

## The Plasticity of Rocksalt and Its Dependence upon Water

R. BOWLING BARNES, *The Johns Hopkins University, Baltimore, Maryland*

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Measurements are reported which show that if a piece of rocksalt be placed in water, the water actually penetrates into the interior of the crystal. A discussion is given of the

rôle played by the water in causing the high degree of plasticity and tensile strength (Joffé effect) characteristic of salt crystals which have been so treated.

A PIECE of rocksalt which has been immersed in water and allowed to dissolve partially exhibits two remarkable properties, namely, a very high degree of plasticity<sup>1</sup> and a noticeable increase in its tensile strength.<sup>2</sup> In spite of the many researches carried out upon this subject, neither of these effects is completely understood, as the exact rôle played by the water and the mechanism of its action remain unknown.

Joffé in a paper in 1924<sup>2</sup> suggested that the entire phenomenon was a surface effect, the water simply serving to remove the dry surface with its minute cracks and fissures. Griffith<sup>3</sup> had shown that the presence of such crevices could easily lead to extremely low values of plasticity and tensile strength, since the forces which one applied to the crystal would be greatly magnified at the inner edges of such fissures. Dry<sup>4</sup> salt, therefore, was assumed to be brittle at room temperature, this brittleness being determined supposedly by the presence of these small crevices.

Polanyi and Ewald<sup>5</sup> took issue with this theory and offered a new explanation of the two effects. According to their views also, the action of the

water was supposed to take place upon the surface of the crystal. They assumed that dry salt was brittle, and that in some manner the water caused the elastic limit actually to be lowered, making the crystal plastic. If, due to some applied stress, a deformation followed, the result was a toughening (Verfestigung) or increase in the tensile strength.

Later on Smekal<sup>6</sup> offered still another theory in an attempt to account for these unusual properties of crystals. He had shown previously<sup>7</sup> that any normal crystal of salt is characterized by the presence of an almost uniformly distributed number of imperfect regions, which he supposed to be either actual little holes, networks of crevices, or simply regions of loosely bound atoms. These he assumed to be the cause of the low values of the tensile strength found in such crystals. Together with Quittner he had shown indirectly (by means of electrical conductivity measurements) that these imperfections made it possible for water to enter the interior of a crystal. This water, they found, caused marked changes in the physical properties of the crystal, making in reality a different crystal out of the original one. The resulting crystal was highly plastic, and as a result of a deformation exhibited high tensile strength values.

These three hypotheses will be referred to as *A*, *B* and *C* respectively. Various experiments have

<sup>1</sup> This was first noted by Engelhart in 1867 while working in the salt mines. See B. K. Kleinmanns, *Phys. Zeits.* **15**, 363 (1914).

<sup>2</sup> A. Joffé, M. W. Kirpitschewa and M. A. Lewitsky, *Zeits. f. Physik* **22**, 286 (1924); **31**, 576 (1925).

<sup>3</sup> A. A. Griffith, *Trans. Roy. Soc.* **A221**, 163 (1920).

<sup>4</sup> Throughout this paper, salt in its normal condition shall be referred to as dry salt. Salt which has been made plastic by the action of water shall be called wet salt. A sample shall be considered plastic when it can be noticeably bent with the fingers.

<sup>5</sup> W. Ewald and M. Polanyi, *Zeits. f. Physik* **28**, 29 (1924); **31**, 746 (1925).

<sup>6</sup> A. Smekal, *Naturwiss.* **16**, 743, 1045 (1928); F. Quittner and A. Smekal, *Zeits. f. physik. Chemie* **B3**, 162 (1929); A. Smekal, *Phys. Zeits.* **32**, 187 (1931); See also E. Schmid and O. Vaupel, *Zeits. f. Physik* **56**, 308 (1929).

<sup>7</sup> See Smekal's chapter in the *Handbuch der Physikalischen und Technischen Mechanik*.

shown, that: (1) dry salt is not absolutely brittle;<sup>8</sup> (2) wet salt is very plastic;<sup>9</sup> (3) the elastic limits for dry and wet salt are quantitatively the same;<sup>10</sup> (4) the interior of wet salt has definitely been changed with respect to that of the dry salt;<sup>11</sup> (5) a purely surface action is improbable;<sup>12</sup> (6) a static effect is not possible.<sup>13</sup> From a comparison of these facts with the requirements of the three theories, it will be seen that *C* most nearly fits all of the experimental facts. The present paper is a report upon some of the author's recent experiments which seem to bear further important evidence in favor of theory *C*, by proving that the crystal in its wet state actually contains water within its interior.<sup>13</sup>

It was reasoned that if theory *C* were correct, a piece of wet salt should show the presence of water throughout its volume, while if *A* or *B* were correct, the sample of salt should show water only upon its surfaces. By means of detecting the characteristic infrared absorption bands of water in the interior of such pieces of salt, this question was decided.

In studying this absorption a rocksalt spectrometer of the customary design was used with a Globar as a source. The radiation from this source, which was operated by a 110 volt battery, was brought to a focus by a concave mirror,  $M_1$ , of 60 cm focal length used at its radius of curvature, allowed to diverge and then concentrated by a second concave mirror upon the first slit of the spectrometer. A piece of normal, dry salt was placed at the radius of curvature of  $M_1$ , and its transmission curve measured from  $1.5\mu$  to  $4.0\mu$ . Immediately afterwards (or preceding), with the salt removed, the energy curve, or transmission

curve of the atmosphere, was measured, and by dividing the respective ordinates of these two curves the percent transmission of the dry salt was obtained. The sample was then placed under water at room temperature until it became very plastic, i.e., until it could actually be bent with the fingers, removed from the water, and its exterior quickly dried. This drying was accomplished by rubbing the crystal thoroughly with a cloth, and then exposing it to a blast of air. To insure further that the absorption found, if any, did not come from a surface layer of water, the two end surfaces were entirely removed by cleaving 1 or 2 mm off of each end of the crystal. The two surfaces through which the radiation had to pass were fresh cleavage surfaces in the dry and in the wet samples, and so in each case should have been strictly comparable. With the plastic crystal in this condition, its transmission was determined as described above.

Comparison of the transmission curves\* for dry and wet samples, Fig. 1, shows that the salt has definitely undergone distinct changes. The amount of absorption in the region where water is known to absorb has definitely increased, showing that water has entered the crystal. The curves shown are typical of almost every sample examined.

#### DISCUSSION OF RESULTS

Since the effect was so small, a great number of samples had to be examined in order to make sure that the increase of absorption had not arisen from some spurious source. The effect of the water vapor and  $\text{CO}_2$  in the atmosphere had to be taken into account, and kept constant, the former absorbing at  $2.66\mu$  and the latter at  $2.7\mu$ .

The method as described above consisted of mapping and comparing three energy distribution curves, namely: curves through the atmosphere, the dry sample and the wet piece of salt. Because of slight differences in the figure of the various cleavage surfaces and slight changes in the focus of the radiation caused by differences in the length and alignment of the samples, these three curves were not strictly comparable so far

<sup>8</sup> F. Blank, *Zeits. f. Physik* **61**, 727 (1930); U. Heine, *Zeits. f. Physik* **68**, 591 (1931); K. H. Domerich, *Zeits. f. Physik* **80**, 242 (1933); A. Smekal, *Phys. Zeits.* **31**, 229 (1930).

<sup>9</sup> See reference 5. E. Schmid and O. Vaupel, *Zeits. f. Physik* **56**, 308 (1929).

<sup>10</sup> K. H. Domerich, *Zeits. f. Physik* **80**, 243 (1933); G. F. Sperling, *Zeits. f. Physik* **74**, 476 (1932).

<sup>11</sup> See reference 7. Smekal and Quittner; E. Schmid and O. Vaupel, *Zeits. f. Physik* **63**, 311 (1931).

<sup>12</sup> U. Heine, *Zeits. f. Physik* **68**, 591 (1931); A. Smekal, *Phys. Zeits.* **32**, 187 (1931).

<sup>13</sup> R. Bowling Barnes, *Phys. Rev.* **43**, 82 (1933); *Naturwiss.* **21**, 193 (1933). Also A. Smekal, *Phys. Rev.* **43**, 366 (1933); *Naturwiss.* **21**, 268 (1933).

\* As will be shown later, these curves were obtained in such manner as to make them purely relative. Hence the values greater than 100 percent.

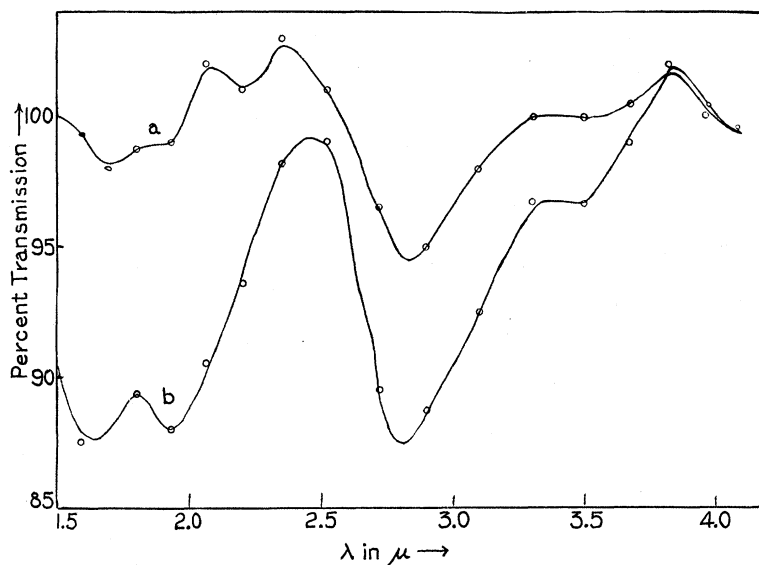


FIG. 1. Transmission curves showing effect of water used in making the sample plastic. (a) 32 mm dry salt; (b) 23 mm wet salt.

as the actual numerical values were concerned. To make them so, the ordinates of the dry and wet curves were each multiplied by a constant factor so as to bring them into coincidence with the respective air curves at some one wave-length. Since neither salt nor water has an absorption band very close to  $4.0\mu$ , the curves were made to check at this point. It was by dividing the respective ordinates of the resulting three curves that the transmission curves discussed were obtained.

One rather interesting fact is shown in all of the curves obtained regarding the transmission of the various pieces of dry salt. These each show quite definitely the presence of water bands, even though the salt had not yet been put into water.<sup>14</sup> With respect to this absorption in the dry condition, samples from Russia, Poland and Michigan behaved very differently. A sample of dry Michigan salt 43 mm long showed at  $2.85\mu$  a transparency of only 60 percent. The same sample when cut to 23 mm length showed 80 percent, and

when 12 mm long only 95 percent transmission. This absorption is surprising although when held up to a light the longest sample showed a very faint haziness, and so probably contained minute droplets of water. These samples were, however, quite brittle when dry, apparently because the water was localized and not uniformly distributed throughout the volume of the crystal.

It is interesting to try to identify the five absorption bands which appeared in this work. Attention must first be called to the fact that the spectra of liquid water, water vapor and water of crystallization show marked differences. Furthermore, granting that some water has actually worked its way through a system of cracks into the interior of the crystal, nothing definite can be said as to whether these molecules then exist as individuals, similar to water of crystallization or as droplets of liquid water. Accordingly, the identification remains somewhat uncertain and incomplete. Fig. 2 shows the locations of the five bands found in these experiments as compared with the known water bands, and those generally ascribed to the OH group. There is little doubt that the absorption found comes from water on the inside of the crystal, although some of the observed bands do not coincide exactly with any

<sup>14</sup> Robertson and Fox (Proc. Roy. Soc. A120, 133 (1918)) in their paper on infrared methods found absorption bands around  $6.25\mu$ . Concerning these they said "Water in or on rocksalt windows seems, therefore, the most likely cause of the bands."

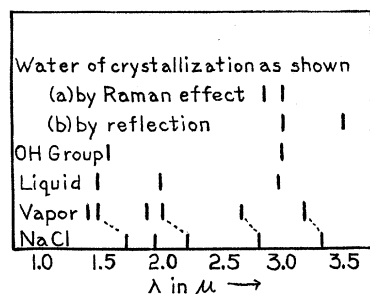


FIG. 2. Comparison of water bands found in salt with known water bands.

known water bands. Whether the shifts indicated in the figure by dotted lines are real and have any meaning cannot be said.

If we assume that this water absorbs just the same as does liquid water an approximation can be made as to the amount of water which has entered the crystal. Aschkinass found for the so-called  $3\mu$  band ( $2.97\mu$ ) an absorption coefficient equal to about 2500. Using this, in the relation that  $J = J_0 e^{-kd}$ , we see that in order to produce the 15 percent drop in the transmission shown in Fig. 1, an equivalent thickness of  $6.4 \times 10^{-4}$  mm of liquid water is necessary. Assuming further that this was dispersed uniformly throughout the crystal, we see that in the 57 mm crystal the density of the water was roughly  $10^{-5}$  g/cc. According to this, the sample used which was  $5.7 \times 2.0 \times 0.5$  cm should have contained about  $5.7 \times 10^{-5}$  g of water. It is, therefore, not impossible that if such a crystal be heated over a long period of time, at a temperature high enough to drive out this water, a difference in its weight before and afterwards could be detected.<sup>15</sup> The above figure,  $10^{-5}$  g/cc, the author realizes is only a rough estimate of the upper limit for the amount of water in such a crystal. Too little is known about the condition of the water to allow any accurate calculation.

It will be noticed also that the greatest increases in the absorption occur at the bands other than the  $2.8\mu$  band. The absorption coefficient of liquid water at this band is about 2500, while at  $1.97\mu$  it is only 123. In the salt, however, the in-

tensities of these bands are very much more nearly equal. Just why this condition holds cannot yet be said.

Since dry salt showed definitely the presence of water absorption bands, it could only be hoped that upon making the samples plastic, some characteristic change in these bands would take place. Fig. 3 shows quite clearly that such a change always occurred, and that it was always an increase in the absorption when the salt was made plastic. A sample of Russian salt 65 mm long was measured while dry (curve *a*). Upon being made plastic, its absorption increased (curve *b*). After having dried out at room temperature for 24 hours, it became brittle and its absorption decreased to that shown in curve *c*. Again it was made plastic, and the absorption shown in curve *d* appeared. Finally the sample, then only 21 mm long, was dried in an oven at  $150^\circ\text{C}$  for 24 hours. Curve *e* was then obtained. Similar cycles were repeated upon other samples with quite similar results.

Control measurements were made which showed that the absorption which we have attributed to the presence of water is a volume effect, and not a spurious effect connected in some manner with the two end surfaces. A sample was measured dry, then made plastic and the increase in the amount of the absorption noted. It was then shown that if this sample were cut in half, this increase in the absorption would decrease decidedly or that it was really a function of the length of the crystal.

It is possible that in some cases part of the radiation in passing through the crystal may have suffered total internal reflection upon the sides of the crystal. It is improbable that this could have falsified the results; however, in order to test this, some of the wet crystals were dried in a blast of air, then immediately dipped into molten paraffin. The two ends were split off and the transmission determined as above. In no case was any difference detected which could have been caused by such total reflections.

The above discussed results show only that the presence of water distributed throughout the volume of the crystal goes hand in hand with the plasticity of rocksalt. Whether the penetration of the solvent into the salt is either necessary or sufficient to make it plastic is not known. That,

<sup>15</sup> Schmid and Vaupel once showed that the density of salt was not changed by more than 0.2 percent by making it plastic.

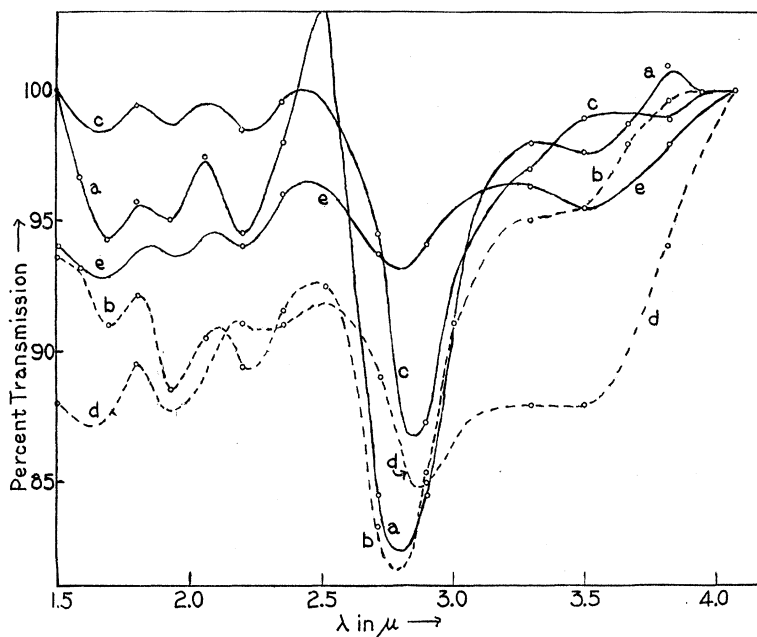


FIG. 3. Showing that water in the interior of a salt crystal always accompanies plasticity. All curves on same sample. (a) 65 mm dry—brittle; (b) 57 mm wet—plastic; (c) 55 mm dried—brittle; (d) 21 mm wet—plastic; (e) 21 mm dry—brittle.

in the case of water at least, it does penetrate is certain, but whether this is also the case when ethyl-alcohol or fuming sulphuric acid is used remains to be seen.

As we mentioned before it has often been shown that there exist no perfect ideal crystals such as the ones postulated by Born in making

his calculations. Smekal and Zwicky have each proposed theories of the structure of real crystals showing their deviations from such ideal crystals. In all probability the water molecules in the experiments described above penetrated the crystals by going into these imperfect regions whatever their nature may have been.