Finally, in connection with the first-mentioned effect to be expected, the case of carbon black is of interest. The diamagnetic susceptibility of this substance is virtually temperature independent[12] and Warren[13] has found, on the basis of x-ray examination, that it consists of graphite of extremely small particle size.

It is a privilege to thank Professor L. W. McKeehan for many helpful discussions during the progress of this work. I am indebted to Yale University for a Sterling Fellowship during the tenure of which this work was done.

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[12] M. Owen, Ann. d. Physik [4] **37**, 657 (1912).

[13] B. E. Warren, J. Chem. Phys. **2**, 551 (1934).

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Dilatations in Rochelle Salt

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The inverse piezoelectric effect of Rochelle salt has been studied by means of mechanical dilatometers. The dilatation of a crystal along a direction 45° to the *b* and *c* axes and 90° to the *a* axis, caused by an electric field impressed in a given direction along the *a* axis, has been found, in general, not to be the same as the dilatation caused by an equal field impressed in the opposite direction. This indicates a permanent electric polarization within the crystal. A prolonged application of voltage along the *a* axis slowly changes this "permanent" polarization, which gives rise to an inverse piezoelectric fatigue effect, and is associated with the fatigue effect as observed by Valasek. Oscillograms showing the rate of deformation of a Rochelle salt crystal were taken. The forms of these curves, for small distortions of the crystal or small applied fields along the *a* axis, are in approximate agreement with the exponential type as required by the theory of Schulwas-Sorokin and Posnov. The relaxation times varied from zero at the Curie points to a maximum approximately midway between the critical temperatures. The thermal expansion of Rochelle salt along the three crystallographic axes was determined through the upper critical temperature. No discontinuities were observed, but a change in the rate of expansion occurred at the Curie point for the *b* and *c* axes.

It has been shown[1] that there is a one to one relation between the change of lattice constant, as measured by x-rays, and the corresponding change of external dimensions as measured by means of a microscope. The effect of x-rays on a Rochelle salt crystal is not a negligible factor. Besides the ordinary yellow coloring of the crystal, due to the x-rays, there occurs a roughening of its surface. A crystal placed in a dry atmosphere will normally become coated with a white dehydrated salt. This will not form where an intense x-ray beam impinges. Thin aluminum foil fastened to a surface of a crystal will tend to disappear under the action of an x-ray beam. Crystals completely painted with a solution of celluloid in amyl acetate, so as to form an impervious coating, had small amounts of liquid form between the crystal and the coating after long exposure to x-rays. These indicate a gradual disintegration of the crystal.

For x-rays, from a copper target excited at 10 ma and 28 kv, incident on the crystal, there was a change of the lattice spacing, (021) planes, of the order of 10^{-5} cm per cm per minute, the rate of which decreased as the time of exposure increased. The reflected spectrum lines broadened as the time of exposure to the x-rays increased, which indicated increasing imperfections in the crystal structure. It was found inadvisable to use a given crystal after it had been exposed to x-rays of the above intensity more than 20 hours.

As mechanical or optical measurements of strain are equivalent to x-ray measurements, there appeared to be no reason for adhering to the x-ray method if more suitable means could be found.

Dilatometers

The dilatometers constructed are shown in Fig. 1. In type *b* the crystal, *A*, was fastened at one end to a hard rubber support by means of celluloid dissolved in amyl acetate, hard rubber

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[1] Vigness, Phys. Rev. **46**, 255 (1934).

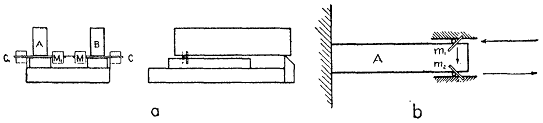

FIG. 1. Dilatometers. A is a material whose coefficient of expansion is being measured. B is a material whose coefficient of expansion is known. M_1, M, m_1, m_2 are mirrors attached to needles. The arrows in Fig. b refer to the path of light. C_1 and C are counterweights.

was used for insulating purposes, the other end of the crystal rolled on two needles as illustrated. Thin sheet rubber was stretched tightly over portions of the surfaces that would otherwise make contact with the needles. This was to insure no slippage and was necessary for all experiments involving a sudden application of an electric field causing a rapid change in length of the crystal.

The second dilatometer (a of Fig. 1) was used only in measuring the thermal expansion of the crystal. Except for the needles and mirrors all parts were constructed of brass. A very similar instrument of quartz was recently described by Clark Williams.[2] The mirrors, M_1 and M, are caused to rotate by the material whose thermal expansion is being studied and by a standard sample, respectively; from the differences in their rotation the differences in their rate of expansion can be determined. Motions or expansions of the rest of the apparatus cancel out. The material used in B was brass, the composition of which was 1/3 zinc and 2/3 copper; the coefficient of expansion[3] for this material is 18.3×10^{-6}. A small lateral scratch was made on both A and B to make a reference line of contact with the knife-edge support. The surfaces upon which the needles roll are made flat and polished. With needles 0.06 cm in diameter and with the distance from the mirrors to the scale 150 cm the amplification per unit length of the crystal, for the type a, is about 5000, for type b there is twice this amplification.

ASYMMETRY OF INVERSE PIEZOELECTRIC RESPONSE

Voigt[4] has shown that for a crystal of the symmetry of Rochelle salt the relations connecting the six strain components and electric field reduce to

$$y_z = d_{14}E_x; \qquad z_x = d_{25}E_y; \qquad x_y = d_{36}E_z;$$

y_z, z_x and x_y are strain components, d_{ij} the piezoelectric moduli and E_x, E_y, E_z the electric field components along the respective axes. For voltage applied along the a axis the change in length per unit length of a crystal, along a direction r, which is perpendicular to the a axis, is

$$\Delta r/r = d_{14}mnE_x,$$

where m and n are the direction cosines of r with respect to the y and z axes.

The above equation shows that the direction of maximum piezoelectric expansion or contraction of a Rochelle salt crystal is in a direction 45° to the b and c axes and 90° to the a axis; crystals were therefore cut with r along this direction. Tin foil electrodes fastened to the crystal by means of Canada balsam xylol solution were used.

That the inverse piezoelectric effect is not the same for the voltage applied in one direction, along the a axis of the crystal, as it is for the same voltage applied in the opposite direction is shown in Fig. 2. A check of the values of strain for corresponding voltages and temperatures shows good agreement between the x-ray and dilatometer measurements.[1] Staub[5] shows a similar lack of symmetry between the change of positive and negative fields along the a axis (actually along a line perpendicular to the (111) planes, which is quite equivalent for purposes of comparison) and the change of the intensity of an x-ray beam reflected from the (111) planes. The

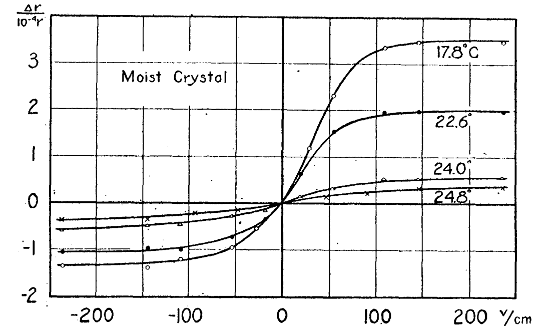

FIG. 2. Nonsymmetrical response of a crystal to voltages impressed in opposite directions along the a axis.

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[2] Clark Williams, Phys. Rev. **46**, 1011 (1934).

[3] International Critical Tables, Vol. 2, page 469.

[4] Voigt, *Lehrbuch der Kristallphysik*, Chapter 8, Leipzig (1910).

[5] Staub, Helv. Phys. Acta **7**, 3 (1934).

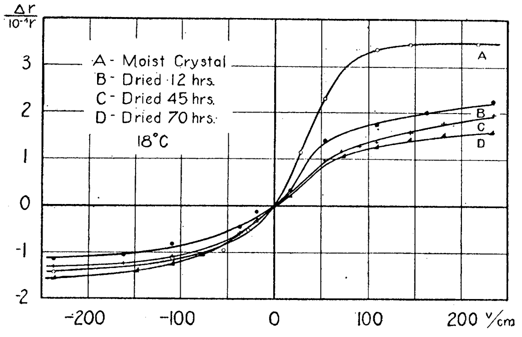

FIG. 3. Inverse piezoelectric displacement as a function of the moisture content of the crystal.

shapes of the curves show that there is not a linear relation between the change in lattice spacing and the change of intensity of the reflected x-ray beam.

The effect of drying a crystal is shown in Fig. 3. The crystal was initially moist and $CaCl_2$ was placed in the crystal chamber for the time indicated. For the dry crystal the inverse piezoelectric strain was quite symmetrical but smaller, on the average, than for the moist crystal.

POLARIZATION AND FATIGUE EFFECT. RELAXATION TIMES

A very prominent characteristic of Rochelle salt crystals is the sluggishness with which the deformation of the crystal takes place when small voltages are applied along the active axis,[5, 6] or when the electric field is removed from this axis. The measurement of the final deformation is made additionally difficult by a gradual creep that may persist for hours.

Rochelle salt crystals about 3.5×1.5×0.5 cm were used in dilatometer type *b* (Fig. 1), the greatest dimension was in a direction 45° to the *b* and *c* axes and the smallest was along the *a* axis. Because of surface conductivity it was not found practicable to keep a saturated solution of Rochelle salt in the chamber containing the crystal, as short circuits would gradually develop between the electrodes of the crystal when voltages were applied for long periods of time. For measurements involving the long applications of voltage $CaCl_2$ was kept in the crystal chamber unless otherwise stated, but in no case were crystals used if they exhibited any physical evidence of dehydration. Kobeko and Kurtschatov[7] state that there is no fatigue effect[8] if liquid (saturated Rochelle salt solution) electrodes are used, and Staub[5] gives the time of relaxation as strongly dependent on the dryness of the crystal. The results given here will correspond to those obtained from a "dry" crystal.

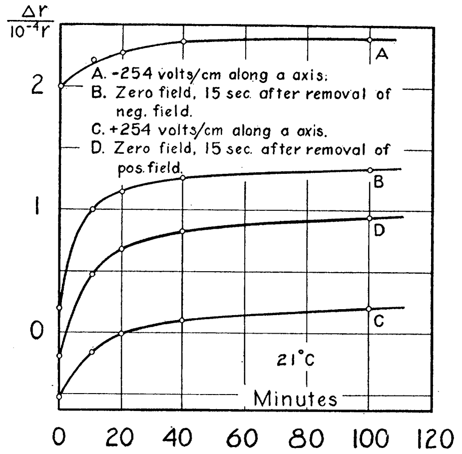

FIG. 4. Gradual polarization of a crystal due to a field of −254 volts per cm along the *a* axis applied continuously, except for short intervals of time necessary to apply a change in voltage and to determine the corresponding change in length of the crystal.

The effect of an application of an electric stress along the *a* axis for a considerable period of time is illustrated in Fig. 4. Previous to this experiment the crystal from which these data were derived had been subjected to an electric stress of +254 volts per cm for several hours. The direction that is called positive is arbitrary. The field was reversed in direction at zero time on the graph, and its effect on the inverse piezoelectric effect, as a function of the time of its application, was studied. It is to be noted that a gradual polarization of the crystal takes place which slowly changes the zero field length of the crystal. The electric field is removed for about 15 seconds for the determination of the length at zero field. This gradual change in the zero field length of the crystal corresponds to a change in a "permanent" polarization of the dielectric. The longer an electric stress is applied in a given

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[6] Schulwas-Sorokin and Posnov, Phys. Rev. **47**, 175 (1935).

[7] Kobeko and Kurtschatov, Zeits. f. Physik **66**, 192 (1930).

[8] By the fatigue effect[9] is meant that as the time of charge of a condenser (Rochelle salt dielectric) is made longer, the quantity discharged in a given time becomes less.

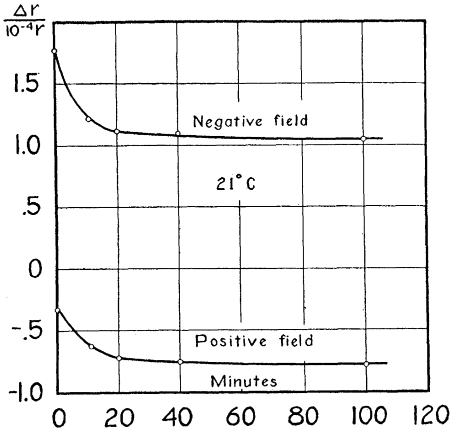

FIG. 5. Fatigue effect. Inverse piezoelectric response due to a negative and positive electric field of 254 volts per cm along the *a* axis. An electric field of −254 volts per cm has been applied for the time indicated on the abscissa, except during the time the voltage was changed in order to determine the inverse piezoelectric response.

direction along the *a* axis, the less will be the deformation caused by a removal of this voltage, and the greater will be the deformation caused by a removal of a field applied a short time (15 seconds) in the opposite direction. This is the fatigue effect[9] expressed in terms of the deformation of the crystal and is illustrated in Figs. 4 and 5.

The rate of change of deformation of a crystal is shown in Fig. 6. In general the rate of relaxation, caused by a removal of the electric field, is less than the rate of deformation caused by electric fields greater than 30 volts per cm. An analysis of curves of these types shows that the sluggishness of the crystal decreases from a maximum, approximately midway between the Curie points, to zero at the Curie points. If a large voltage (greater than 100 volts per cm) is applied along the *a* axis, the crystal deforms very rapidly to a point that appears very near saturation; but a creep may begin after this initial deformation that is caused by a gradual change in the permanent polarization of the crystal. For small values of field (less than 40 volts per cm) it is predicted by Schulwas-Sorokin and Posnov[6] that these curves will be of a simple exponential type.

The first of the oscillograms illustrate very markedly the difference in the inverse piezoelectric response to positive and negative electric fields of equal magnitudes along the *a* axis. The ordinate scale for all the curves of Fig. 6 is the same.

Schulwas-Sorokin and Posnov suppose that the motion of an electric dipole with respect to the lattice can be represented by the equation

$$v\dot{x}_4 + c_{44}x_4 = M_4,$$

where v is a constant of viscosity, c_{44} an elastic constant, x_4 is the shear strain, and M_4 is the applied mechanical stress (shear, corresponding to x_4). There would be a similar equation for an applied electric stress. The electric field is assumed to be zero. The equation is obviously correct only for small values of stress, as it assumes that the final value of displacement is a linear function of the stress. This is approximately true (Fig. 2) if the stress is limited to the equivalent of 40 volts per cm.

For the relaxation times as are represented from data derived from curves of the type shown in Fig. 6, we have assumed that M_4 and the electric field are zero; i.e., we remove the stress, thus

$$v\dot{x}_4 = -c_{44}x_4.$$

The displacement $\Delta r/r$ is proportional to the strain x_4, as the displacement is in a direction 45°

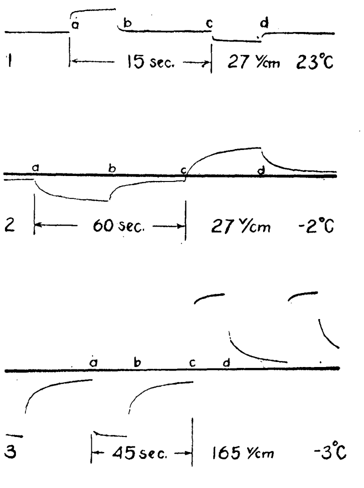

FIG. 6. Oscillograms of the dilatation of a crystal as a function of time. An electric field is applied along the *a* axis at *a*, this field is removed and the crystal faces short circuited at *b*, the field is applied in the opposite direction at *c*, and at *d* the field is again made zero.

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[9] Valasek, Phys. Rev. **24**, 560 (1924).

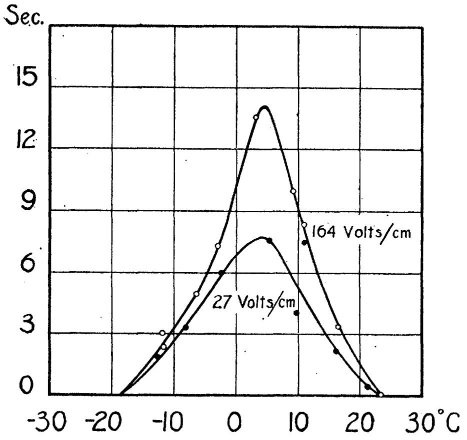

FIG. 7. Relaxation times.

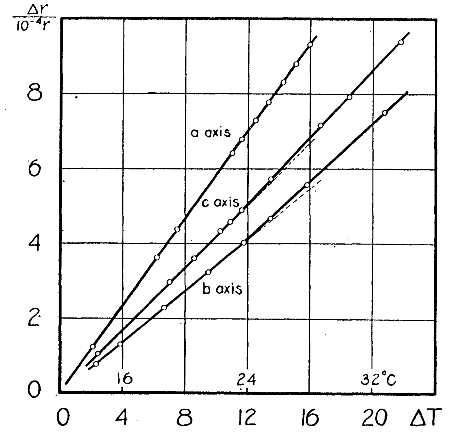

FIG. 8. Thermal expansion of a Rochelle salt crystal along the three crystallographic axes.

to the b and c axes. Therefore in Fig. 7 it is assumed that

$$\Delta r/r = Ke^{-t/\theta},$$

which is a solution of the above equation. The constants have been adjusted to fit the relaxation curves of the type shown in Fig. 6. These curves plotted on semilogarithmic paper appear as fairly straight lines except for the steepest portion of the curves, where the rate of deformation is too great. In Fig. 7 the time constant, $t=\theta$, has been plotted as a function of the temperature. From the experimental data there appear to be three relaxation times of quite different orders of magnitude. A very short time, which makes the crystal suitable for microphones or loudspeakers, a time of the order of a few seconds, which is represented in Fig. 7, and a time in the order of minutes, which is apparent in the fatigue effect and which is illustrated in Figs. 4 and 5.

THERMAL EXPANSION

Valasek[10] has determined the temperature coefficient of expansion along the three crystallographic axes of Rochelle salt and states that no abnormal change in the rate of expansion was observed at the critical points.

The dilatometer, type a Fig. 1, was used to determine the rate of expansion through the upper critical temperature. No elaborate precautions were made in order that the absolute magnitude of the coefficient of expansion might be determined, though the values should be correct within two percent. Temperature was measured by means of a thermometer placed in the crystal chamber. It was found necessary to wait approximately one hour after the thermometer had reached a steady value before a measurement of the expansion of the crystal could be taken. This meant that the time necessary for the apparatus to come to an equilibrium temperature was about 6 hours.

From data of the type shown in Fig. 8 the coefficients of expansion along the three principal axes are found to be

$a = 58.3\times10^{-6}$ From +12°C to +35°C
$b = 35.5\times10^{-6}$ From +12°C to +24°C
$= 39.7\times10^{-6}$ From +24°C to +35°C
$c = 42.1\times10^{-6}$ From +14°C to +24°C
$= 43.6\times10^{-6}$ From +24°C to +34°C.

This shows a change in the rate of expansion along the b and c axes at the upper Curie point. The anomaly of the specific heat at the upper critical temperature[11, 12] leads one to expect a corresponding anomaly in the coefficient of expansion.[12]

In conclusion I wish to express my sincere appreciation to Dr. Joseph Valasek, under whom I have been privileged to work, and Dr. Henry A. Erikson, chairman of the department of physics, for their helpful advice and for their assistance in obtaining the materials necessary for this work.

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[10] Valasek, Phys. Rev. **20**, 639 (1922).

[11] Kobeko and Nelidow, Physik. Zeits. d. Sowjetunion **1**, 382 (1932).

[12] Rusterholz, Helv. Phys. Acta **8**, 39 (1935).