REFLECTION OF CADMIUM AND ZINC ATOMS FROM SODIUM CHLORIDE CRYSTALS

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Abstract

A beam of zinc atoms reflected from a sodium chloride crystal is in part specularly reflected. The specular beam was investigated: (1) by measuring the velocity distribution of the atoms composing the specular beam; and (2) by examining the specular beam after reflection from a second crystal. A difference in angle of 22.5 between the two crystals does not greatly reduce the intensity of the specular beam. It is concluded that if velocity selection or a space-grating type of reflection of zinc is present it is not very pronounced.

Double reflection experiments of cadmium from sodium chloride crystals have been repeated and apparently evidence for both space and surface-grating phenomena found in certain cases. It is suggested that individual differences in crystals may be an important factor in causing these differences.

Introduction

The wave-particle dualism of an atom required by the new quantum mechanics has for some time been investigated by the reflection of atoms from a crystal or ruled grating.[1]

In a paper by Ellett, Olson and Zahl[2] it was shown that a beam of uncharged cadmium atoms undergoes reflection from a sodium chloride crystal such that the specular beam consists of atoms possessing for the most part a velocity within a definite range. They suggest that the phenomenon may be due to a space-grating type of reflection. A formula of the type

$$\lambda = \frac{h}{mv} = 2d\left(1 - \frac{\phi}{\frac{1}{2}mv^2} - \cos^2\theta\right)^{1/2}$$

may be made to fit their data if ϕ, the average potential energy of the cadmium atom within the crystal, is not taken as constant but as varying with the angle of incidence. As further evidence for a velocity selection the same writers show that a beam of cadmium atoms incident on a first crystal of sodium chloride is not specularly reflected from a second crystal unless the angle the incident beam makes with both crystals is the same or nearly the same.

The reflection experiments of Knauer and Stern[3] who used helium and molecular hydrogen incident on sodium and potassium chloride crystals, indicate the presence of a surface diffraction phenomenon. Estermann and

[1] See J. B. Taylor, Phys. Rev. **35**, 375 (1930) for a more complete list of references.

[2] A. Ellett, H. Olson and H. Zahl, Phys. Rev. **34**, 493 (1929).

[3] F. Knauer and O. Stern, Zeits. f. Physik **53**, 779 (1929).

Stern[4] find that the reflection of helium and molecular hydrogen from crystals of lithium flouride conclusively shows the cross-grating nature of the diffraction. Johnson[5] has found that atomic hydrogen reflected from lithium flouride produces a pattern which satisfies simple cross-grating formulae.

Ellett and Olson[6] have shown that a beam of sodium atoms incident on sodium chloride gives no indication of specular reflection. Taylor[1] has worked with alkali metals other than sodium and finds no specular reflection of lithium, potassium or caesium from crystals of sodium chloride or lithium flouride. There is also no evidence of specular reflection of cadmium or arsenic from crystals of orthoclase or flourite.[2]

It is difficult, at this stage of the problem to conceive why some atoms and molecules should be reflected from crystal surfaces in accordance with surface-grating theory while a heavier atom such as cadmium should penetrate at least apparently through several reflecting layers of the crystal and be specularly reflected only if the atom's initial velocity corresponds to a certain wave-length. There is also the question why in certain cases no reflection occurs at all.[7]

It is not the purpose of this paper to attempt a solution of the problem. The apparent necessity for the consideration of two distinct phenomena adds considerable complexity to the general case of the reflection of atoms and molecules from crystals.

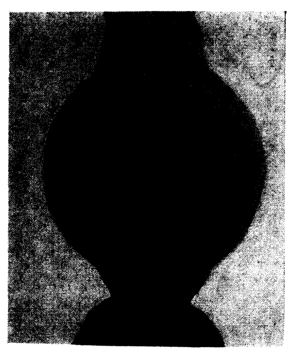


Fig. 1. Specular deposit obtained with zinc reflected from sodium chloride at an angle of 45°.

Experimental

I. Reflection of zinc from sodium chloride.[8]

A beam of zinc atoms issuing from a molybdenum boiler at 600°C is

[4] I. Estermann and O. Stern, Zeits. f. Physik **61,** 95 (1930).

[5] T. H. Johnson, Phys. Rev. **35,** 1432 (1930).

[6] A. Ellett and H. Olson, Phys. Rev. **31,** 643 (1928).

[7] Taylor suggests in the case of the alkali metals mentioned above that the presence of no reflection may in part be due to the ease of absorption of these metals on surfaces.

[8] A preliminary report of part of the work on zinc herein described was read at the Christmas meeting of the American Physical Society at Des Moines.

in part specularly reflected when incident upon a freshly cleaved clean sodium chloride surface. This was determined by placing a crystal within a bulb which was surrounded by liquid-air, a defined beam of zinc atoms entering through a small opening and striking the crystal surface. Since all atoms after leaving the crystal must strike a liquid-air cooled surface every atom could be accounted for. Fig. 1 shows a specular spot thus obtained when the crystal surface was set at 45° relative to the direction of the incident beam. The specular spot is not sharply outlined and fades into a back-ground of diffusely scattered atoms which possess a maximum on the normal to the crystal surface. It will be remembered that random scattering results in a distribution according to the well-known cosine law.

II. Direct measurement of the velocity distribution of the atoms composing the specular beam.

The apparatus employed was essentially the same as that by which the velocity distribution of cadmium atoms after reflection was measured.[2]

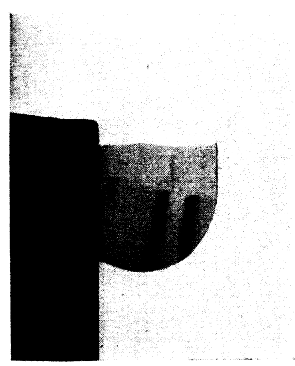


Fig. 2. A typical deposit obtained with specularly reflected zinc after passing through the velocity-analyzer.

Briefly, the atoms after reflection from a large area of the crystal surface were all condensed except a narrow beam which passed through a slit placed very close to the first disk of a rotating sectored-disk velocity-analyzer.[9] The atoms which passed through the defining slit and were moving in a direction appropriate to the velocity of the analyzer passed through the sectored disks and were condensed on a liquid air cooled glass surface. Rotation of the analyzer first in one direction and then the other resulted in the formation of two deposits. Fig. 2 shows a photograph of a typical set of deposits obtained in this manner. Microphotometer curves of the deposits when translated into relative density gave the velocity distribution of the atoms contributing to the deposits. Such curves for zinc reflected from sodium chloride

[9] J. A. Eldridge, Phys. Rev. **30**, 931 (1927).

are shown in Fig. 3,[10] together with the rate of rotation of the disks, the geometric outline and the velocity corresponding to the observed separation of the deposits. The best mean values for the velocities corresponding to different angles of incidence are given in Table I.

TABLE I. *Experimental values of the velocities of a specular beam of zinc atoms reflected from crystals of sodium chloride.*

θ	vel (m/sec)			Average
22.5°	763	736	761	753
45.	666	672	683	674
67.5	712	689	695	699

It is a question as to how much weight may be assigned to these measured values of the velocities. The resolving power of the apparatus was considerably lower in the case of the high-speed zinc atoms than in that of the much slower cadmium atoms. A monochromatic (single velocity) beam would

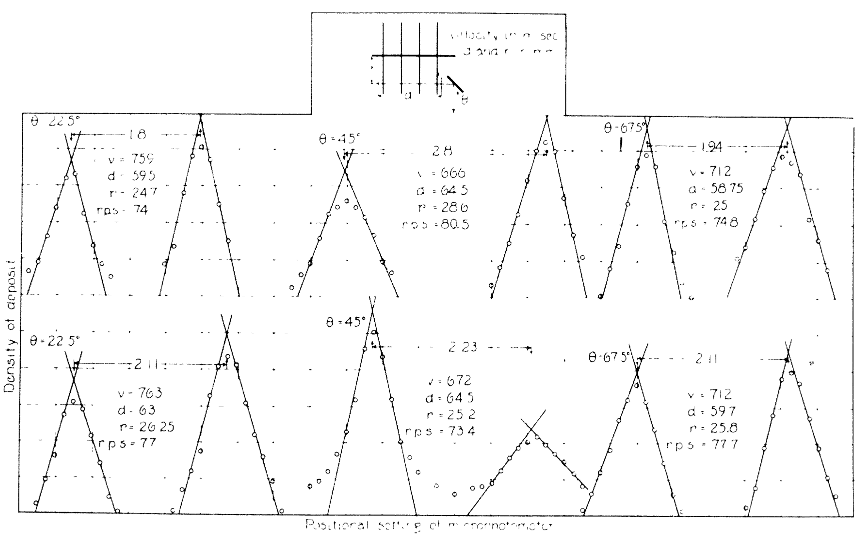


Fig. 3. Density curves obtained from deposits such as are shown in Fig. 2.

give a velocity distribution closely resembling the triangles of Fig. 3, but due to the low resolving power a beam of zinc atoms possessing a Maxwell distribution of velocities would also give an approximate triangle not very much wider at the base. The isosceles appearance of the velocity triangles is different from a curve produced by a Maxwell distribution of velocities, but

[10] Approximate relative densities were obtained with a microphotometer-density curve experimentally calibrated for cadmium. This was deemed permissible since the density of the lines was not great enough to cause specular reflection of light. That is, the deposits could be considered as made up of an aggregate of individual scattering centers. In regions of such low density the calibration curve for cadmium plotted on semi-logarithmic paper is quite linear.

other than that the measurements offer no strong evidence for the presence of velocity selection.

III. Multiple reflection of zinc from sodium chloride.

If a space-grating type of reflection occurred resulting in the specular beam being made up of atoms possessing nearly equal velocities, then reflection from a second crystal should be total if the angles were the same and the specular reflection should drop off as the angle of the second crystal is changed. The rate at which the specular beam dropped off as a function of the change in angle would be a measure of the resolving power of the crystal for the atoms in question.

A description of the type of apparatus used may be found in an earlier reference to some similar experiments with cadmium.[2] Aside from some differences in the way the atom gun was mounted the methods were identical.

Runs were made, first with both crystals making an angle of 45° with respect to the incident beam, and second with the first crystal at 45° and the

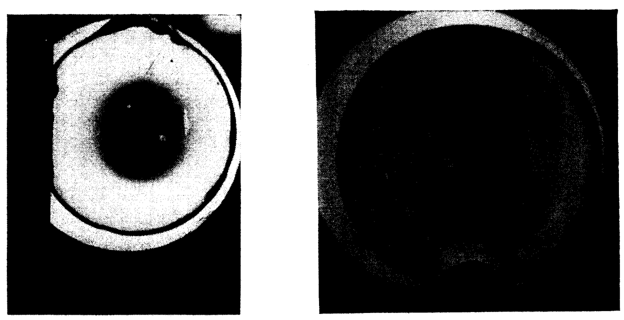


Fig. 4. (a) Specular deposit of zinc obtained after double reflection from sodium chloride, the incident beam making an angle of 45° with both crystals. (b) Same as (a) except the beam was incident on the second crystal at 22.5°.

second at 22.5°. The alignment of both crystals was taken care of optically by sending a beam of light over the path to be traversed by the atoms. Since the measurements of II indicate a maximum velocity difference when the crystals are set at 45° and 22.5°, it would be under these conditions that selective reflection should be in greatest evidence.

In Fig. 4(a) is shown a specular deposit condensed on the walls of the bulb surrounding the second crystal, both crystals set at 45°.[11] The deposit was several times dense enough to be opaque yet there was no trace of any diffuse back-ground. At a conservative estimate, at least 95 percent of the atoms incident on the second crystal were specularly reflected. The presence of almost total reflection differs considerably from all experiences with zinc

[11] Microphotometer curves of these specular deposits were not made because of their opacity to ordinary light. An attempt to obtain a density picture by means of x-rays greatly reduced by the characteristic absorption of the metal was not successful.

reflected from one crystal. Cosine scattered atoms become in evidence, in the case of single crystal reflection, soon after the appearance of a specular spot.

Fig. 4(b) is a photograph of a deposit made under identical conditions except that the second crystal was set to receive the beam from the first at an angle of 22.5°. The specular deposit is quite evident together with a faint diffuse back-ground which was entirely lacking in the runs made with equal angles. (Photographic comparison of course only serves as an approximation).

A comparison of (a) and (b) of Fig. 4 indicates that if one is to consider velocity selection as the explanation of these phenomena then the resolving power of sodium chloride for zinc must be extremely low. Following the x-ray analogy, the low resolving power shown by the reflection of zinc could be explained by assuming that the incident zinc atoms penetrate but very few of the reflecting planes of the crystal. If it be assumed that no selective reflection was present it will then be necessary to introduce some other explanation as to why the zinc atoms when both angles are equal, are almost totally reflected from the second crystal but not from the first.

In Fig. 4(b) a dense thread-like line can be seen to twist around the lower edge of the specular deposit. This curious structure appeared as though it was formed by a very dense "ray of zinc" which slowly moved through an irregular path and finally stopped after doubling back. The small circular spot which represents either the terminus or the start of the trace was many times heavier than either the thread-like deposit or the specular deposit. It has been observed but once. No explanation can be put forth at this time.

IV(a). Multiple reflection of cadmium atoms from sodium chloride.

It was considered desirable to repeat the experiments on double reflection of cadmium[2] since the experiments on zinc discussed in III gave no conclusive evidence of velocity selection.

In Fig. 5(a) is shown a typical specular deposit condensed on the walls of a liquid-air cooled bulb surrounding the second crystal, both crystals being set at 45°. Within one or two percent the entire incident beam was found to go into the specular deposit. The deposit was many times dense enough to be opaque.

In Fig. 5(b) is shown a photograph of a deposit produced under indentical conditions except that the beam from the first crystal was incident on the second at an angle of 22.5° with the surface. A specular deposit is clearly in evidence but the boundary is not well defined and there is present considerable diffuse scattering having a maximum on the normal to the reflecting area of the crystal. The rim of the hemisphere due to the random scattered atoms is clearly discernible. Approximately 50–65 percent of the beam incident on the second crystal was specularly reflected, the remaining atoms contributing to the diffuse back-ground.

The absence of any random scattered atoms when the crystals are set at equal angles and the presence of such atoms when the angles are different indicate that selective reflection is present though not in so marked a degree as found in cases previously reported.

A curious phenomenon was observed in the particular run illustrated by Fig. 5(b). Almost on the normal to the surface of the second crystal a quite noticeably dense rectangular deposit appeared. In Fig. 5(c) is shown this deposit, the specular deposit of Fig. 5(b) appearing at the edge of the photograph.

Because of the incident beam having the shape of a cone it is hard to conceive of any mechanism whereby a square deposit could be obtained by ordinary reflection or even evaporation from the crystal surface. However, since the crystal was fastened to the heating unit by means of fine copper

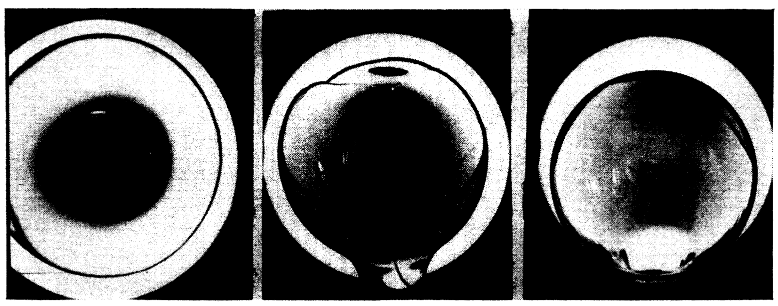


Fig. 5. (a) Specular deposit of cadmium obtained after double reflection from sodium chloride, the incident beam making an angle of 45° with both crystals. (b) Same as (a) except the beam was incident on the second crystal at 22.5°. (c) Curious rectangular deposit found almost on the normal to the crystal surface.

wires which passed over the unused region of the crystal some of the atoms (when the second crystal is set at 22.5° relative to 45° for the first) would strike the wires after reflection since the diffusely scattered atoms spread over a complete hemisphere. There is no reason to believe however, that these atoms which leave the crystal at grazing angles would be scattered in any way but at random. Even if these atoms were in some way directed towards and contributed to the rectangular deposit the few atoms intercepted would hardly account for the number found in this deposit.

This phenomenon has not been observed in any case other than when the first crystal was at 45° and the second at 22.5°, and in fact, it has been observed but twice under these conditions.

IV(b). Multiple reflection of cadmium atoms using the same set of crystals for different angles.

All atomic reflection experiments so far reported in this paper have been made with crystals freshly cleaved before each run. Immediately after cleavage they were mounted, placed into position for the experiment and the air pumped from the system. Out-gassing by heating was never commenced until shortly before the run. In a word, such a treatment and direct comparison after wards assumes equal behavior of all sodium chloride crystals under like conditions.

The experiments described here differ from those of III and IV(a) in that the apparatus was so designed that the reflected beam from the second crystal could be studied as a function of the angle of incidence using the same set of crystals for the comparison.

The essential features of the apparatus are brought out in Fig. 6. A beam of cadmium atoms defined by a system of liquid-air cooled slits strikes the first crystal which is fixed at 45°. A portion of the specularly reflected beam is re-defined by a second opening and then passed to the second crystal which is mounted on a ground-glass joint so that the angular relation between the incident beam and the crystal surface can be varied. The second specularly reflected beam is thrown on to the liquid-air cooled surface of a

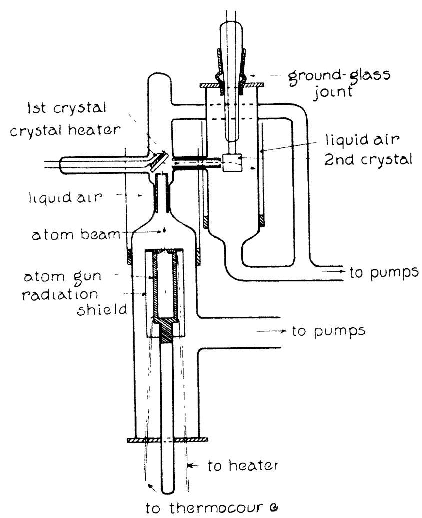


Fig. 6. Apparatus used for experiments described in IV (b).

glass cylinder. Two angles were studied during a run, the crystal being thrown over from one position to another at ten minute intervals to compensate for any change in the density of the atomic beam. A complete run took about three hours or one and one-half hours at each angle. At the end of a run the glass cylinder was cut up and the deposits studied with the help of a microphotometer.

Because of the lack of time only two runs have been made with the apparatus. In the last of the two runs it was found that even when the second crystal was at 18° relative to 45° no trace of selective reflection occurred. The greater number of atoms contributed to the specular deposit with but little indication of random scattering.

In Fig. 7 are shown the microphotometer curves across the central sections of the specular deposits when the first crystal was held at 45° and the second alternately changed from 45° to 18°. The curves were not drawn to represent relative density because the central portions of the deposits so closely approached opaqueness that the cadmium microphotometer-density curve was not applicable. The relative slopes however, and the breadth of the deposit would not be greatly altered even if a translation were made. The

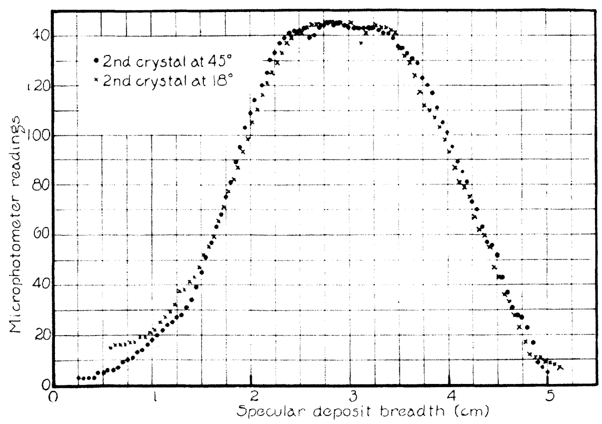


Fig. 7. Microphotometer curves across central sections of specular deposits shown in Fig. 8.

agreement of the two curves is within the limits of the microphotometer error.

In Fig. 8(a) and (b) the photographs of the two specular deposits are shown. These pictures were taken by means of reflected light unlike the transmitted light photographs of the other deposits shown earlier. In Fig.

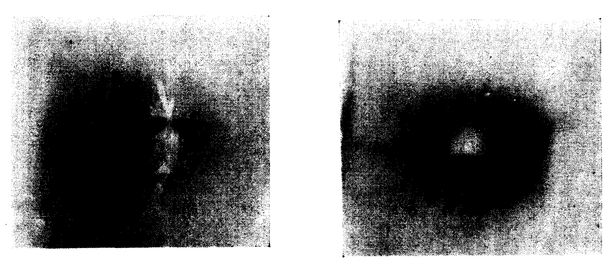


Fig. 8. Reflected light photographs of specular deposits obtained with apparatus shown in Fig. 6. (a) Both crystals set at 45°. (b) First crystal at 45° and the second at 18°.

8(a) is shown the result obtained when both crystals were set at 45°. Quite noticeably, two lines streak across the central part of the deposit. The microphotometer faintly records the broader line as a decrease in density. Fig. 8(b) represents the situation obtained when the second crystal was at 18° relative to 45° for the first. A curved broad line traces around the lower edge of the deposit. This line is also recorded as representing a decrease in actual density. Other than this principal line three curved streamers can be distinguished leaving the central spot. It is difficult to say more than this. The pattern is very faint and if the missing part of a symmetrical pattern is present it does not appear on the photograph, neither does it show up on the original.

These deposits suggest what may be evidence of a surface-grating phenomenon.

Discussion

The double reflection experiments with zinc described in III show no positive evidence for velocity selection as a function of the angle of incidence Moreover, since the measured velocities of specularly reflected zinc fall closely in the region of the most probable velocity of zinc at that temperature they cannot be considered with the same degree of confidence as the similar cadmium measurements which gave values considerably off the most probable velocity.

It may perhaps be a coincidence, but if values for ϕ be calculated by substitution of the measured velocities of zinc into the equation mentioned earlier, then values are obtained which closely approximate those for cadmium at similar angles. The values obtained for both zinc and cadmium are contrasted in Table II. The agreement is quite close but whether this carries any significance is not known.

Table II. *Calculated values of ϕ for zinc and cadmium.*

θ	22.5°	45°	67.5°
$\phi_{Zn}10^{14}$	4.4	12.1	22.2
$\phi_{Cd}10^{14}$	4.84	13.2	19.6

The appearance of two distinct phenomena in the case of cadmium after multiple reflection from sodium chloride was rather surprising. It was believed that all runs were made under identical experimental conditions. The crystals, however, were not laboratory grown but were the natural mined product and although a critical selection was made of each crystal before it was used, it cannot be said the crystals were perfect. Unfortunately, each group of experiments described was made with crystals cleaved from different blocks. It is possible that individual differences in crystals of sodium chloride may in part be responsible for the differences in results as reported herein. It is of interest to note in this connection that Dempster[12] has found that in reflecting positive ions from surfaces of calcite great differences have appared with two different crystals.

Whether or not reflection from two different crystals is necessary for producing patterns as shown in Fig. 8 is not known at present though such patterns have never been observed from single crystal reflection. It may be that reflection from the first crystal removed atoms of such velocities as would have made the pattern obscure had a single reflection alone been

[12] A. J. Dempster, Phys. Rev. **35,** 1405 (1930).

recorded. The absence of any appreciable diffuse back-ground of random scattered atoms for either angle is an indication that the reflection was not devoid of some velocity selection Experience from single crystal reflection invariably has shown that with a specular deposit equivalent in density to those of Fig. 8 there is always present a considerable diffuse back-ground. In fact, early experiments[2] show but 17 percent of the incident beam contributing to the specular deposit. There is reason to believe, however, that considerable variation from that specific percentage takes place depending on the crystal.

The incompleteness of the patterns of Fig. 8(a) and (b) makes it difficult to attempt to fit the data with cross-grating formulae. It is probable that a clearer pattern may result if the crystal be oriented so that rows of similar ions run parallel and perpendicular to the plane of the incident beam. The present experiment was with alternate positive and negative ions parallel and perpendicular to the plane of incidence.

Conclusions

No general conclusions can be drawn concerning the above experiments. More data are first necessary. The problem of the reflection of heavy atoms from crystals is far from a satisfactory solution. It appears that what was first thought to be a case of space-grating reflection with velocity selection depending on the wave-length of the atom now spreads into a problem of greater complexity.

The writer wishes to express his appreciation to Professor A. Ellett under whose direction this work was carried out and to the Research Department of the General Electric Company who so kindly furnished the molybdenum guns used in the experiments with zinc.

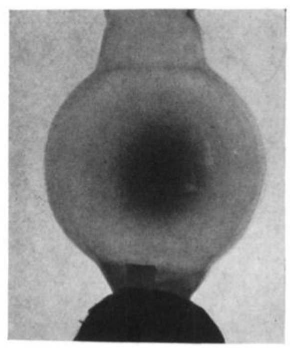


Fig. 1. Specular deposit obtained with zinc reflected from sodium chloride at an angle of 45°.

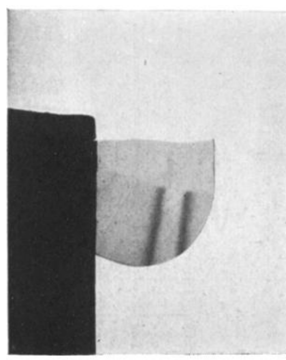
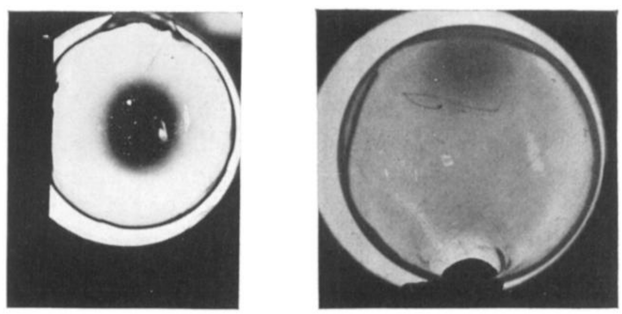


Fig. 2. A typical deposit obtained with specularly reflected zinc after passing through the velocity-analyzer.



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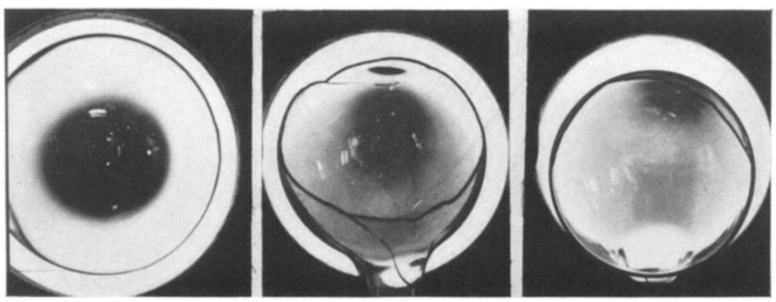

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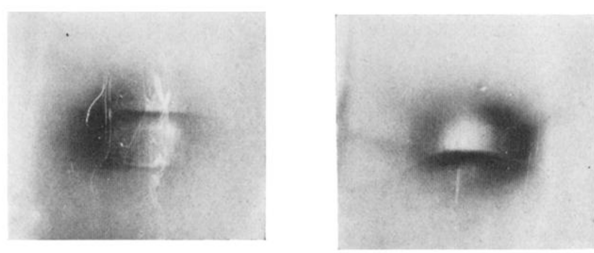

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