METALLIC REFLECTION FROM ROCK-SALT AND SYLVITE IN THE FAR ULTRA-VIOLET

By A. H. Pfund

Abstract

From the rapid rise of the dispersion curve of rock-salt and sylvite in the ultra-violet, the existence of regions of anomalous dispersion in the Schumann region have been long anticipated. By using a specially constructed vacuum tube in connection with a vacuum spectrograph the regions of metallic reflection for NaCl and KCl were found. From these results an estimate was made of the wave-lengths of the true resonance frequencies. The values, 1547A for NaCl and 1581A for KCl, are in remarkable agreement with those previously calculated by Herzfeld and Wolf.

THE development of dispersion formulas by Helmholtz, Ketteler, Lorentz, etc., has made it possible to calculate, from the known dispersion curve of a substance, the characteristic frequencies for the "vibrators" which give rise to anomalous dispersion and metallic reflection. The experimental verification of these formulas has been carried out largely by Rubens and his co-workers as a result of their study of the residual rays from quartz, rock-salt, etc., in the infra-red. More recently Herzfeld and Wolf[1] have calculated the "resonance" wave-lengths of anomalous dispersion in the ultra-violet for the halides of the alkali metals. The present work[2] was undertaken for the purpose of putting these predictions to an experimental test. The existence of "resonance frequencies" is indicated by absorption bands. Due, however, to the great width of these absorption bands for other than extremely thin layers, it was deemed more expedient to search for regions of metallic reflection.

The vacuum spectrograph was made to accommodate a one-meter concave grating. This was ruled with 15,000 lines per inch and yielded a dispersion of approximately 17.4A per mm. In its original form the spectrograph suffered from the defect that but a single exposure could be recorded on the photographic plate. Fortunately, the opening which received the plate-holder was cylindrical in shape, hence a modified film-holder of the type shown in Fig. 1 could be used to advantage. Since the slit as well as the lines on the grating were

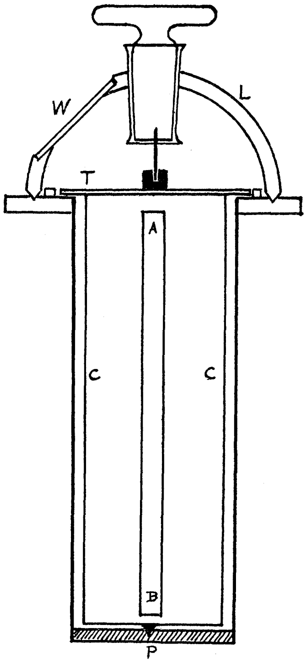

Fig. 1. Film holder.

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[1] Herzefeld and Wolf, Ann. d. Physik **78,** 35 (1925).

[2] A preliminary notice announcing the discovery of a band of metallic reflection for rock-salt was published in "Science" June 17, 1927.

horizontal, the spectrum was projected in a vertical direction through a vertical slot in the outer cylinder *AB*. An ordinary kodak film was wrapped around the inner cylinder *C* and was given the usual coating of mineral oil. This cylinder, which rested on a conical pivot *P*, could be rotated from without by means of the glass stopper and barrel, which were cemented into the steel dome *L*. A strip of brass was cemented into a slot cut in the stopper and was made to engage the slotted rod *M*. So as to be able to observe the rotation of the film-holder for successive exposures a window *W* was inserted in the steel dome. Then also, coarse graduations were cut on the top *T* of the film-holder. As a result it was found possible to record at least twenty-five equally spaced exposures on the same film. The departure of the cylindrical surface from the true focal plane of the grating seemed to exert but a negligible effect for present purposes.

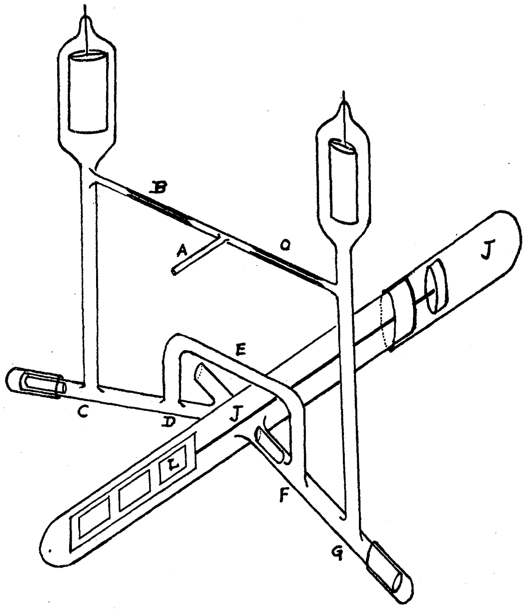

Fig. 2. Diagram of apparatus.

Since it was necessary to record radiations which had been reflected from the surface of the material under investigation and, also, to record "direct" or unreflected radiations, a vacuum tube of special design was employed. As shown in Fig. 2 the gas was admitted through the usual fine capillary into the tube *A*. So as to prevent the direct passage of the discharge, the tubes connected to *A* were constricted to a diameter of one half mm, or less at *B* and *O* and were wrapped externally with tinfoil. Further, to force the discharge to pass through the arm *E* and not through the large tube *J*, the following expedient was adopted: two lengths of glass tubing of about 4 cm each were introduced, respectively, into the arms *CD* and *FG*. Each of these short tubes was sealed off at one end and was supplied with a cylinder of soft iron so as to be susceptible of being moved by means of an external magnet. As shown in the figure, whenever it became necessary to reflect light from the crystal surface, the one tube was moved between *D* and *J*—thus closing this path. The other short tube was moved out of the path of the discharge. Obviously to make use of the direct beam, the relative positions of the two short tubes were interchanged.

The crystals or mirrors to be studied were attached to a metal plate *L* which was constrained to move in "ways." The plate was connected to a thin rod which terminated in a cylinder of soft iron. By means of an external magnet it was possible, therefore, to bring either a mirror or a clear opening in front of the spectrometer slit.

Preliminary spectrograms showed that the entire region from about 3000 to 1000A could be obtained from a mixture of hydrogen and oxygen. Since the electrolysis of water gives rise to a highly explosive mixture, a gas generator was devised which not only eliminated all danger from explosion, but which made it possible to generate hydrogen and oxygen separately or together. The arrangement of parts is shown in Fig. 3. The electrolyte fills the two large outer tubes as well as the central tube *C*, which contains some mercury. A pair of platinum wires *P* less than 1 mm apart is inserted into the tube above the mercury and is connected in parallel with the pair of electrodes *A* (used to generate a mixture of hydrogen and oxygen). As is obvious, the gases generated force the mercury into contact with the free ends of the platinum wires—thus short circuiting the current through *A* and hence, stopping the liberation of gases. Since the electrodes are entirely submerged the danger of an explosion is eliminated. In case the gases are to be generated separately, use is made of the other electrode *B*—the wires at *P* being now connected in parallel with *A* and *B*.

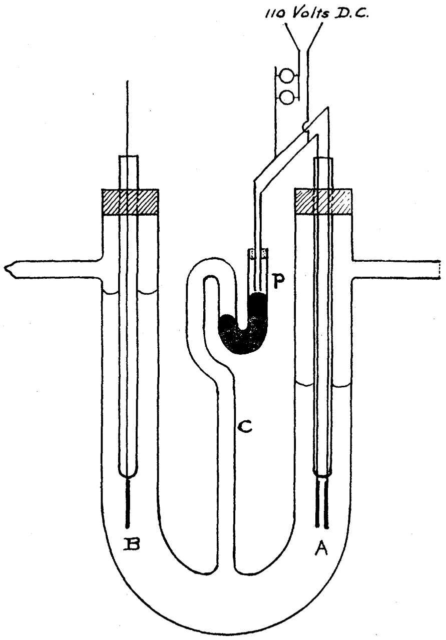

Fig. 3. Gas generator.

The spectrograph was usually exhausted to a pressure of 0.01 mm. At first much time was lost in attempting to obtain reflection spectra from artificially polished surfaces of rock-salt. However, as soon as natural cleavage planes were employed, excellent records were obtained. Not only is the ultimate polish of cleavage planes very high, but the immunity to clouding in consequence of exposure to water vapor is greatly increased. The times of exposure for the "direct" beams was from one to eight minutes while, for the "reflected" beam the exposure was of the order of one hour. Because of imperfections in the crystal surface, failure to secure perfect alignment, etc., a direct comparison of the intensities of the direct and reflected beams was found not to yield correct results. Since, however, the spectrograms include also the region around 2000A, in which refractive indices and, hence, reflecting powers are known, it was possible to correct for all imperfections and to obtain correct results in the regions of short wave-length.

The actual photographs obtained from cleavage planes of rock-salt (NaCl) and sylvite (KCl) are shown in Fig. 4. It is evident that NaCl has a very pronounced reflection maximum at 1581A, while KCl has a similar maximum at 1616A. Thus the existence of vibrators which occasion the great dispersion of the above substances in the ultra-violet has been established.

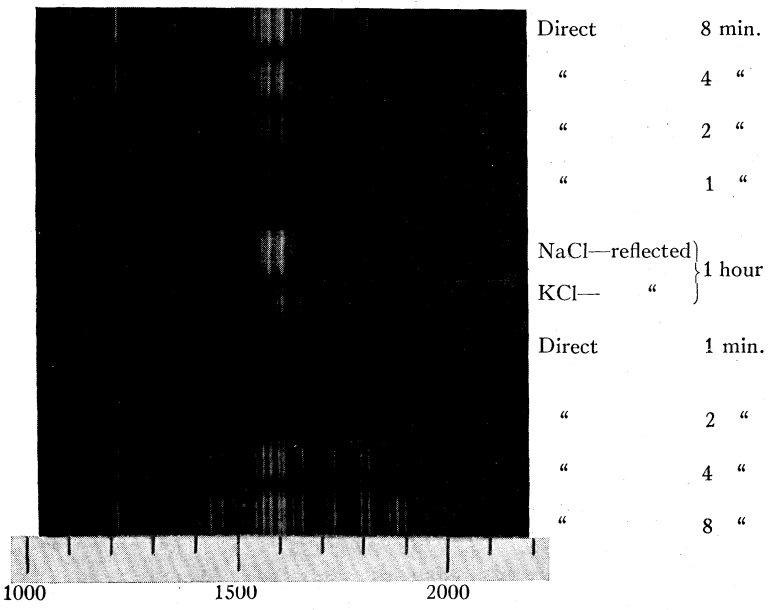

Fig. 4. Photographs of reflection from the cleavage planes of rock salt and sylvite.

As is well known, the region of maximum reflection lies at a wave-length somewhat greater than that of the true center of the absorption band. A tentative estimate of the wave-length of this absorption band was made by taking the wave-length lying midway between the region of maximum reflection and the region on the short wave-length side at which the reflecting power drops, virtually, to zero. According to these estimates the absorption bands are located at 1547A for NaCl and at 1581A for KCl. While not clearly brought out in the reproduction in Fig. 4, it is evident from the finer detail revealed by the negatives that a second maximum in the region of

1100A is being approached. This point is to be cleared up as soon as the work shall have been extended into the region of still shorter wave-lengths.

Among the possible modes of vibration within a crystal, the following may be cited: (1) Vibrations of the nuclei relative to one another. The free periods of these vibrations lie in the far infra-red. Their wave-lengths are 70.2μ for NaCl and 61.7μ for KCl.[3] (2) Nuclear vibrations within a complex positive or negative ion. These vibrations which lie between 6 and 15μ were definitely identified by the writer[4] as originating within the complex negative ion of sulphates and nitrates. (3) Electronic vibrations due to electrons in the outer shells (present work.) (4) Electronic vibrations due to electrons in the inner shells (x-ray region.)

Concerning the vibrations of electrons in the outer shell, it may be stated that Herzfeld and Wolf[1] have predicted the wave-lengths of these resonance frequencies for the halides of the alkali metals. Furthermore, they have been able to identify a given vibrating electron with the positive or negative ion in the crystal lattice. Their results[1] are as follows:

	λ_1 Calc.	λ_2 Calc.	λ_3 Calc.	λ_3' Observed
NaCl	342A (Na ion)	936A (Cl ion)	1543A (Cl ion)	1547 ± 8A
KCl	515A (K ion)	975A (Cl ion)	1580A (Cl ion)	1581 ± 8A

From these data it is evident that the results observed for λ_3' agree within the limits of experimental accuracy with those calculated. Furthermore, the predicted shift of the band for KCl toward the red with respect to that for NaCl, is verified.

In addition to the preceding the following substances were likewise examined: crystalline quartz, glass, calcite, potassium bichromate, zinc sulphide, gold and speculum metal. As for the non-metallic substances, it may be stated that, while none revealed reflection maxima as sharply defined as those of NaCl and KCl, the existence of broad maxima, particularly in the case of calcite, is anticipated. These will require a microphotometer for detailed study. While the reflecting powers of gold and speculum decrease continuously in the region of shorter wave-length, the reflecting power of quartz is on the increase. These results confirm earlier ones[5] which demonstrated the superiority of crystalline quartz over metals in the region of short wave-lengths.

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[3] Fuchs and Wolf, Zeits. f. Physik **46,** 511 (1928).

[4] A. H. Pfund, Astrophys. Jl. **24,** 19 (1906).

[5] A. H. Pfund, J.O.S.A. **12,** 467 (1926).

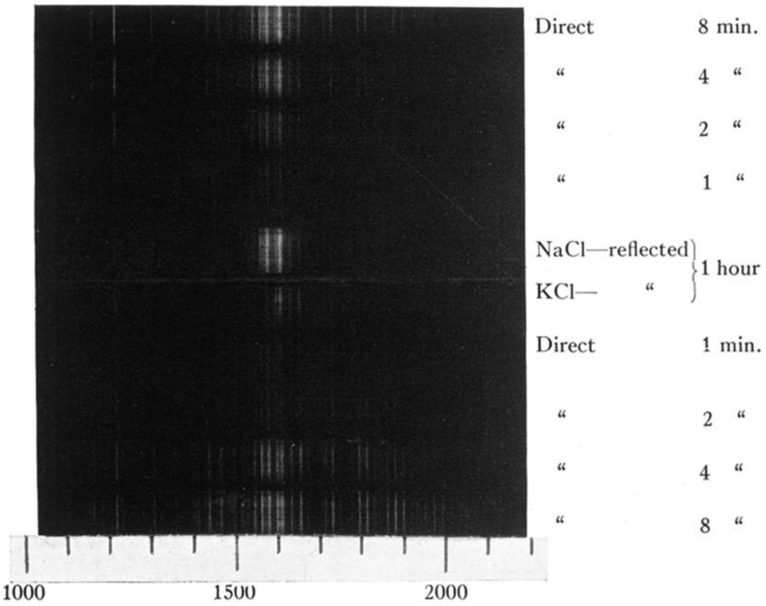

Fig. 4. Photographs of reflection from the cleavage planes of rock salt and sylvite.