atoms or under circumstances such that the effective mass of the crystal is small we may expect to find evidence of a transfer of energy. The experiments now to be described, on the reflection of mercury atoms from alkali halide crystals, we believe are best understood as a case of space-grating reflection accompanied by an energy transfer by no means negligible.

METHOD

The distribution of heavy atoms scattered from crystal surfaces has been investigated previously[6,7,8] by condensing the scattered atoms upon a liquid-air cooled surface surrounding the scattering crystal. The use of this method is limited practically to metals which are solid at ordinary temperatures and not too readily oxidized on exposure to air. Even in these cases there is some difficulty in interpretation of the results. Over a limited range of densities microphotometer transmission curves may be used to obtain the relative number of atoms in various parts of the deposit, but of course, heavy deposits are completely opaque while very light deposits on the other hand evaporate so rapidly that it is impossible to obtain significant transmission curves. A further serious difficulty with the deposit method is that the scattering crys-

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[8] H. A. Zahl, Phys. Rev. **36**, 893 (1930).

tal must be removed from the apparatus between runs, so that it is not possible to say that its condition is the same in two runs.

In the experiments now to be described the relative numbers of mercury atoms scattered in various directions by alkali crystals were measured by means of an ionization gauge. This made it possible to study the effects of change in the angle of incidence, temperature of the scattering crystal, and temperature of the incident beam all in a single run.

APPARATUS

The apparatus used, shown schematically in Figs. 1 and 2, resembles in its general outlines an ordinary x-ray spectrometer, and in fact must be adjusted just as is such a spectrometer. That is to say the crystal must rotate about an axis in the plane of its face, and this axis must lie in the center of the incident beam of atoms, the latter being defined by the boiler opening and the liquid-air cooled slit just below the crystal. The axis about which the ionization gauge is rotated must be colinear with the axis of rotation of the crystal. These adjustments were effected by placing a closely fitting needle into the projecting aperture of the gauge and adjusting the needle and gauge supports so that the point of the needle appeared to remain stationary when the gauge was rotated about its axis. In a similar manner the crystal mounting was adjusted so that its axis of rotation lay in the plane of the crystal face. Coincidence of the two axes of revolution was then secured by adjusting the supports carrying the ground glass joints by means of which rotation was effected. The adjustment was finally checked optically. A beam of light from a source placed directly below the boiler aperture was reflected from the crys-

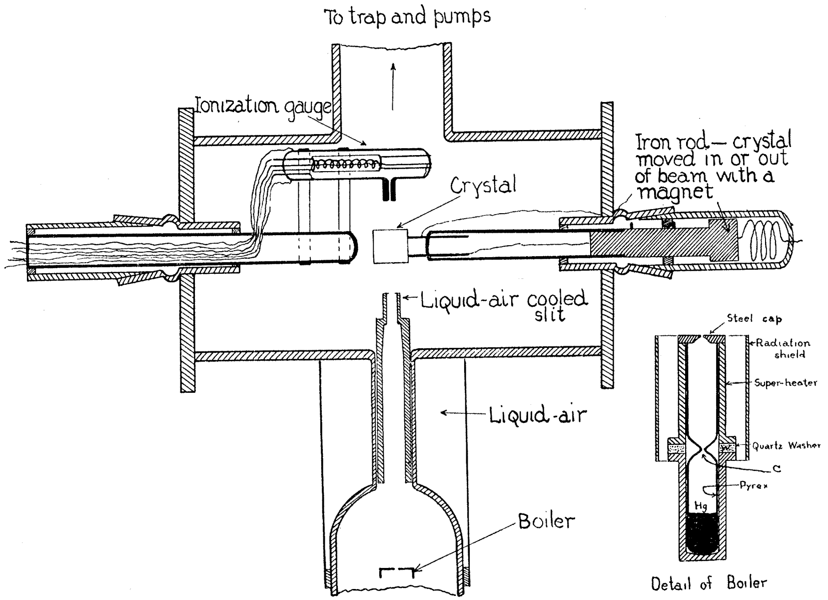

Fig. 1. Diagram of apparatus.

tal and must then pass through the aperture of the ionization gauge for all positions of the crystal and proper relative position of the gauge.

The operation of the ionization gauge as a pressure measuring device is too well known to require discussion here. Johnson[9] has considered its application to the measurement of molecular beams but found it unreliable because of difficulties which he ascribed to adsorption. We have had no difficulty with phenomena of the type reported by Johnson provided the gauge is sufficiently outgassed.

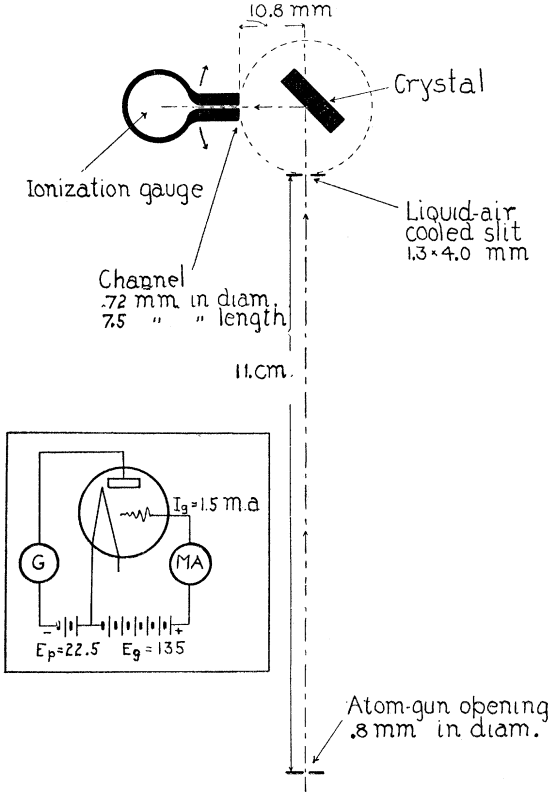

Fig. 2. Essential details of beam system. Insert shows electrical scheme of ionization gauge used.

The elements of the gauge were those of an ordinary 'peanut' vacuum tube with the filament replaced by 1 mil non-thoriated tungsten wire. These were enclosed in a glass envelope having a volume of about 6 cc, to which was sealed a capillary side tube 0.72 mm in diameter and 7.5 mm long. This aperture was arranged so that the atoms of the incident beam struck the opposite glass wall of the gauge instead of striking the metal parts directly. Since the point opposite the aperture is struck by more mercury atoms than any other part of the gauge it is here that adsorption should first occur and as mercury is

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[9] T. H. Johnson, Phys. Rev. **31**, 103 (1928).

probably less readily adsorbed on clean glass than on metal the gauge was arranged in this manner.

About the outside of the gauge was wound a heater to aid in out-gassing and to reduce adsorption, but it was not required for the latter purpose as heat generated by the filament kept the gauge sufficiently hot, once it had been well out-gassed. The positive ion current due to residual gas was in all cases less than one half of one percent of that obtained when the gauge was placed into the main beam. That adsorption of mercury on the gauge walls was not appreciable may be seen from the fact that upon removing the gauge from the main beam the galvanometer returned to its zero within thirty to forty seconds. This was with the electron current reduced so that the main beam gave only 500 mm deflection. When the gauge was used for measuring the much less intense scattering its sensitivity was increased by a factor of 2.6 by increasing the electron current.

The gauge aperture offers to the molecular beam entering the gauge no impedance whatever and admits to the gauge the same number of molecules from the beam as would a thin walled circular aperture of the same area provided the incident beam has negligible divergence. To molecules escaping from the gauge, however, the aperture offers an impedance 9 times as great as would a thin circular aperture of the same area, and the pressure produced in the gauge by a given incident beam of small divergence is increased by just this factor. This of course applies only under circumstances such that the mean free path is long compared to the length of the gauge aperture so that collisions between molecules of the entering beam and molecules escaping from the gauge may be neglected.

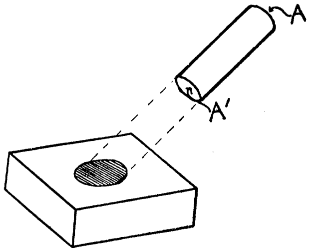

Fig. 3. Illustrating situation when gauge is used to measure the scattering from a crystal.

The situation when the gauge is used to measure the scattering from a crystal is somewhat more complex and may be more readily discussed with the aid of a diagram, see Fig. 3. Molecules leaving any part of the shaded area within a cone whose solid angle is virtually constant and equal to A/r^2 will enter the gauge without impedance, and in addition some fraction of the molecules coming from this same area with directions lying between this cone and the cone defined by the area A' will also enter. Outside the shaded area the solid angle within which molecules may enter without striking the walls of the gauge aperture drops off rapidly but molecules may of course enter the gauge from parts of the crystal surface from which it is not possible to see directly into the gauge, and to calculate the fraction of such molecules entering might be rather difficult. This difficulty may be avoided by using a narrow incident beam so that the entire area of the crystal struck by the incident atoms lies close to the axis of the gauge aperture. Otherwise the area of the crystal from which molecules enter the gauge will increase as the gauge is moved away from the crystal normal. With the dimensions of the present apparatus this condition was not met for angles of incidence (measured from the crystal face) less than 25 or 26°.

Fig. 4 shows the distribution of atoms scattered from a heated glass surface when the incident beam made an angle of 31° with the surface. From the surface of an amorphous substance such as glass we would expect random scattering so that the number of molecules scattered into an infinitesimal cone of solid angle $d\omega$ making an angle θ with the crystal surface is proportional to sin $\theta d\omega$. That is to say, the readings of the ionization gauge when plotted on polar coordinate paper should lie on a circle whose center is on the normal to the scattering surface. The full curve in Fig. 4 is a circle having its center on the normal to the glass surface. A systematic departure is noticeable, and in fact as the broken curve shows, the observed points lie very closely on a circle whose center is 3° off the normal. This probably does not indicate any such systematic departure from cosine scattering, but merely means that the direction of the normal to the glass surface was not accurately known. This curve represents the first observations made with the apparatus and the optical method of checking alignment had not yet been developed.

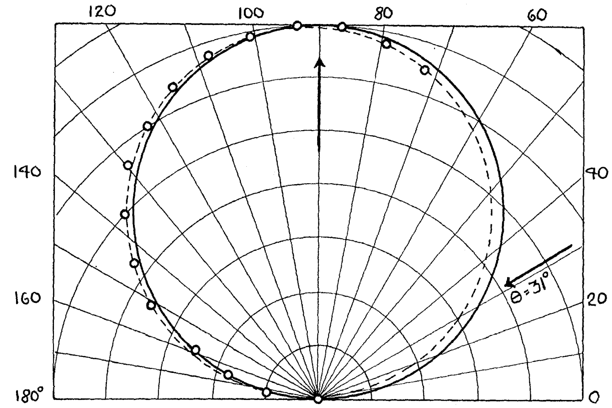

Fig. 4. Distribution of mercury atoms from a glass surface, glass heated to 350°C, beam temperature of 170°C.

Further, if mercury atoms are scattered from glass according to the cosine law the reading of the gauge when standing on the normal to the crystal surface should be the same for all angles of incidence, provided the entire width of the surface struck by the incident beam is equally effective. At small angles of incidence as was mentioned above it is to be expected that the illuminated section of the glass will become so wide that some parts of it will not be effective, especially when the gauge stands on or near the normal. Figure 5 shows readings of the gauge placed on the normal to the glass surface plotted against the angle of incidence. These readings are constant as far as 30° while at 20° the reading has dropped about 5 percent.

Interpreting gauge readings as in Fig. 4, amounts to assuming that the galvanometer deflection is proportional to the number of atoms entering the gauge, and for low pressures this is the characteristic behavior of the ionization gauge. As a check it is worth mentioning that the reading of the gauge when placed in the main beam was proportional to the vapor pressure as calculated from the vapor pressure temperature equation, which is quite accurately known for mercury.

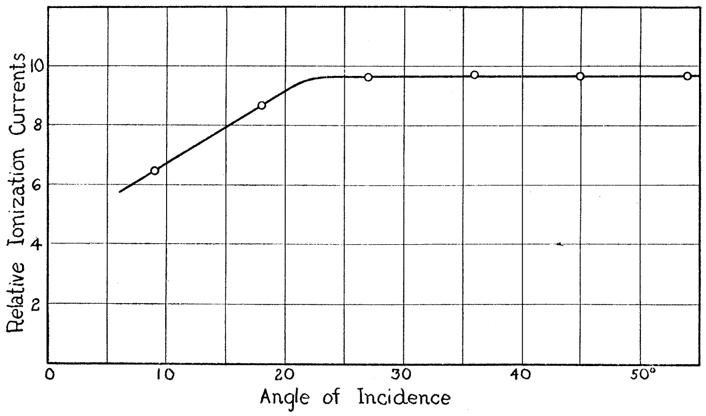

Fig. 5. Readings of gauge when placed on the normal to the glass surface plotted against the angle of incidence.

Fig. 6 shows the readings of the gauge as it was swept through the incident beam. This does not give the distribution of intensity in the beam, as the center of rotation of the gauge is far removed from the point from which the molecular beam diverges, but the fact that the curve is symmetrical does show that the axis of rotation of the gauge lies near the center of the incident beam. The fact that 6–7° rotation of the gauge away from the maximum is required to bring the gauge reading back to zero does not mean that the incident beam had this great divergence, but merely that the gauge required to be rotated this amount to swing the opening of the gauge channel clear

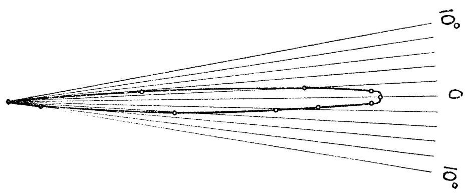

Fig. 6. Direct beam (uncorrected).

of the beam, for as long as the channel opening remains in the beam some molecules striking the walls of the channel will enter the gauge.

The width of the incident beam deduced from the movement of the gauge channel opening required to clear it is just what would be expected from the relative sizes and positions of the boiler aperture and upper defining slit. The details of construction of the boiler are shown in Fig. 1. The upper and lower halves insulated by the quartz washer *w* could be heated separately so that the vapor pressure of the mercury in the boiler could be controlled by regulating the temperature of the lower half of the boiler while the velocity with which the mercury atoms left the boiler could be increased by super-heating the upper half. The constriction *c* served to reduce diffusion of atoms between the two sections of the boiler so that the vapor in its passage through the upper section might more nearly attain a velocity distribution characteristic of the temperature at which the walls of this super-heater were maintained. It is not to be expected that the molecules escaping from this boiler possess a Maxwell distribution of velocities, for at the pressure maintained in the boiler (4–7 mm Hg) the free path is much shorter than the diameter of the boiler orifice. However, as long as the amount of mercury escaping from the boiler is proportional to the boiler pressure it may be expected that deviations from a Maxwell velocity distribution will not be extremely large, as both the reduction in the quantity of gas escaping and the deviation from the Maxwell distribution are due to the same cause, namely collisions occuring in the vicinity of the orifice.

The results presented in the next section will show that the distribution of atoms scattered by a crystal is affected by the velocity distribution in the atomic beam. That is, the changed velocity distribution brought about by super-heating is immediately evident in the changed distribution of scattered atoms while on the other hand the scattering is not affected by changes in boiler pressure, at least as long as the boiler pressures are kept below the value at which the beam intensity ceases to be proportional to boiler pressure, and this in itself may be taken to indicate that the velocity distribution in the beam is approximately independent of boiler pressure over the range in question.

EXPERIMENTAL RESULTS

(1) *Reflection of Mercury from Rocksalt as a Function of the Angle of Incidence*

Fig. 7(a, b, c, d, e, f, g) represents the results obtained during a single run, the curves therefore being representative of but one crystal. The angle of incidence was changed in 9° steps from 18 to 72° (the angle referred to is always measured from the crystal surface). The circles are single experimental points and could be repeated to within two or three percent. For all the curves the crystal temperature[10] was maintained at 350° C while the incident beam

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[10] Ellet and Olson[6] have found that in the region of this temperature outgassing of NaCl seems to be almost complete. J. H. Frazer (Phys. Rev. **34,** 644 (1929)) has also found, in agreement with Ellett and Olson, that at 330°C the thickness of adsorbed gas on the surface of an NaCl crystal appears to have reached a minimum.

was held at 170° C. In the curves the arrows indicate: (1) the direction of the incident beam; (2) the position the maximum of the reflected beam should occupy if the reflection were specular and total; and (3) the normal to the crystal surface.

Consider Fig. 7(a). The beam strikes the crystal at an angle of 18°. A_1 represents the curve obtained by sweeping the gauge over the crystal surface. If we consider the atoms after leaving the crystal surface as a combination of random scattered atoms and those definitely inclined in a specular direction then the experimental curve should allow separation into two such components. Moreover, since the degree to which cosine scattered atoms are present is surely limited by the intensity in the regions of the normal and particularly by the intensity on the side of the normal opposite to the reflected beam, an estimate of the cosine scattered atoms can be obtained. The circle marked A_3 represents the estimate of the number of atoms scattered according to the cosine law. Belief in the validity of such a procedure is strengthened when upon subtracting the cosine scattered atoms from the curve A_1 a quite symmetrical curve A_2 is obtained as the second component. It can be seen that the directed curve A_2 obtained after the subtraction is considerably displaced from the position it would occupy if the atoms contributing to this curve were specularly reflected.

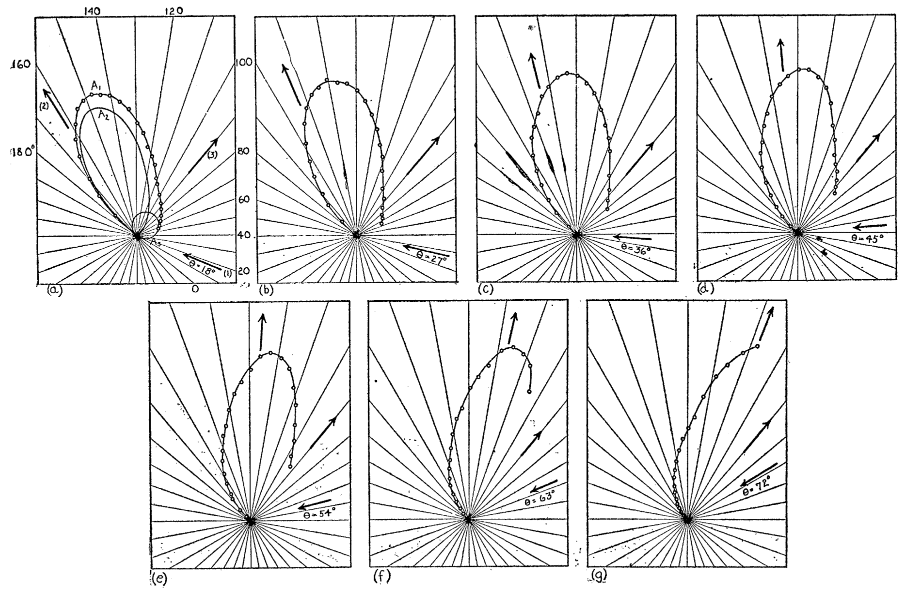

Fig. 7 (a, b, c, d, e, f, g). Distribution of mercury atoms from NaCl as a function of the angle of incidence, crystal at 350°C, beam at 170°C.

For greater angles of incidence, i.e., Fig. 7 (b, c, d, e, f, g) the cosine correction has not been applied since the movement of the gauge was restricted by the upper defining slit and what end points were available in the region of the crystal normal contained increasing numbers of directed atoms making an approximation to the number of random scattered atoms comparatively uncertain at larger angles of incidence. It is for this reason that most of the work to be described has been done at small angles of incidence.

It should be noted, however, since correcting the experimental curves consisted simply in subtracting the area of the estimated circle, that unless an impossible cosine circle falling beyond the experimental points be chosen the

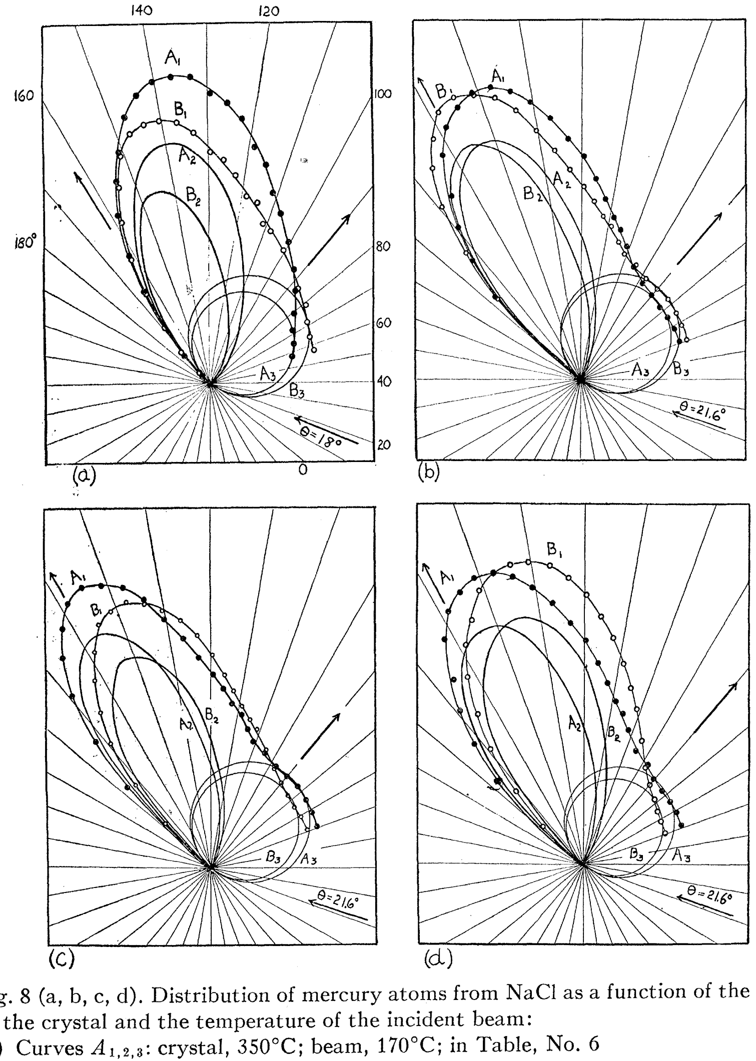

Fig. 8 (a, b, c, d). Distribution of mercury atoms from NaCl as a function of the temperature of the crystal and the temperature of the incident beam:

(a) Curves $A_{1,2,3}$: crystal, 350°C; beam, 170°C; in Table, No. 6
$B_{1,2,3}$: crystal, 50°C; beam, 170°C; in Table, No. 5
(b) Curves $A_{1,2,3}$: crystal, 350°C; beam, 500°C; in Table, No. 4
$B_{1,2,3}$: crystal, 50°C; beam, 500°C; in Table, No. 2
(c) Curves $A_{1,2,3}$: crystal, 50°C; beam, 500°C; in Table, No. 2
$B_{1,2,3}$: crystal, 50°C; beam, 170°C; in Table, No. 1
(d) Curves $A_{1,2,3}$: crystal, 350°C; beam, 500°C; in Table, No. 4
$B_{1,2,3}$: crystal, 350°C; beam, 170°C; in Table, No. 3

effect of any such correction applied to curves such as 7(b) and (c) would not move the experimental beam into the specular position. On the basis of the data shown in Fig. 7, and three more similar runs not shown but given equal weight, (it was not deemed advisable to average results since individual crystals showed distinct differences) it appears that up to angles of at least 45° the corrected curve is not specular.

(2) *Effect of Temperatures of Scattering Crystal and of Boiler Upon the Scattering of Mercury Atoms by Sodium Chloride Crystals*

The effect of varying separately the temperatures of crystal and boiler is shown in the four curves a, b, c, d of Fig. 8. In the case of Fig. 8(a) the beam emerging from a boiler at a constant temperature of 170° C was incident at an angle of 18° upon a crystal at 350° C (Curves $A_{1,2,3}$) and 50° C (Curves $B_{1,2,3}$). The effect of the same change of crystal temperature when the boiler is maintained at 500°C is shown in Fig. 8(b) in which $A_{1,2,3}$ and $B_{1,2,3}$ are for crystal temperatures of 350°C and 50°C, respectively. The angle of incidence was in this case 21.6°.

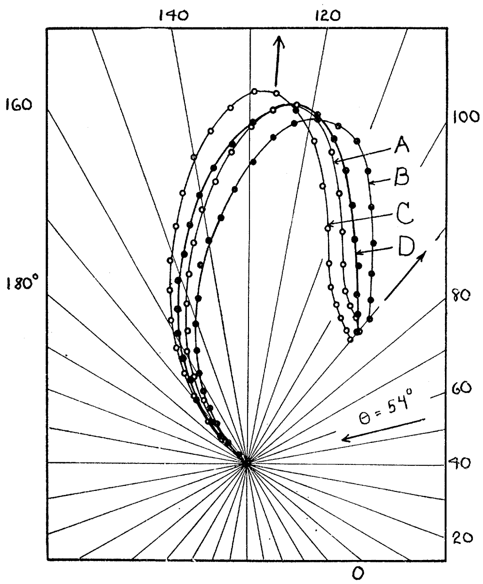

Fig. 9. Distribution of mercury atoms from NaCl as a function of the crystal temperature and the temperature of the incident beam, angle of incidence equals 54°.

Curve A: crystal, 50°C; beam, 170°C; in Table, No. 15
B: crystal, 350°C; beam, 170°C; in Table, No. 16
C: crystal, 50°C; beam, 500°C; in Table, No. 17
D: crystal, 350°C; beam, 500°C; in Table, No. 18

The effect of changing the boiler temperature while that of the crystal is maintained constant may be seen in Fig. 8(c and d). In Fig. 8(c), $A_{1,2,3}$ and $B_{1,2,3}$ are for boiler temperatures of 500°C and 170°C with the crystal maintained at 50°C while in 8(d) we have the corresponding situations with the crystal at 350°C.

We note the following changes which have occurred in all cases of NaCl studied: (1) The position of the maximum shifts towards a smaller angle (closer to the specular position) with decrease in crystal temperature. (2) The number of atoms scattered at random increases with a decrease in crystal temperature. (3) The corrected beam definitely becomes narrower with decrease in crystal temperature. (4) The position of the maximum shifts towards a smaller angle with increasing beam temperature.

That the same changes occur at larger angles of incidence may be roughly seen in Fig. 9 (*A*, *B*, *C*, *D*). Here the incident beam makes an angle of 54°

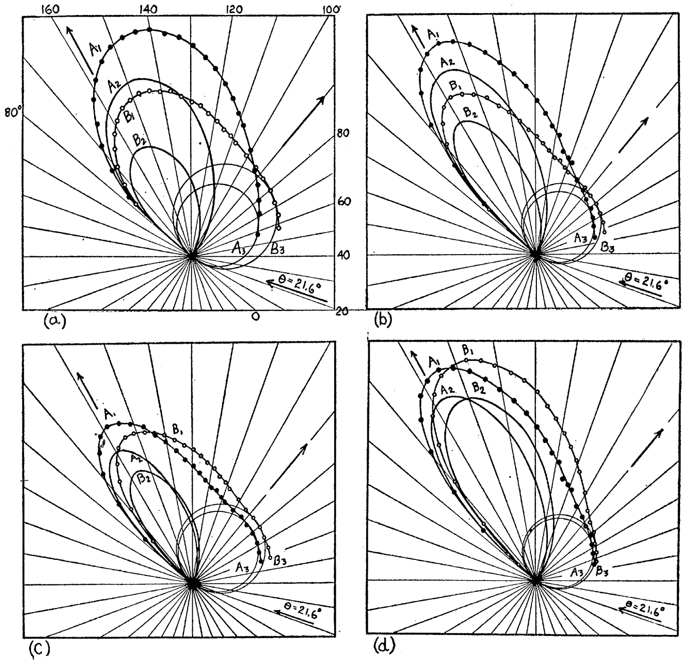

Fig. 10 (a, b, c, d). Distribution of mercury atoms from KBr as a function of the crystal temperature and the temperature of the incident beam.
(a) Curves $A_{1,2,3}$: crystal, 350°C; beam, 170°C; in Table, No. 8
$B_{1,2,3}$: crystal, 50°C; beam, 170°C; in Table, No. 7
(b) Curves $A_{1,2,3}$. crystal, 350°C; beam, 500°C; in Table, No. 10
$B_{1,2,3}$: crystal, 50°C; beam, 500°C; in Table, No. 9
(c) Cruves $A_{1,2,3}$. crystal, 50°C; beam, 500°C; in Table, No. 9
$B_{1,2,3}$: crystal, 50°C; beam, 170°C; in Table, No. 12
(d) Curves $A_{1,2,3}$: crystal, 350°C; beam, 500°C; in Table, No. 10
$B_{1,2,3}$: crystal, 350°C; beam, 170°C; in Table, No. 11

with the crystal surface. The conditions represented by the curves *A*, *B*, *C*, and *D* are given under the illustration. There has been no attempt to separate these curves into directed and random scattered components but the changes in the positions of the maxima are evidently quite similar to those which occur at smaller angles.

(3) *Reflection of Mercury from KBr and KCl*[11] *as a Function of Temperatures of Crystal and Beam.*

Fig. 10(a, b, c, d) and Fig. 11 are representative of the data available on KBr and KCl. Comparisons are made in the same way as in Fig. 8. The general form of these curves and the effects produced by changing crystal and boiler temperatures are evidently the same as in the case of NaCl discussed in detail above. For KI, however, the situation is quite different.

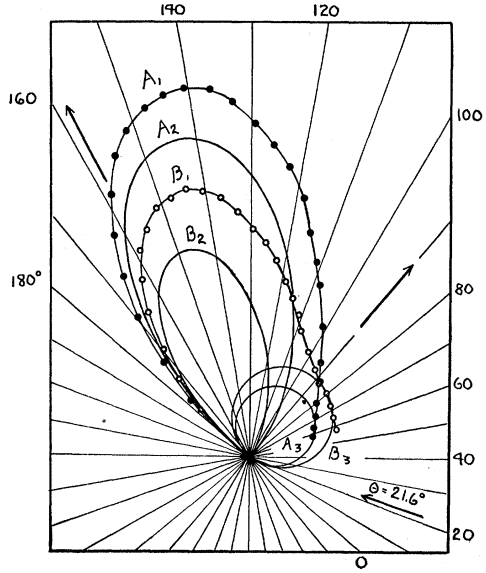

Fig. 11. Distribution of mercury atoms from KCl as a function of the temperature of the crystal.

Curves $A_{1,2,3}$: crystal, 350°C; beam, 170°C; in Table, No. 13
$B_{1,2,3}$: crystal, 50°C; beam, 170°C; in Table, No. 14

(4) *Reflection of Mercury from KI*

A crystal of KI heated to a temperature of 350°C was found to scatter an incident beam of mercury quite closely following the cosine law. In Fig. 12 is shown a case in which a beam of mercury was incident upon the crystal surface at an angle of 36°. The broken line is the circle upon which the points would fall were the cosine law followed. The experimental points through which the full line is drawn suggest that the scattering in this case is of a cosine nature with no indication of directed scattering.

(5) *Calculation of Directed and Random Scattered Atoms*

To obtain the relative number of atoms contributing to the cosine scattered and quasi-specular beam the following procedure was employed.

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[11] The crystals of KBr, KCl and KI used in these experiments were kindly furnished us by Professor H. M. Randall of the University of Michigan.

It was found that the corrected beams A_2 and B_2 could be quite well represented by curves of the form

$$I = I_{\max} \cos m\theta$$

where m is some number chosen to fit the particular curve. m was always greater for lower crystal temperatures. These curves with properly chosen values of m can be fitted so closely with the experimental curves that intensities obtained from them by integration are considered to be accurate to within the limits of experimental error.

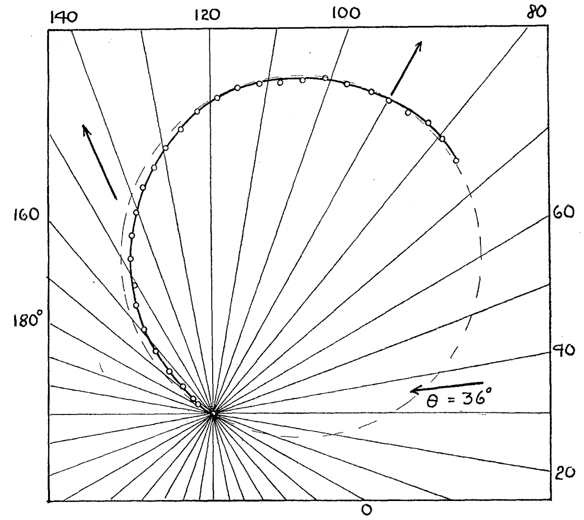

Fig. 12. Distribution of mercury atoms from KI: crystal, 350°C; beam, 170°C.

In Fig. 13 is shown a typical case in which cos 3θ has been used to represent a curve obtained with a NaCl crystal at 50°C and a cos 2.5θ curve to represent the case of the same crystal at 350°C. The dots represent the corrected experimental points.

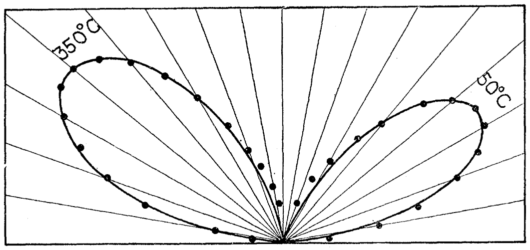

Fig. 13. Typical agreement obtained between corrected experimental curves and curves having form cos $m\theta$.

On the following basis one may write for the total relative intensity of the corrected quasi-specular beam

$$I_2 = 2I_{2(\max)} \int_0^{\pi/2m} \int_0^{\pi} \cos m\theta \sin \theta d\phi d\theta \qquad (1)$$

where $I_{2(\max)}$ is the corrected galvanometer reading on the maximum of the directed curve.

By the same integration we obtain the relative number of atoms contributing to the cosine beam, i.e., I_3, by putting $m=1$ and letting $I_{3(\max)}$ be the diameter of the circle representing these atoms.

To check on the accuracy of such integrations the following procedure is available. If the beam temperature is kept constant and curves are obtained for two different crystal temperatures the total number of atoms scattered must remain the same in both cases since the gauge records all atoms whether in the cosine or directed beam. The degree to which the following equation is true when experimental values are substituted serves as a check on the assumptions made during the integration.

$$I_{A_2} + I_{A_3} = I_{B_2} + I_{B_3} \tag{2}$$

where A and B represent different crystal temperatures, the beam remaining constant.

(6) *Discussion of the Table*

In the Table are presented the results available at this time. In column (1) is given the type of crystal. The numbers to the left of the crystal formula represent different crystals. Strict comparison outside of each parallel set of data is thus permissible only if this crystal identification number is the same, comparison then being restricted to changes in angle and relative percentages in the cosine and directed beam, since in changing the beam temperature it was not feasible to obtain exactly equal vapor pressure at the gun opening for the two different velocity distributions.

In column (2) is given the figure identification. In other words, if there is a number listed in this column corresponding to a certain curve then the experimental points of this run are plotted in one of the illustrations and may be identified by the corresponding number in the figure caption.

Column (4) lists the location of the maximum of the corrected directed beam while in column (6) is given the change in this maximum due to the change in crystal temperature given in column (5).

The value of m for which cos $m\theta$ showed the best agreement with the directed beam is given in column (8). Columns (9) and (10) list the values of the relative intensities of cosine and directed scattering obtained as explained above. Column (11) shows to what degree equation (2) holds when values listed in (9) and (10) are substituted into this equation, thereby giving an approximation to the magnitude of the error introduced by the integrations.

In column (12) are listed the relative percentages of atoms contributing to the directed beam.

(7) *Reflection of Mercury from NaCl as a Function of the Vapor Pressure at the Gun Opening*

The work discussed up to this point has been done with the same apparatus under essentially constant conditions. Recently, the present writers

TABLE . *Reflection of mercury from crystals of sodium chloride, potassium chloride, potassium bromide and potassium iodide.*

1 Crystal	2 Figure Identification Number	3 Angle of Incidence	4 Angle of Reflection	5 Temperature of Crystal	6 Change in Angle of Reflection Due to Change in Crystal Temperature	7 Temperature of Mercury Beam	8 Curve Describing Directed Beam	9 Intensity of Directed Beam	10 Intensity of Cosine Beam	11 Total Intensity	12 Percent of Atoms Contributing to Directed Beam
(1) NaCl*		21.6°	31.5°	50°C	5.9°	170°C	cos 2.5θ	13.2	23.9	37.1	35.6%
		21.6	37.4	350		170	cos 2.25θ	19.1	19.7	38.8	49.3
(2) NaCl	1	21.6	30.	50	4.5	170	cos 2.9θ	7.	25.65	32.65	21.4
	3	21.6	34.5	350		170	cos 2.5θ	10.55	22.8	33.35	31.7
(2) NaCl		21.6	27.	50	3.5	375	cos 3θ	7.66	25.97	33.63	22.8
		21.6	30.5	350		375	cos 2.7θ	9.85	21.6	31.45	31.3
(2) NaCl	2	21.6	25.	50	2.5	500	cos 3θ	7.87	29.3	37.17	21.2
	4	21.6	27.5	350		500	cos 2.7θ	9.48	26.9	36.38	26.
(3) NaCl		21.6	32	50	4.	170	cos 2.7θ	7.21	35.8	43.01	16.8
		21.6	36	350		170	cos 2.25θ	10.3	32.2	42.5	24.2
(3) NaCl		21.6	29	50	3.5	375	cos 3θ	7.35	30.3	37.65	19.5
		21.6	32.5	350		375	cos 2.7θ	10.15	30.	40.15	25.3
(4) NaCl	5	18	36	50	6.	170	cos 3θ	4.36	21.1	25.46	17.1
		18	42	350		170	cos 2.5θ	7.57	17.9	25.47	29.7
(5) NaCl		18	32	50	5.	170	cos 3θ	7.93	20.6	28.53	27.8
		18	37	350		170	cos 2.5θ	13.2	15.8	29.	45.5
(6) NaCl		18	35	50	6	170	cos 3θ	6.26	19.	25.26	24.8
		18	41	350		170	cos 2.5θ	12.1	11.8	23.9	50.7
(7) NaCl		18	27	50	4	170	cos 3θ	4.16	9.25	13.41	31.
		18	31	350		170	cos 2.5θ	7.7	8.55	16.25	47.4
(8) NaCl		18	27	50	5	170	cos 3θ	4.95	10.3	15.25	32.4
		18	32	350		170	cos 2.5θ	8.75	8.7	17.45	50.1
(9) NaCl		18	40	350		170	cos 3θ	5.73	13.1	18.83	30.4
(10) NaCl		18	38	350		170	cos 2.5θ	10.4	16.7	27.1	38.4
(11) NaCl		18	30	350		170	cos 2.5θ	7.12	10.7	17.82	39.9
(12) KCl	14	21.6	33	50	3.1	170	cos 2.5θ	12.4	33.6	46.	26.9
	13	21.6	37.4	350		170	cos 2.2θ	23.2	26.1	49.3	47.
(13) KBr	7	21.6	27.5	50	5.5	170	cos 2.25θ	8.39	34.4	42.79	19.6
	8	21.6	33	350		170	cos 2θ	15.9	27.	42.9	37.1
(14) KBr	12	21.6	27	50	3.	170	cos 2.8θ	5.9	29.4	35.3	16.7
	11	21.6	30	350		170	cos 2.5θ	11.5	24.5	36.	31.8
(14) KBr	9	21.6	22	50	3	500	cos 3θ	5.8	24.4	30.2	19.2
	10	21.6	25	350		500	cos 2.8θ	8.88	21.5	30.38	29.3
(15) KI	19	36	(Incident beam scattered according to the cosine law)								
(16) NaCl	15	54	55.5**	50	6	170					
	16	54	61.5	350		170					
(16) NaCl	17	54	51.	50	5.5	500					
	18	54	56.5	350		500					
(17) NaCl		45	53	50	5.5	170					
		45	58.5	350		170					
(18) NaCl		45	52.5	50	7.5	170					
		45	59.	350		170					
(19) NaCl		54	49.5	50	6	170					
		54	55.5	350		170					
(20) NaCl		54	54.	50	5	170					
		54	59.	350		170					

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* The numbers in column 1 denote different individual crystals. If the crystal position has not been changed the numbers in column 1 are the same. Thus the three sets of data opposite (2) NaCl were taken with the same crystal which was kept fixed while the crystal and beam temperature were varied.

** The remainder of the angles listed in this column represent the peak of the uncorrected beam.

and Mr. R. R. Hancox have experimented with other ionization gauges resulting in the development of a gauge of greater sensitivity which could be used with considerably lower vapor pressures. In brief, with 20 m.a. electron current coupled with increased ionization efficiency, an increase in sensitivity over the old gauge by a factor of about 25 was obtained.

In Fig. 14 is shown a group of curves taken with this new gauge. The reflecting crystal was NaCl, the incident beam making an angle of 20° with the crystal surface. In the case of curves *A* and *B*, the crystal was held at a temperature of 350°C while for curve *C* the temperature of the crystal was approximately 100–150°C. The vapor pressures at the gun opening for *A*, *B* and *C* were 0.5, 2 and 10 mm, respectively.

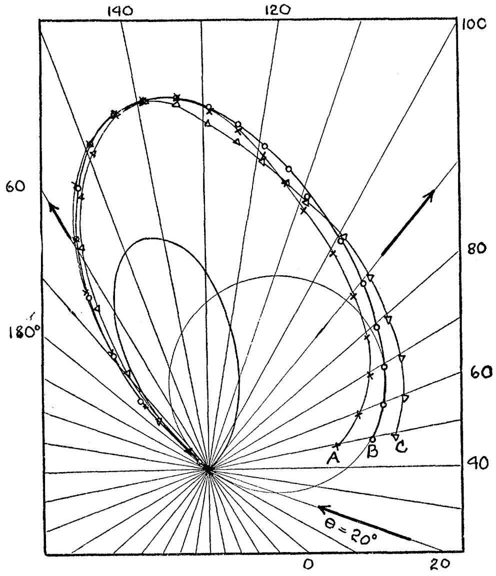

Fig. 14. Reflection of mercury from NaCl as a function of the vapor pressure at the gun opening: *A*, 0.5 mm of Hg; *B*, 2 mm; *C*, 10 mm.

It can be seen that over this range of vapor pressures the general character of the curves remains the same. The curve *C* which is taken at a lower crystal temperature has changed in agreement with the findings discussed earlier. The amount of random scattering in the case of this particular crystal is rather large but other crystals of NaCl have been found which give similar results.

It is evident from Fig. 14, though the mean free path at the gun opening for a pressure of 0.5 mm is small compared to the diameter of the opening, there is little change brought about when the pressure is increased further by a factor of 20. This increases our confidence in the assumption that in the incident atomic beam deviations from a Maxwell distribution of velocities are not great under the conditions described earlier.

(8) *Rotation of the Plane of the Crystal*

A second experiment using the new gauge was as follows: The crystal was mounted so that during a run it could be rotated on an axis perpendicular to the plane of the crystal face. Thus runs could be made under comparable conditions with the crystal oriented so that rows of alternate ions were parallel and perpendicular to the plane of the beam while by a rotation of 45° rows of similar ions could be brought into this position.

In Fig. 15 curve *A*, rows of alternate ions are parallel and perpendicular to the plane of the beam while curve *B* is taken under identical conditions save that the crystal was rotated in its plane through 45° bringing rows of similar ions parallel and perpendicular to the plane of the beam. Curve *C* represents a half-way position. For these data the crystal was held at 350°C, the beam was incident at 19° and the pressure at the gun opening was 1 mm.

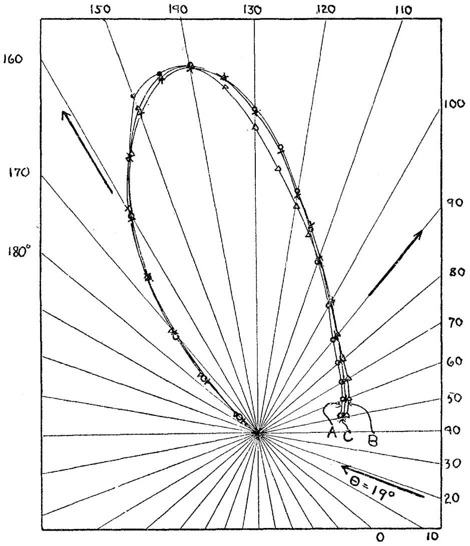

Fig. 15. Distribution of mercury atoms from NaCl as the crystal is rotated about an axis perpendicular to the plane of its face.

Clearly, if there are any changes brought about by change in crystal orientation, they are quite small and beyond the accuracy of the present method of experiment.

Summary and Discussion

Zinc and cadmium atomic beams incident upon rocksalt give rise to directed reflection which for large angles of incidence is specular, at least within the limits of accuracy of the deposit method used in studying the phenomena. Even with these lighter atoms, however, observations at small angles of incidence (6–10°, measured from the crystal surface) have shown unmistakable departures from specular reflection. It seems very probable that the process involved in the reflection of these lighter elements is the same which gives rise to the various phenomena reported in this paper for the case of mercury. However, the deviation of the directed reflected beam from the direction of specular reflection appears to be considerably greater with mercury than with either cadmium or zinc.

The mechanism involved in the reflection process must then account, qualitatively at least, for the following facts:

(1) The existence of a directed beam.

(2) The deviation of the direction of maximum intensity in this beam from the direction of specular reflection.

(3) The decrease of this deviation with higher beam and lower crystal temperatures and with lighter atoms.

(4) Better definition of the directed beam (narrowing of the beam) at low crystal temperatures, accompanied by an increase in the relative amount of random scattering.

The existence of directed scattering is sufficient to show that the scattering process is not merely condensation and re-evaporation. The possibility of reflection because of the abrupt change in potential energy at the crystal boundary must be considered. Johnson[12] has pointed out that this process is analogous to that of reflection of light from an imperfect (slightly rough) mirror and has considered that the effect of increased thermal agitation at higher crystal temperatures will produce the same effect as increased roughness of the mirror. That is to say it should result in increased random (cosine) scattering. In the present experiments the opposite effect has been observed. That is, the intensity of cosine scattering is always greatest at low crystal temperatures.

Another factor which might enter at low temperatures is the formation of a gas layer on the crystal surface, and this would lead to increased cosine scattering. It would not however account for the fact that the definition of the directed beam is better at low crystal temperatures and this increased definition or narrowing of the beam is quite consistently observed. Neither is it evident how the presence of a gas layer could account for the maximum of the directed scattering being shifted towards the direction of specular reflection.

There remain the possibilities of scattering processes analogous to surface and space-grating diffraction in optics. The wave-lengths of the heavy atoms with which we deal here are so short that we could scarcely expect surface-grating phenomena except perhaps at grazing incidence. At first sight there is the same objection to space-grating phenomena, but we must remember that in this case there occurs in the wave equation a quantity[13,7] whose effect is analogous to that of the refractive index in optical problems. Moreover in the case where the change in potential energy at the crystal boundary corresponds to the existence of repulsive forces the refractive index

$$\mu = (1 - \phi/\tfrac{1}{2}mv^2)^{1/2}$$

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[12] T. H. Johnson, J. Franklin Inst. **210,** 135 (1930).

[13] Bethe, Naturwiss. **15,** 787 (1927).

is less than unity so that it will operate to increase the apparent wave-length inside the crystal. This perhaps requires us to imagine that the atoms reflected from the crystal penetrate through several layers of the crystal lattice, and to this we must admit an intuitive repugnance. However, the chief basis of this reaction may be merely our intuitive "billiard ball" picture of the atom, leading us to imagine that such a process must lead to disruption of the crystal.

If we may be permitted to lay aside this objection for the moment we can show that the space-grating picture possesses certain advantages in that it appears to give a fairly good qualitative representation of the experimental facts, for it is apparent that for suitably small values of the refractive index there might arise phenomena closely analogous to the familiar Bragg reflection of x-rays, and this is the most obvious explanation of the existence of specular reflection. The concept of the resolving power of the crystal for de Broglie waves, determined essentially by the number of crystal planes effective in scattering, appears as a possible explanation of the fact that the directed beam is more sharply defined and relatively less intense at lower crystal temperatures, for decreased thermal agitation of the crystal should increase its resolving power in this case just as in the optical case. The fact that the direction of maximum intensity in the directed beam does not coincide with the direction of specular reflection suggests that the effective refractive index may be a complex quantity as it is in the optical case when absorption is taken into account.

The ideas advanced by Duane[14] and Compton[15] in connection with x-ray diffraction may lead to a clearer picture, as the emphasis is placed on the particle rather than the wave aspect of the situation and the application of our ordinary notions of conservation of momentum and energy is more evident. The relative translatory motion of a crystal and an atom is periodic as displacement through a distance equal to the lattice space brings the system back to its initial configuration. The quantization[16] of such a periodic motion leads at once to equations which have the form of Bragg's x-ray equation if h/mv is interpreted as a wave-length.

The mass of the crystal entering into the equations expressing the laws of conservation of energy and momentum is the mass of that part which behaves as a rigid body, i.e., suffers no distortion. Scattering in which momentum and energy are communicated to a group of atoms acting as a rigid body has been called by Williams[17] coherent scattering or the atoms are said to scatter coherently. This is a convenient term, suggesting as it does the close connection between the wave and the particle aspects of the situation. From the equations of conservation of energy and momentum it is at once evident that the larger the portion of the crystal which scatters coherently the less

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[14] W. Duane, Proc. Nat. Acad. Sci. **9**, 158 (1923).

[15] A. H. Compton, Proc. Nat. Acad. Sci. **9**, 359 (1923).

[16] P. Jordan, Zeits. f. Physik **37**, 376 (1926).

[17] E. J. Williams, Proc. Camb. Phil. Soc. **24**, 343 (1928).

will be the energy communicated to the crystal and the more nearly will the direction of rebound of the reflected atom make an angle with the crystal surface equal to the angle of incidence. Increased thermal agitation of the crystal at higher temperatures will reduce the size and mass of the coherently scattering groups, and the reflection will depart more and more from the specular direction. It is evident too that for a given size of coherently scattering groups the deviation from the specular direction will be less for light atoms, all of which is in accord with observation.