leraas functions yields an upper limit which converges to the true eigenvalue E_0, and their proof can easily be extended to show that the lower limit must also converge to E_0 provided $E_0 < \alpha \leq (E_0 + E_1)/2$. The spread between the limits in either (7) or (8) is, however, much greater than the experimental error, so that it cannot be said that complete finality in the helium problem has yet been reached. To carry the approximation farther would be very laborious. Nevertheless, it is probable that E_0 lies close to the Hylleraas value -1.45187, for, as mentioned above, the upper limit is almost certainly a better approximation than the lower limit at any stage of the process, and further, the trend of the values in Table II indicates that the upper limit sequence has converged much more nearly to its limiting value than has the lower limit sequence. However, the fact that the convergence of the latter has also slowed up considerably in going from the sixth to the ninth approximation indicates that possibly E_0 does not lie quite so close to the Hylleraas value as has been generally supposed. On the other hand, the Hylleraas value agrees very closely with the experimental value when the small corrections due to relativity and nuclear motion are included.[18]

[18] H. Bethe, reference 15, 359.

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The Effect of a Direct Electric Field on the Laue Diffraction Photograms

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The effect of a direct electric field (d.e.f.) on the Laue photograms of silica, mica and gypsum crystals has been investigated. It was found that under the action of a d.e.f. (1) the intensity of the Laue reflections is increased, (2) the central spot (which is caused by the rays passing directly through the crystal and the rays reflected backward) is made narrower. If the d.e.f. was applied to the crystals through Al coatings deposited by evaporation on both surfaces of the crystals, the narrowing of the central spot increased only up to a certain intensity of the d.e.f. used. In this case also a time influence was observed. That is to say, if the d.e.f. was applied for a longer time or if sufficiently aged Al coatings were used, the difference in the central spot with and without the d.e.f. disappeared. It was proved that the observed narrowing of the central spot is caused by the alternations provoked in the crystal lattice itself by the d.e.f. and not by the specific properties of the Al coatings. This was done by using instead of the Al coatings obtained by evaporation thin foils of Al pressed on both crystal surfaces for the application of the d.e.f. In this case also the narrowing of the central spot was observed but no time influence was found. The observed phenomena are explained partly by the perfection of the crystal lattice, partly by the shift of the positive and negative ions of the crystal and the positive metallic ions of the deposited Al coatings, which take place in a d.e.f.

MANY authors have studied the influence of electric oscillations, generated in piezoelectric crystals by means of an alternating electric field, on the intensities and the structure of the Laue reflections.[1] It has been found that under the action of electric oscillations the intensity of the Laue spots increases in their intermediate parts, which are due to the reflection of the interior part of the oscillating crystal plate under investigation. Besides this, Fox and Fraser[2] have ascertained that at the same time a widening of the central spot mainly due to the primary x-ray beam takes place. An explanation of these observed phenomena was given[3] by assuming that the perfection of the crystal lattice is disturbed by electric oscillations not only on both surfaces of the crystal plate but also in its interior part which thus contributes to the increase of the intensity of the Laue reflections.

[1] E.g., Fox and Carr, Phys. Rev. **37**, 1622 (1931); Colby and Harris, Phys. Rev. **43**, 562 (1933); Fox and Cork, Phys. Rev. **38**, 1420 (1931); Barrett and Howe, Phys. Rev. **39**, 889 (1932); Nishikawa, Sakisaka, Sumoto, Phys. Rev. **43**, 363 (1933); Jauncey and Deming, Phys. Rev. **48**, 462 (1935).

[2] Fox and Fraser, Phys. Rev. **47**, 15 (1935).

[3] Langer, Phys. Rev. **38**, 573 (1931); **49**, 206 (1936).

In this case the width of the wave-length range ($\Delta\lambda'$) reflected from the continuous incident x-radiation is greater than that ($\Delta\lambda$) of a crystal at rest. The central spot is formed not only by rays passing directly through the crystal but also by rays reflected backward. Dispersion of these rays is greater, the greater is $\Delta\varphi'$ as calculated on the basis of $\Delta\lambda'$, from the Bragg equation. As a result of this, a widening of the central spot in the case of an oscillating crystal takes place. The influence of the imperfection of the crystal lattice on the structure of Laue reflections was then affirmed by results obtained both for crystals with a perfect lattice (silica) as compared with those for crystals with imperfect lattice (rock-salt). This was further proved with crystals whose lattices were intentionally disturbed to a depth of 0.1 mm by polishing[4] the crystal with emerald, and finally with crystals whose lattices were disturbed as the result of an uneven drop of temperature or uneven mechanical strains.[5] Conversely the effect of the perfection of the crystal lattice was investigated by gradually etching away the imperfect surface layers.[2]

As for the influence of a d.e.f. on the crystal lattice, Német[6] found by the Bragg method differences in the intensities of the lines only in the case of Rochelle salt and ice, whereas the differences for the majority of other crystals lay within the limits of experimental errors. The differences in intensity obtained by Hengstenberg[7] and Bennett[8] for crystals with and without the action of a d.e.f. are similarly not of such magnitude as to be compared with the results obtained in the present investigation. Dolejšek and Jahoda[9] also did not observe any appreciable change in the intensity of reflection when they studied the changes of the value of the grating constant under the influence of a direct electric field.

The aim of this work is to show the results obtained when we investigated the influence of a d.e.f. on the structure of Laue reflections and of the central spot for the case of piezoelectric (silica) and apiezoelectric (mica, gypsum) crystals.

The direct electric field was applied to the plates of the crystals by means of aluminum coatings which were deposited directly on both surfaces of the crystal plates by the evaporation of aluminum in high vacuum. These aluminum coatings were deposited so thinly, that on exposure they showed practically no Debye-Sherrer interferences corresponding to the characteristic radiation of the anode of the x-ray tube. As the source of x-rays, a Roentgen tube with Cu anode and Lindemann windows was used; at a voltage of 40 kv and a current of 10 ma the time exposures were 15 minutes.

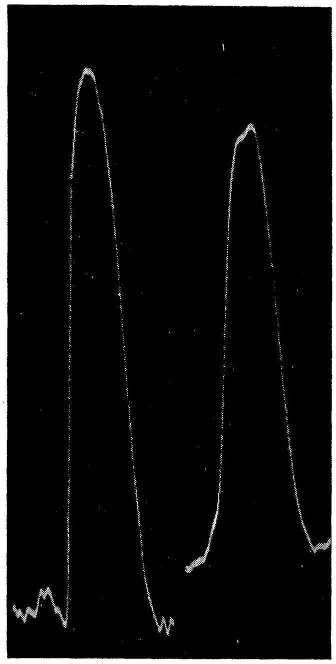
Experimental Results

(1) Silica

The influence of the d.e.f. was studied on two silica plates cut vertically to the electric axis. Their thickness was 0.4 and 0.1 mm, respectively. The potential differences applied amounted to 400, 600, and 1000 volts, which correspond to an intensity variation of the electric field of 1×10^4 to 1×10^5 volts/cm.

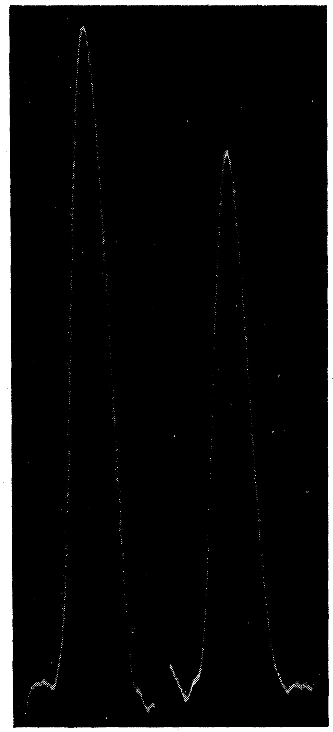
It was found that the lattice of silica gives in the d.e.f. Laue reflections which are more sharp and intense than when no electric field is applied. The corresponding microphotometric curves obtained for a plate 0.4 mm thick with a potential difference of 400 and 600 v are shown on Figs. 1 and 2. It can be seen from Fig. 1 (potential difference of 400 volts; Laue reflection corresponding to such a large value of φ that reflections from both surfaces can be discerned) that on applying a d.e.f. not only the intensity of Laue reflections is increased but also the ratio between the intensities reflected from both surfaces is slightly changed. From the microphotometric curve *a* of the spot obtained without the action of the d.e.f. is to be seen that the rocking curve has two maxima of which the right one is higher than the left, as a result of the fact that at larger values of φ the rays reflected from the surface of the crystal opposite to the film have to pass a longer way through the crystal and thus are more absorbed than the rays which go directly through the crystal and are reflected from the face of the crystal turned toward the film. On the other hand

[4] Barrett, Phys. Rev. **38**, 832 (1931).
[5] Nishikawa, Sakisaka, Sumoto, Phys. Rev. **38**, 1078 (1931).
[6] Német, Helv. phys. Acta **8**, 97 (1935).
[7] Hengstenberg, Zeits. f. Physik **58**, 345 (1928).
[8] Bennett, Phys. Rev. **36**, 65 (1930).
[9] Dolejšek and Jahoda, Comptes rendus (in print).



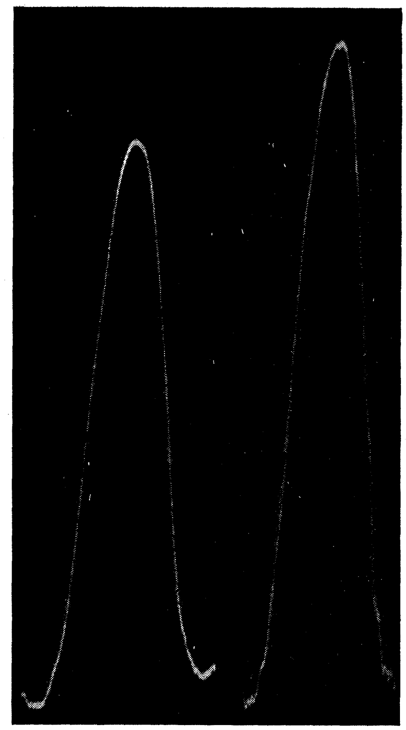
(b) (a)

FIG. 1. Microphotometric curves of Laue reflection in silica plate 0.4 mm thick. (a) Without electric field; (b) under action of electric field, 400 volts.



(b) (a)

FIG. 2. Microphotometric curves of Laue reflection in silica plate 0.4 mm thick. (a) Without electric field; (b) under action of electric field, 600 volts.



(a) (b)

FIG. 3. Microphotometric curves of Laue reflection in mica. (a) Without field; (b) under action of field.

the photometric curve of the same spot under the action of the d.e.f. *b* shows a total increase of the intensity and a change in the ratio between the intensities of both maxima. Under the electric field the left and right maxima of the spot are of equal height. Thus the left maximum corresponding to the reflection from the crystal surface connected with the positive pole of the electric source was slightly increased in relation to the maximum due to reflection from the crystal surface connected with the negative pole of the electric source. As mentioned above, the application of an alternating electric field to silica plates effects on the contrary an increase of the intensity mainly in the intermediate part of the Laue spot which lies between both maxima; i.e., an increase of the reflection power of the inner part of the crystal plate takes place.

Besides this we investigated the influence of etching on the sharpness and intensity of the Laue reflections. In agreement on the whole with Fox and Fraser we ascertained that after etching the crystal plate with 40 percent HF for 15–30 minutes neither the sharpness nor the intensity of Laue reflections is appreciably changed and that after more prolonged etching a sharpening and a simultaneous decrease of the intensity takes place. There is however no appreciable difference between the photograms obtained by means of a plate etched with 40 percent HF for long time as, e.g., for 3 or 20 hours.

(2) Mica

For the experiments analogous to those performed with silica, mica plates 0.07 mm thick were used. The potential difference varied within the limits of 400 to 1000 volts which correspond to an intensity of the electric field of 6×10^4 to 1.4×10^5 volts/cm. For mica similarly as for silica an increase of the intensity and sharpness of the Laue spots under the action of a d.e.f. was observed as is evident from the microphotometric curve in Fig. 3 which shows the rocking curve of a Laue spot when tension is (b) or is not applied (a). In this case the microphotometric curve indicates (cf. silica) not only the increase of both maxima corresponding to the reflections from both surfaces of the plate but also the change of the ratio of both maximum intensities. The maximum due to the reflection from the crystal surface connected with the positive pole of the electric source is increased more than that due to reflection from the surface connected with the negative pole when the d.e.f. is applied.

We observed also for mica crystals an influence of the d.e.f. on the width of the central spot. Under the influence of a d.e.f. on mica crystals this spot diminished as can be seen from Fig. 4(a) and (b); however this diminution continued only to a certain potential difference applied. The magnitude of the diminution of the central spot was dependent on the direction of the rays in respect to the direction of the electric field. The central spot was appreciably narrowed when the rays entered the crystal through the coating connected to the negative pole and left it through the coating connected to the positive pole. However, if the crystal of mica used had been coated with metal a long time before the experiment, or if the electric field was applied to the crystal for a longer time, the difference between the central spot with and without the application of d.e.f. disapeared.[10]

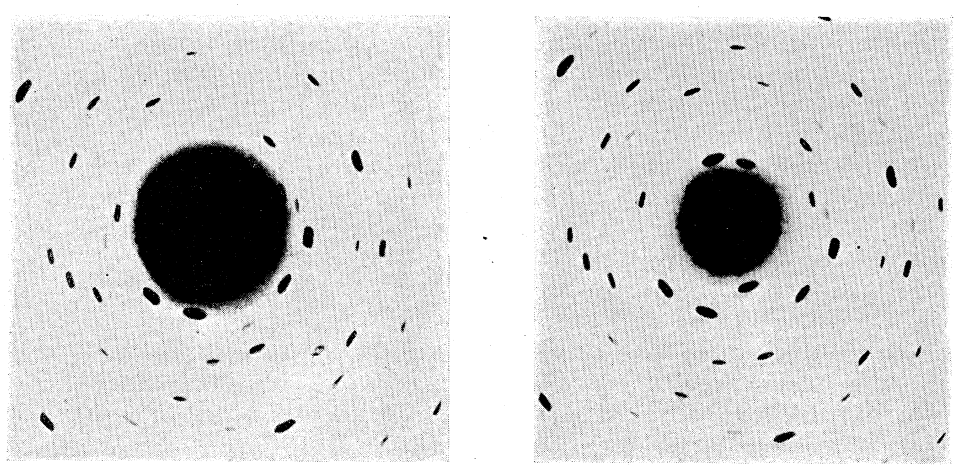
(3) Gypsum

Phenomena analogous to those observed in mica were also found for gypsum but they were much less distinct and thus nothing definite can be said about them.

(4) The influence of aluminum coatings in general on all crystals

It was ascertained that the deposition of aluminum coatings on the surfaces of all three mentioned minerals, i.e., silica, mica, and gypsum effects an appreciable increase in the intensity of that part of the spots which corresponds to reflections from both surfaces of the crystal plates. Because the intensity of reflection increases from both crystal faces whereas the intensity of reflection from the inner layers of the crystal remains unchanged, the spots appear much more in contrast than in the case when the

[10] In the case of silica the influence of the d.e.f. on the narrowing of the central spot could not be studied. We worked with silica earlier than with mica, and arranged our experiments in such a manner that the rays entered the crystal through the metal coating connected with the positive pole of the source. With this arrangement the influence of the d.e.f. on the central spot is insignificant as we proved later in the case of mica. When later with opposite connections and with mica, a marked narrowing of the central spot as a result of the application of a d.e.f. was observed, we could not undertake analogous experiments with silica since all coatings were already aged and other silica plates were not available.



(a) (b)

FIG. 4. Laue pattern for mica. (a) Without field; (b) under action of field.

Al coating is washed off. From the microphotometric curves of the Laue spot corresponding to the mica plate coated and uncoated with aluminum in Fig. 5(a) and (b), respectively, it can be seen that both maxima of blackening corresponding to the reflections from both surfaces of the crystal plate are increased when the coated plate is used (Fig. 5a), and further that the ratio of these maxima has been quite changed by coating the plate. At the same time it was determined that coating mica with Al has the effect of widening the central spot (the respective photograms are not reproduced here since they are similar to those in Fig. 4).

Discussion of the Results

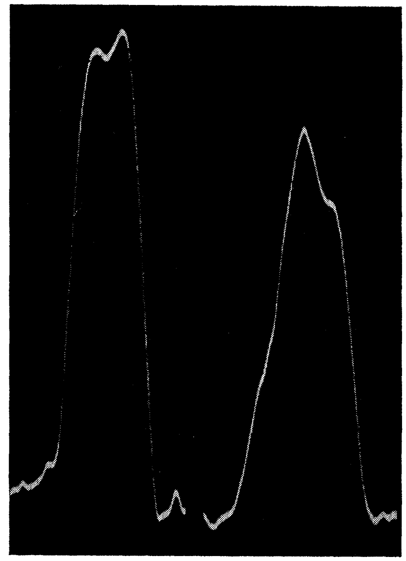
In order to explain our findings occurring when a d.e.f. is applied to certain crystals it is necessary to presuppose that under the influence of a d.e.f.:

(1) A perfection of the lattice, in the inner part of the crystal takes place,[11]

(2) That on the crystal-aluminum interface the positive and negative ions of the crystal penetrate into both Al coatings connected with the negative and positive poles of the electric source, respectively,

(3) That the metallic ions of Al penetrate into the crystal from the coating connected with the positive pole of the electric source.

The perfection of the crystal lattice caused by the influence of a d.e.f. explains the observed sharpening of Laue spots and the narrowing of the central spot. In order to confirm that the central spot under the action of the d.e.f. is really affected by the perfection of the crystal lattice and not by some specific properties of the Al coatings, we used thin leaves of aluminum pressed to both surfaces of the crystal plate in place of these coatings. Also in this case when the d.e.f. was applied, the central spot became narrower. This can serve as a proof that the narrowing of the central spot in a d.e.f. is caused by a perfection of the lattice itself and not by the nature of the coatings themselves.



(a) (b)

Fig. 5. Microphotometric curves of Laue spot from mica. (a) Coated with aluminum; (b) uncoated.

The observed increase of the intensity of Laue reflections from both crystal faces under the influence of an electric field can be explained by the penetration of positive and negative ions from the crystal lattice into both aluminum coatings. When a d.e.f. is applied, negative ions from the crystal lattice on the aluminum-crystal border are shifted towards the Al coatings connected with the positive pole and the positive ions towards the coatings connected with the negative pole of the electric source; thus at both faces of the crystal plate a layer of a very imperfect lattice is formed.

As long as the intensity of the applied d.e.f. does not exceed a certain value, the ions remain shifted from their normal positions while the d.e.f. is acting and when the d.e.f. is removed they go back to their original positions. This formation of layers with disturbed lattices when a

[11] Such an arrangement of the "lattice" of fluids in a d.e.f. was observed by R. L. McFarlan (Phys. Rev. **35**, 1469–75 (1930)) and F. C. Todd (Phys. Rev. **44**, 787–793 (1933)) who found an increase in the intensity of the main maximum for nitrobenzene under the influence of a d.e.f. This effect is explained as caused by the more regular arrangement of the molecules. Német, reference 6, however, did observe by means of the Bragg method a decrease of the intensity of the reflection lines when a d.e.f. was applied to the crystal of Rochelle salt. He explains this fact by a disarrangement of the lattice. But it has to be taken into account that his observations (made by the Bragg method) concern only the surface of the crystal where the regularity of the lattice and the equilibrium of the lattice forces are mostly disturbed. Thus under the influence of the d.e.f. changes of a very different nature from those in the inner part of the crystal with which we are dealing can occur. Besides this, in the case of ice, he used an artificial reflecting surface.

d.e.f. is applied explains the increase in the intensity of Laue reflections from both surfaces as it was observed.

The formation of layers with imperfect crystal lattice should oppose to a certain degree the narrowing of the central spot provoked by the total perfection of the crystal lattice. According to the experiments the narrowing of the spot provoked under the influence of the d.e.f. by the perfection of the inner crystal lattice prevails, however, over the broadening of the spot caused by the penetration of ions into the thin surface layers.

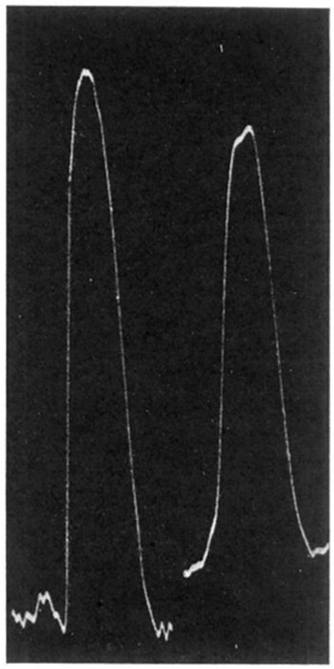
Finally the third assumption, i.e., the penetration of positive metallic Al ions from the coating connected with the positive pole of the electric source into the crystal lattice explains the increase of the intensity of Laue reflections from the crystal face connected with the positive pole, and the dependence of the narrowing of the central spot on the direction of the incident x-rays in respect to the orientation of the electric field. This is due to the circumstance that under the influence of the d.e.f. the shift of the positive Al ions from the coating connected with the positive pole towards the crystal lattice forms on the respective Al crystal border a layer with greatly disturbed lattice. As a result of this, at the Al crystal border close to the positively charged coating there will be a thicker layer with a disturbed lattice than on the face connected with the negative pole, where on the contrary the disturbance of the lattice is produced only by the penetration of positive ions from the crystal into the Al coating, since the Al ions from the coating cannot penetrate into the crystal. Therefore it is to be expected that those parts of the Laue spots which correspond to the reflections from the crystal face connected with the positive pole should be more intense than those which correspond to the reflections from the face connected with the negative pole. This was observed.

By means of the penetration of metallic Al ions into the crystal lattice the dependence of the narrowing of the central spot on the direction of incident rays with respect to the orientation of the d.e.f. can be also explained. If the rays enter the crystal through the coating connected with the negative pole then the rays reflected from the strongly disturbed part of the lattice ($\Delta\varphi'$) situated on the opposite face of the crystal are practically inefficacious as to the back reflection. Thus the narrowing of the central spot under the influence of the d.e.f. which was distinctly determined for mica, is much more pronounced than in the case where the rays enter the crystal through the coating connected with the positive pole, in which case on the contrary more rays reflected from the strongly disturbed part of the lattice contribute to the back reflection, so that the influence of the perfection of the lattice is to a great extent counteracted. This confirms our experimental results.

If, however, the intensity of the d.e.f. applied exceeds a certain value or if it is applied long enough, the ions leave their normal positions permanently and the difference between photograms taken with or without the application of the d.e.f. disappears, as was observed. The same result is obtained if the coatings on the crystal are sufficiently aged. In such cases atoms of aluminum penetrate permanently into the crystal lattice by their own diffusion.

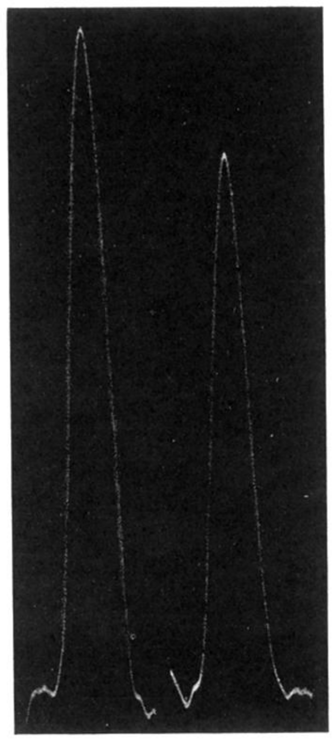
Finally the observed increase of the intensity of Laue reflections and the broadening of the central spot for crystals coated with aluminum in respect to those with the aluminum coating washed off, can be explained in the following way: atoms of aluminum deposited from aluminum vapors in high vacuum on both surfaces of the crystal plate arrange themselves in sufficiently thin layers according to the lattice of the crystal. In this way, on both surfaces of the crystal whose lattices already are almost ideally imperfect—as is known—thin layers of aluminum are formed whose lattices are still more imperfect and which therefore show on a Lauegram very intense reflections and a widening of the central spot.

In conclusion the authors wish to express their indebtedness to Professor V. Dolejšek, Director of the Institute of Spectroscopy of Charles University for valuable suggestions and criticisms of this work.



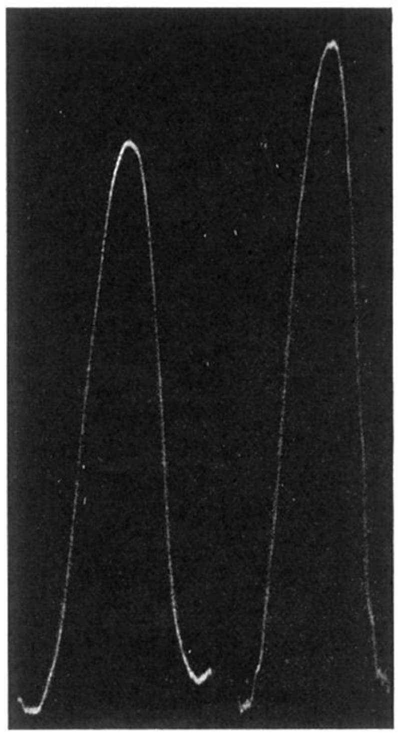
(b) (a)

FIG. 1. Microphotometric curves of Laue reflection in silica plate 0.4 mm thick. (a) Without electric field; (b) under action of electric field, 400 volts.



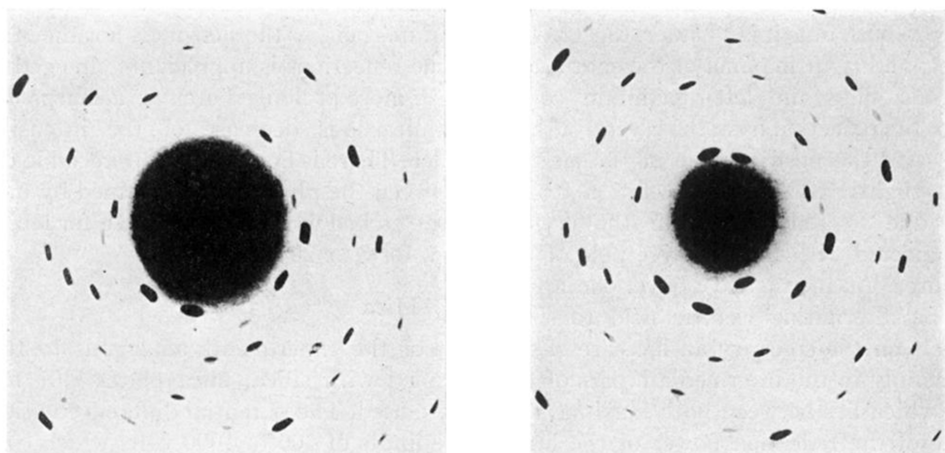
(b) (a)

FIG. 2. Microphotometric curves of Laue reflection in silica plate 0.4 mm thick. (a) Without electric field; (b) under action of electric field, 600 volts.



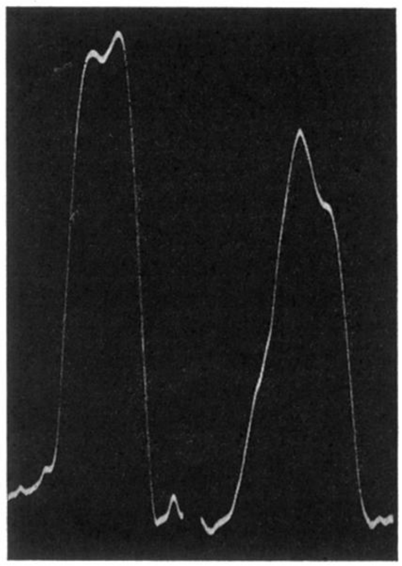
(a) (b)

FIG. 3. Microphotometric curves of Laue reflection in mica. (a) Without field; (b) under action of field.



(a) (b)

FIG. 4. Laue pattern for mica. (a) Without field; (b) under action of field.



(a) (b)

Fig. 5. Microphotometric curves of Laue spot from mica. (a) Coated with aluminum; (b) uncoated.