### A New Method of Producing Negative Ions

In some recent experiments on the bombardment of metal surfaces with positive ions, negative ions formed at the surface by the positive ion impacts were observed. The apparatus used was an adaptation of the Dempster type mass spectrograph in which the negative particles formed could be analysed. Platinum targets were used in most cases and the impacting ions were of lithium (chiefly  $Li_7^+$ ) produced by a spodumene source on a hot filament. The positive ions were accelerated through 500 volts to the target where any negative particles formed would be driven back to the first slit of the mass spectrograph with the same velocity as the impinging positives. Identification of the negative particles was made from the calibration of the spectrograph with known positive ions. All experiments were made in a good vacuum of the order of 10<sup>-6</sup> mm of mercury.

In this way negative ions of  $OH^-=17$  and  $Cl^-=35$  were found to result from the bombardment with positive lithium ions. Secondary electrons were also observed together with two ions which were probably  $H_1^-$  and  $H_2^-$ : the latter two ions were not easily analysed due to the width of the slits and the small values of the magnetic field at which they were observed. For platinum targets which had not been outgassed the negative OH ion was strong and steady over a period of several hours; its intensity was of the same order of magnitude as the electron emission. The H1 and H<sub>2</sub> ions accompanied the OH ion, H<sub>1</sub> being several times as intense as H2. The Cl ion was not resolved into its components and was not always observed; its presence was more noticeable when the target was coated with spodumene showing that it probably arose from some chance contamination of the target. Strong outgassing of the platinum target did not affect the electron emission but caused the negative ions to disappear.

This method of forming negative ions while of interest in itself may also be of importance in interpreting related experiments. It is possible that in studies of ionization and secondary electrons produced by positive ions this type of emission may contribute to the effects observed. The general presence of water vapor in most metals and compounds will probably give rise to negative ions as well as electrons while the negative chlorine ion indicates that other substances may form other ions under the influence of positive ion bombardment.

Negative ions have been observed previously by J. J. Thomson<sup>1</sup> and O. H. Smith<sup>2</sup> as the retrograde rays formed in discharge tubes. These ions, presumably of  $H_2^-$  and  $O_2^-$ , were formed just in front of the cathode by gas molecules acquiring a negative charge. O. W. Richardson<sup>3</sup> and H. A. Barton<sup>4</sup> have reported a few cases of negative ions formed by direct heating of the salt. Very recently Mueller and Smyth<sup>5</sup> have reported negative hydrogen and hydroxyl ions formed by electron impacts in apparatus containing water vapor. Further work on this type of emission is being carried out and will be reported on later.

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<sup>1</sup> J. J. Thomson, "Rays of Positive Electricity," pp. 137–138.

<sup>2</sup> O. H. Smith, Phys. Rev. 7, 625 (1916).

<sup>8</sup> O. W. Richardson, "Emission of Electricity from Hot Bodies."

<sup>4</sup> H. A. Barton, Phys. Rev. 26, 360 (1925).

<sup>6</sup> D. W. Mueller and H. D. Smyth, Program of Schenectady Meeting, American Physical Society, Abstract 11, Aug. 26, 1931.

# Variations in the Grating Constant of Calcite Crystals

With the development of the double crystal spectrometer for measuring x-ray wavelengths and the use of the high precision photographic spectrometers now employed, the question of a possible variation in the grating constant of calcite is of considerable importance. Also the chemical purity and density of the crystals should be examined. In the present experiments optically clear crystals have been secured from four localities, Iceland, Spain, Montana, and Argentina. The crystals were carefully cleaved and the part of the surface used for diffracting the x-rays was almost free from "steps." Small pieces of each crystal were cut from a region very close to the part of the crystal used and a chemical

TABLE I.

Crystal	Silica	Alumina	Ferrous oxide	Manganous oxide	Magnesium oxide	Calcium carbonate
Iceland Montana Argentina Spain	absent absent absent 0.004%	absent absent absent absent	$\begin{array}{c} 0.006\%\\ 0.005\\ 0.006\\ 0.007\end{array}$	$\begin{array}{c} 0.007\% \\ 0.011 \\ 0.010 \\ 0.006 \end{array}$	absent absent absent absent	99.98% 99.97 99.97 99.98

analysis of these pieces has been made. The results of these analyses are shown in Table I. Thus chemically there appears to be very little difference between the various samples.

A preliminary determination of the density of each crystal indicated that the density was the same for all crystals within 1 part in 4000. A more precise determination of the densities will be made before a final report of the experiment is given.

The spectrometer was a high precision double crystal spectrometer built by the Société Génevoise. An attempt was made to calibrate the circle with a telescope but no consistent error of as much as 0.5'' was found. This was just about the error of setting the cross hairs in the telescope. A more precise method of testing the circle was as follows: The diffracting angle of the same crystal in the 4th order was determined in three 120° positions of the circle. These agreed to within 0.4'' with an average variation of 0.2''. This average diffracting angle has been used as the absolute value and all other measurements have been made relative to this.

The first crystal of the spectrometer was an Iceland calcite set to diffract the  $K\alpha_1$  line of molybdenum over the main axis of the spec-

trometer. This crystal was made parallel to the spectrometer axis to within 1' of arc. The surface of the second crystal was mounted on the axis and parallel to it to within 5" of arc. The correction which must be made in the measured diffraction angle, due to the height of the slits, was determined experimentally in the 4th order. This agreed, however, very closely with the calculated correction. The correction for the thermal expansion of the crystal has been made using Larsson's value1  $(\alpha = 1.09 \times 10^{-6})$  of the expansion coefficient. The results are for a crystal temperature of 18°C. In calculating the wave-lengths the theoretical value of the index of refraction  $(1-\mu=1.85\times10^{-6})$  has been used and the grating space of the crystal was assumed to be 3.02904A in the first order.

The results given for the 4th order are much more reliable than any others. Eight independent determinations have been made on each crystal in the 4th order and the average variation in each case was about 0.2". In each of the other orders only two or three determinations have been made and the average

<sup>1</sup> Larsson, Inaugural-Dissertation, Uppsala 1929.

Order	Iceland	Montana	Argentina	Spain				
$\begin{array}{c}1\\2\\3\\4\\5\end{array}$	6° 42' 35.4'' 13° 30' 44.9'' 20° 31' 0.3'' 27° 51' 34.0'' 35° 44' 28.5''	$\begin{array}{c} 6^{\circ} \ 42' \ 35. \ 6'' \\ 13^{\circ} \ 30' \ 45. \ 2'' \\ 20^{\circ} \ 31' \ 1.3'' \\ 27^{\circ} \ 51' \ 34. \ 6'' \\ 35^{\circ} \ 44' \ 30. \ 8'' \end{array}$	$\begin{array}{c} 6^{\circ}.42'35.5''\\ 13^{\circ}.30'45.7''\\ 20^{\circ}.31'1.1''\\ 27^{\circ}.51'34.7''\\ 35^{\circ}.44'29.9''\end{array}$	6° 42' 35 .3'' 13° 30' 45 .3'' 20° 31' 0.8'' 27° 51' 34 .4'' 35° 34' 29 .9''				
Wave-lengths.								
1 2 3 4 5	0.707833A 0.707827 0.707832 0.707830 0.707830 0.707827	$\begin{array}{c} 0.707838\\ 0.707831\\ 0.707831\\ 0.707841\\ 0.707834\\ 0.707838\end{array}$	$\begin{array}{c} 0.707837\\ 0.707836\\ 0.707839\\ 0.707835\\ 0.707835\\ 0.707834 \end{array}$	$\begin{array}{c} 0.707832\\ 0.707832\\ 0.707836\\ 0.707833\\ 0.707833\\ 0.707834 \end{array}$				

Diffraction angles.

variation was from 0.2'' to 0.5''. The average wave-length as given by the 4th order is

## $M_0K\alpha_1 = 0.707833A$

Compton<sup>2</sup> has recently reported a precise determination of the diffraction of the  $MoK\alpha_1$ line in the 4th order using calcite. His value of the diffracting angle is 27° 51' 32.9" or a wave-length 0.707824A as calculated above. This is considerably smaller than any of my results, however, Larsson's results1 agree very closely with the present values obtained with the Iceland crystal.

<sup>2</sup> Compton, Phys. Rev. 37, 1694 (1931).

## Thermocouples of Longitudinally and Transversely Magnetized Wires

Recently (Phys. Rev. 38, 179, (1931)) William H. Ross has performed some experiments designed to give the thermal emf between longitudinally and transversely magnetized elements of the same ferromagnetic substance. In these experiments a short length of wire was placed parallel to the magnetic field between the poles of an electromagnet. At each end of this short length the wire was bent at right angles, so that two long segments came out parallel to each other from between the poles of the magnet. These long ends were connected to a galvanometer. The two bends between the magnet poles were kept at different temperatures and when the magnet was excited a thermoelectromotive force was observed.

We may consider that the circuit contains three thermoelectrically distinct metals:----(1) longitudinally magnetized metal, (2) transversely magnetized metal, (3) unmagnetized metal. Assume the junctions of (3) and (2) to be situated at the edges of the magnet poles. These junctions will then be at different temperatures as a result of conduction of heat along the wires, and the resultant emf will be partly due to the combination of (2) and (3).

The index of refraction of the x-rays in the crystal has been calculated from the 1st and 2nd orders and the 1st and 4th orders. The average values for all crystals are

1st and 2nd order  $(1-\mu) = 1.90 \times 10^{-6}$ 1st and 4th order  $(1-\mu) = 1.86 \times 10^{-6}$ .

These values are in fair agreement with Larsson's<sup>1</sup> results but differ considerably from the value  $(1-\mu) = (2.10 \pm 0.15) \times 10^{-6}$  reported by Compton.<sup>2</sup>

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The title of the paper by Ross implies the existence of only the elements (1) and (2).

Of course, practically, there is no sharp line of demarcation between the elements (2) and (3), but the results are essentially unchanged in the experiment where a temperature gradient in a nonuniform magnetic field replaces the sharp boundary considered above.

Another point of view would consider the longitudinal thermomagnetic potential differences in the transverse sections of wire. The total emf would then involve an integration over a varying magnetic field and a varying temperature gradient.

These considerations are brought forward in order to point out the difficulty of interpreting in a simple way the experiments of Ross. There are conflicting experiments in this field of research and it is highly desirable to keep the various elements clearly segregated in any particular experiment in order to make comparison possible with other results.

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> Houston, Texas, September 7, 1931.