The Elastic, Dielectric and Piezoelectric Constants of Heavy-Water Rochelle Salt[1]

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(Received October 30, 1939)

Crystallization of Rochelle salt from heavy water raises the upper Curie point of the material by 11°C and lowers the lower point by 5°C, but leaves the other properties substantially unchanged.

THE unusual behavior of Rochelle salt in exhibiting an extraordinarily high dielectric susceptibility for fields along the *a* axis between two critical temperatures (Curie points) has been the subject of numerous investigations.[2] This paper presents the results of dynamic measurements of the elastic, electric and piezoelectric constants of Rochelle salt crystallized from heavy water (deuterium oxide).

I. Preparation of Crystals and Measurement of Low Frequency Dielectric Constant

To prepare the samples for measurement, 65 grams of dehydrated Rochelle salt, which had been kept at 100°C for eight hours in vacuum and then at room temperature over dehydrite until the residue reached constant weight, were dissolved in 100 grams of 99.5 percent heavy water. The resulting solution is somewhat supersaturated at ordinary temperatures. Crystal plates were then grown one at a time from this solution at room temperature in a square cell fitted with horizontal glass plates spaced about 100 mils by glass spacers, seeded with ordinary Rochelle salt seeds of the desired orientation.

Two such plates perpendicular to the *a* axis, about 2 square centimeters in area, were used for measurements of dielectric constant at 1000 cycles per second. From these plates the surface irregularities were polished with carborundum and machine oil, the resulting powdery surface was dissolved off in the growing solution, warmed to unsaturation, and a fresh surface was crystallized on for about five minutes. Electrodes of tin foil were affixed with petrolatum and the plates were freely suspended in the temperature-controlled glass tubes. Measurements were made with an oscillator and impedance bridge, at a peak voltage gradient of approximately 35 volts per centimeter. The resulting measurements are shown in Fig. 1, where similar measurements on a similarly prepared plate of ordinary Rochelle salt are shown for comparison. The substitution of heavy water for ordinary water in the crystal has raised the upper Curie point by about 11°C and has lowered the lower point by about 5°C.

The upper Curie points of crystals grown from solution in 50 percent and 20 percent heavy water were found to lie at 26.6°C and about 24°C, respectively.

II. Measurements of the Dynamic Properties of Heavy-Water Rochelle Salt at High Frequencies

In order to measure dynamically the dielectric and piezoelectric properties of an *a* or X-cut heavy-water Rochelle salt crystal, a bar was cut with its length at 45° from the *Y* and *Z* axes and having the dimensions, length = 20.62 mm, width = 4.24 mm, thickness = 2.01 mm. These dimensions were chosen so that no secondary resonances appeared near the main one. The crystal was gold-plated by a modified evaporation process, and its resonance and antiresonance frequencies were measured as a function of temperature. These frequencies plotted

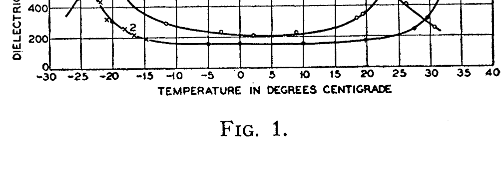

FIG. 1.

[1] A preliminary description of this work is published in a Letter to the Editor in the August 15, 1939 issue of the *Physical Review*.
[2] H. Mueller, Phys. Rev. **47**, 175 (1935).

for a crystal one centimeter long are shown on Fig. 2 by the curves A and B. Curve C shows a measurement of the resonant frequency of the same crystal (with the plating removed) placed in an air-gap holder with a large air-gap.

The relation between the resonant and anti-resonant frequencies and the electromechanical coupling factor k has been discussed at length in a former paper.[3] It is there shown that the electromechanical coupling factor k defined by the equation

$$k=\frac{d_{14}}{2}\left(\frac{4\pi}{Ks_{22}'}\right)^{\frac{1}{2}} \tag{1}$$

determines the ratios of the resonant and anti-resonant frequencies to the natural mechanical resonant frequency (measured as usual without plating on the crystal) according to the curves shown on Fig. 3. In Eq. (1), d_{14}, K and s_{22}' are the open circuit constants, i.e., d_{14} is the piezoelectric constant measured with a high impedance electrical instrument, K is the dielectric constant of the crystal clamped, while s_{22}' is the inverse of Young's modulus measured without plating on the crystal.[4]

Comparing the curves of Figs. 2 and 3, the electromechanical coupling k is easily evaluated and is shown on Fig. 4. To determine the piezoelectric constant d_{14}, we need to know the elastic constant s_{22}' and the dielectric constant K of the clamped crystal. The elastic constant of the crystal free from plating can be determined from the measured frequency of the crystal in an air-gap holder (curve C of Fig. 2) by using the equation

$$f_m=\frac{1}{2l}\left(\frac{1}{\rho s_{22}'}\right)^{\frac{1}{2}}, \tag{2}$$

where l is the length of the crystal and ρ the density. By pycnometer methods Mr. W. L. Bond finds the density of heavy-water Rochelle salt to be

$$\rho=1.830\pm0.003. \tag{3}$$

Hence, the value of s_{22}' as a function of temperature can be calculated from Eq. (2) and is shown as curve s_{22}' of Fig. 4. To determine the dielectric constant K, crystals were cut so small that they had no resonances in the frequency range of interest and their capacitances were measured as a function of the temperature. The dielectric constant K_F of the crystal free to move is shown on Fig. 5. These measurements are at a considerably higher frequency than those of Fig. 1 and show a lower value. The clamped dielectric constant K has been shown[5] to be

$$K=K_F/(1-k^2). \tag{4}$$

Hence, from Fig. 5 and curve k, Fig. 4, the dielectric constant K can be evaluated and it is shown as curve K of Fig. 4. Since we have evaluated k, s_{22}' and K, the value of d_{14}, the piezoelectric constant, can be evaluated and is shown as curve d_{14} of Fig. 6. In general between the Curie points, d_{14} has a lower value for dynamic measurements than ordinary Rochelle salt, but above the upper Curie point it has a higher value.

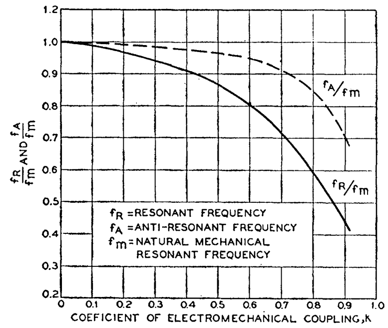

FIG. 3.

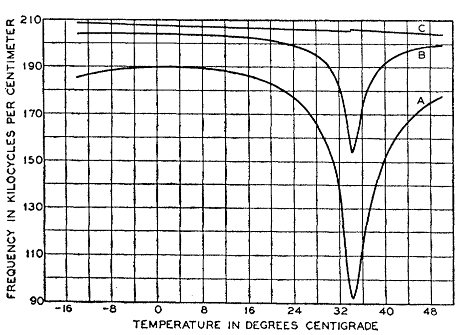

FIG. 2.

[3] W. P. Mason, Phys. Rev. **55**, 775 (1939).

[4] It should be pointed out that to agree with the definition given by Voigt, the constant d_{14} should be measured with a low impedance electrical instrument while the elastic constant s_{22}' should be measured with plating on the crystal and this short-circuited. Both quantities as defined by Voigt can be obtained from those shown on Figs. 4 and 6 by dividing d_{14} and s_{22}', respectively, by $(1-k^2)$.

[5] See reference 3, Eq. (55).

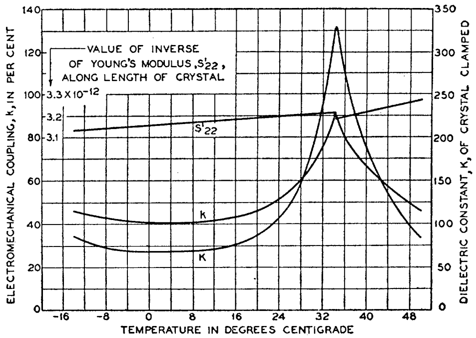

FIG. 4.

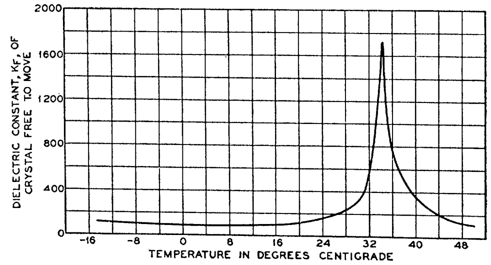

FIG. 5.

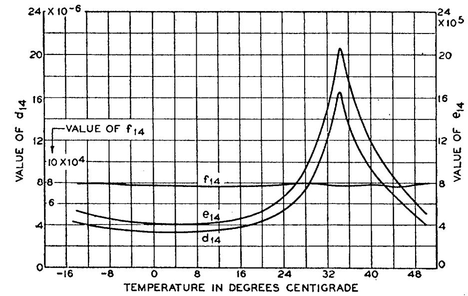

FIG. 6.

Another piezoelectric constant, e_{14}, is often used, which is related to d_{14} by the equation

$$e_{14}=d_{14}/s_{44}, \tag{5}$$

where s_{44} is the shear elastic constant. This was measured for a heavy-water crystal and found to be nearly the same as for ordinary Rochelle salt, namely

$$s_{44}=7.98\times10^{-12}. \tag{6}$$

The value of e_{14} can then be determined and is shown on Fig. 6 by curve e_{14}. It was shown in the paper referred to above that another piezoelectric constant, f_{14}, relating the piezoelectric stress and the applied charge density, was more closely related to the usually measured constants than either d_{14} or e_{14} and furthermore, was nearly a constant for all temperature and frequency conditions. The value of f_{14} is

$$f_{14}=4\pi e_{14}/K \tag{7}$$

and is plotted as curve f_{14} of Fig. 6. The value 7.8×10^4 is nearly the same as for ordinary Rochelle salt. This indicates that the piezoelectric stress caused by the attraction between the bound charges in the material and the applied charge is the same for both Rochelle salts and that their difference in behavior is caused by the difference in the clamped dielectric constants of the two materials.

The difference in the clamped dielectric constant, in particular the lower value between the two Curie points, is accounted for by the wider separation of the Curie points.

Some measurements were also made on Y-cut and Z-cut crystal plates (perpendicular to the b and c axes, respectively) in order to determine the other two piezoelectric constants. By cutting crystals at 45° from the other crystallographic axes and repeating the process described above, the following constants were measured:

Y-Cut Crystals at 30°C

k	K_F	K	s_{11}'	d_{25}	e_{25}	f_{25}
0.305	18.0	16.3	9.93×10^{-12}	220×10^{-8}	6.67×10^4	5.14×10^4

This crystal has a somewhat larger piezoelectric effect than the corresponding ordinary Rochelle salt crystal. Over a temperature range the piezoelectric constant d_{25} increases slightly with temperature.

The measurements for the Z-cut crystal are:

Z-Cut Crystal at 30°C

k	K	s_{11}'	d_{36}	e_{36}	f_{36}
0.107	10.4	4.2×10^{-12}	40.1×10^{-8}	3.97×10^4	4.80×10^4

The constants are very similar to those for an ordinary Z-cut Rochelle salt crystal.

The authors are indebted to Drs. S. O. Morgan and G. K. Teal for suggesting this work, to Dr. G. T. Kohman for the low frequency dielectric constant measurements, and to Mr. W. L. Bond for his measurements of density.