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The Effect of Hydrostatic Pressure on the Susceptibility of Rochelle Salt

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The electric susceptibility of Rochelle salt has been studied as a function of both temperature and hydrostatic pressure. Both the upper and lower critical temperatures are altered by the pressure, but the pressure coefficients for the alterations are different in the two cases. An attempt is made to correlate the experiment with statistical mechanical theory, but it is found that the theory is not sufficiently explicit to provide a quantitative explanation of the results.

THE anomalous variation of the electric susceptibility of Rochelle salt in the temperature range from −40°C to +40°C is so well known as to require little comment. Suffice it to say that as the temperature is increased from −40°, the dielectric constant rises to an effectively infinite value at −18°, remains infinite to +24°, then falls rapidly to normal values. This phenomenon has been exhaustively investigated by Mueller[1] and others. The behavior is thus characterized by two critical temperatures, −18° and +23.7°, the explanation of which has been semi-quantitatively discussed by Fowler.[2] According to his theory, the effects are due to polar molecules within the crystal lattice: the lower critical temperature marks the onset of free dipole rotation, while the upper marks the point at which thermal agitation prevents universal alignment of the dipoles.

In the present paper, we measure the susceptibility as a function of temperature and hydrostatic pressure to 10,000 atmospheres over the temperature range −20° to +60°. The pressure is found to produce a marked alteration of the critical temperatures; this effect is studied to an accuracy of ±0.1°C and ±10 kg/cm². The apparatus is simple and conventional. Pressure is developed within a steel cylinder whose inside dimensions are roughly $\frac{5}{8}''\times 8''$. The equipment for producing the pressure has been exhaustively described by Bridgman.[3] The steel cylinder containing the specimen was surrounded by an oil bath whose temperature could be varied at will. The liquid used for developing the pressure was petroleum ether.

Tinfoil electrodes were cemented to the proper faces of the Rochelle salt crystals, and one lead was brought out of the pressure chamber through an insulated plug; the other lead was grounded. The crystal was freely suspended by its leads, which were as tenuous as possible, in order to eliminate mechanical constraints. The capacity from the insulated lead to ground was measured by means of a General Radio Company type 216 capacity bridge, used in a substitution method. The voltage on the crystal was controlled at 2.0 r.m.s. volts, 1000 cycles. No bias potential was used. Stray capacity effects were eliminated by a blank run made on a piece of glass similar in size and shape to the crystals used. No change in capacity with pressure was detected in this case; accordingly the correction amounted to a constant capacity to ground, which was subtracted from the capacity as measured in order to compute the true capacity of the crystal.

The crystals were furnished through the kindness of the Brush Development Company. Three crystals were used, whose dimensions were:

I. $0.424\times 0.970\times 3.65$ centimeters,
II. $0.356\times 0.869\times 2.27$ centimeters,
III. $0.313\times 0.904\times 2.54$ centimeters.

In all cases the shortest dimension lay along the "a" axis, and the electrodes were, of course, attached to the large faces. No attempt was made to study the effect of pressure on the normal values of the susceptibility which one obtains at right angles to this axis. The crystals are extremely fragile, and unfortunately the data from all three specimens had to be combined in order to get a complete picture of the behavior. It was

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[1] Hans Mueller, Phys. Rev. **47**, 175 (1935).

[2] R. H. Fowler, *Statistical Mechanics*, second edition (Cambridge University Press, 1936) p. 816 *et seq.*

[3] P. W. Bridgman, *The Physics of High Pressure* (Bell and Sons, 1931).

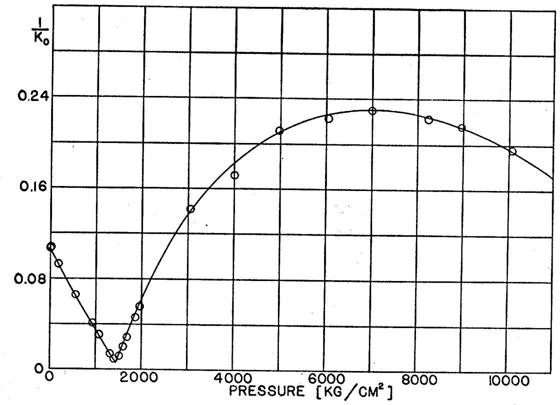

FIG. 1. The reciprocal susceptibility of Rochelle salt as a function of pressure at 40°C.

found that a relatively small but sudden change in pressure would almost invariably crack the crystal.

The absolute accuracy of the values obtained for the susceptibility is not high, partly because of the small specimens, partly because of the relatively large corrections for stray capacity, necessitated by the proximity of the specimen to the steel cylinder. Where it is possible to compare the results obtained with those of Mueller, our susceptibilities agree with his to better than 5 percent. The points observed, however, fell upon curves sufficiently smooth to enable one to estimate the position of the critical points to the accuracy of the temperature and pressure measurements. The runs were made at constant temperature, and the pressure was varied in steps of 1000 atmospheres, except where additional points seemed desirable. Considerable time was required to establish satisfactory thermal equilibrium after a change in pressure, particularly in the regions where the dielectric constant was extremely sensitive to small thermal changes.

Figure 1 shows the data obtained in the run at 40.0°. Following Mueller, the reciprocal susceptibility, $1/k_0$, is plotted. Of course the susceptibility in the critical region (above 1500 atmos. in this particular case) is a somewhat arbitrary quantity, since here the dielectric constant is effectively infinite, the material showing hysteresis and the other properties characteristic of the "ferromagnetic" state. On the other hand, outside the critical region, the properties are quite well defined, the observed dielectric constant being independent of both frequency and field strength. Fig. 2 shows the family of curves of which Fig. 1 shows only a single example. It will be noted that

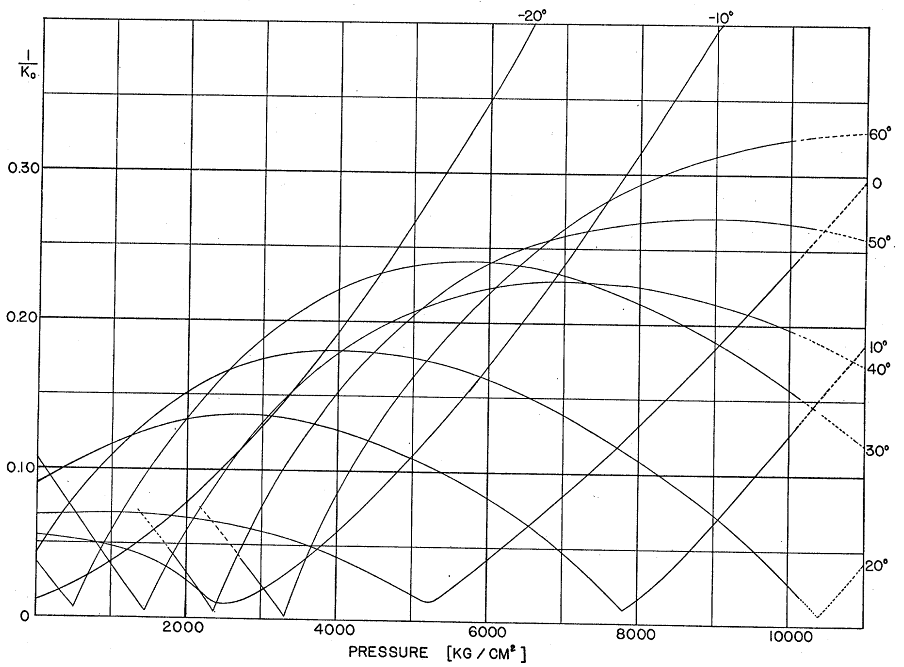

FIG. 2. The reciprocal susceptibility of Rochelle salt as a function of pressure for temperatures from −20°C to +60°C.

above 20°, the lower critical temperature occurs at too high a pressure to be observed. While it would have been possible to carry the measurements to a somewhat higher pressure, the general behavior of the critical points is so well illustrated in the low pressure range that it seemed hardly worth while. It is of some interest to note that as the temperature is increased, the height of the maximum to which the observed dielectric constant rises becomes larger and larger, i.e. $1/k_0$ approaches zero more and more closely. A value of k_0 of 80 was actually observed at 60°, and only the limitation of the bridge prevented the observation of an even larger apparent susceptibility.

No attempt has been made to "fair" the curves of Fig. 2 by plotting the data in the $1/k_0-T$ plane. Close examination of Fig. 2 will reveal that irregularities would appear in such a plot; these are due to the fact that the several specimens used did not give perfectly concordant results. Nevertheless the curves are sufficiently accurate to allow one to determine the position of the critical points with some confidence.

Figure 3 shows the loci of the critical points in the $T-P$ plane. The loci are approximately straight lines, and are adequately represented by the equations

$$\begin{aligned} T_u &= 1.073\times10^{-2}\,p+24.5, \\ T_l &= 3.769\times10^{-3}\,p-19.4. \end{aligned} \tag{1}$$

The critical temperatures at one atmosphere do not agree with Mueller's as well as one would desire, but the discrepancy is doubtless to be traced to the definition of the critical temperature. For the purposes of the present paper it is assumed to lie at the break in the curves shown in Fig. 2.

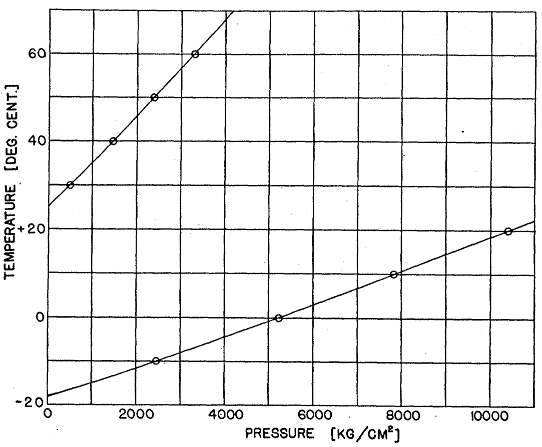

FIG. 3. The critical temperatures of Rochelle salt as a function of pressure.

Figure 2 shows clearly that a discontinuity exists in the temperature and pressure derivatives of the reciprocal susceptibility. It is a matter of pure geometry to deduce an analog of the Clausius-Clapeyron equation, *viz.*

$$\frac{dp}{dT}=-\frac{[(\partial/\partial T)(1/k_0)]_1-[(\partial/\partial T)(1/k_0)]_2}{[(\partial/\partial p)(1/k_0)]_1-[(\partial/\partial p)(1/k_0)]_2}, \tag{2}$$

where the subscripts denote values of the derivatives taken on either side of the discontinuity, and dp/dT gives the slope of the locus of the discontinuity in the $T-P$ plane. For our purposes it is of more interest to extend the straight parts of the curves of Fig. 2 until they intersect the p-axis. We then note that

$$\frac{dT}{dp}=-\frac{(\partial/\partial p)(1/k_0)}{(\partial/\partial T)(1/k_0)}, \tag{3}$$

where now the partial derivatives indicate the slope of the lines where they intersect the axis, and where dT/dp gives the slope of the locus of these intersections, which is nearly the same as what we have plotted in Fig. 3. The latter formula permits a correlation between the present results and those of Mueller. For the upper critical temperature our data yield (extrapolating to 1 atmos.) $(\partial/\partial p)(1/k_0)=-6.1\times10^{-5}$, while Mueller's results for the same temperature and pressure give $(\partial/\partial T)(1/k_0)=5.6\times10^{-3}$. Thus $(dT/dp)_u=1.09\times10^{-2}$. By a similar calculation for the lower temperature, one finds $(dT/dp)_l=2.5\times10^{-3}$. The agreement with Eq. (1) is most satisfactory for the upper critical temperature. In the other case one must remember that the discontinuity is not well marked, and that the extrapolation of both our data and Mueller's to a zero value of $1/k_0$ is far from a precise mathematical process.

The alteration observed in the critical temperatures is to be attributed in some way to the distortion of the lattice under pressure. Most methods of straining the crystal introduce mechanical constraints which, as Mueller has pointed out, completely remove the dielectric anomaly. In applying hydrostatic pressure, however, the only constraint introduced is the viscous reaction of the pressure medium, which at most would be expected to produce a gradual diminution of the anomalous behavior as the liquid becomes more viscous with pressure. Hence the effect of constraints can hardly be cited to account for the phenomenon observed.

Turning to Fowler's theory, we find a formula for the dielectric constant

$$\eta = 1 + \frac{4\pi}{\gamma}\frac{1-\beta T/2T_1}{(T_1/2\beta T_u)-1+(\beta T/2T_1)}, \tag{4}$$

where the critical temperatures are

$$T_1 = \beta W_0/k \quad \text{and} \quad T_u = \gamma n\mu^2/3k.$$

Here W_0 is the energy of the molecular field in the absence of dipole rotation, β is a parameter, roughly equal to $\frac{1}{2}$, which serves to distinguish between rotating and nonrotating dipoles, n is the number of dipoles in unit volume, μ is the dipole strength, γ is the so-called "Lorentz factor" appearing in the formula $F' = F + \gamma P$ which gives the effective field in terms of the applied field and the polarization, and k is Boltzmann's constant. The lower critical temperature is determined by the onset of free dipole rotation; the upper by strict analogy with the Weiss-Langevin theory of ferromagnetism.

As the lattice is strained by pressure, we expect that, to a rough approximation, the expressions determining the critical temperatures will depend in some way upon the volume. If we assume that these expressions are proportional to some power of the volume, we arrive at the conclusion

$$TV^\delta = \text{constant}, \tag{5}$$

where T is either critical temperature, and δ may be expected to have different values in the two cases. The data obtained permit the calculation of the exponent δ for both cases on the assumption that the curves of Fig. 3 are those described by Eq. (5). For since the compressibility and thermal expansion are known at atmospheric pressure, we may easily compute the slopes of the curves defined by Eq. (5) where they intersect the T axis. The slopes are

$$dT/dP = T\delta\kappa/(1+T\delta\alpha),$$

α and κ being the volume coefficient of thermal expansion and the compressibility, respectively. Bridgman[4] gives the compressibility as 60×10^{-7} kg/cm^2, and the thermal expansion as given in the *International Critical Tables* is 143×10^{-6}. Taking $T_1 = 254°$ and $T_u = 297°$ we, find

$$\delta_1 = 2.7 \quad \text{and} \quad \delta_u = 8.4.$$

Thus at the lower critical temperature we conclude that

$$\beta W_0 \sim V^{-2.7}.$$

Such variation of βW_0 is at least within striking distance of what one would expect, for β is a loosely defined quantity, and might change somewhat as the lattice is distorted, while W_0 would fall off as the third power of the distance for a linear array of dipoles.

At the upper critical temperature, on the other hand,

$$\gamma n\mu^2 \sim V^{-8.4}.$$

In this case, $n \sim V^{-1}$, but even so the conclusion seems inevitable that $\gamma\mu^2 \sim V^{-7.4}$. It is to be noted that both the compressibility and the thermal expansion of Rochelle salt are strongly aeolotropic, but even so, it is difficult to see how $\gamma\mu^2$ can vary so remarkably with changes in volume.

The somewhat crude application of Fowler's theory as outlined above indicates that no really satisfactory quantitative explanation of the effects observed can be given until more exact data are available on the crystal structure and the arrangement of the dipoles within the lattice. In particular a theory which will permit accurate calculation of the factor, γ, seems highly desirable. While nothing in the experiment contradicts any part of the theory, it must be admitted that the theory does very little in the way of reproducing the experimental facts.

In conclusion it is a pleasure to acknowledge the counsel of Professor Bridgman in carrying out the experimental part of the work, and of Dr. John Bardeen in the discussion of the theoretical aspects of the problem.

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[4] P. W. Bridgman, Proc. Am. Acad. **64**, 51 (1929).