Caris for assisting with the measurements, and the Perkin-Elmer Corporation for graciously allowing us to use their 100-milliwatt helium-neon gas laser.

---

*Contribution No. 1022.

[1] J. Frenkel, Phys. Rev. 37, 17, 1276 (1931).

[2] See R. S. Knox, Theory of Excitons (Academic Press, Inc., New York, 1963), Chap. IV.

[3] O. Simpson, Proc. Roy. Soc. (London) A238, 402 (1956).

[4] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters 10, 400 (1963).

[5] P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, J. Chem. Phys. 39, 1127 (1963).

[6] A Ronchi ruling is a grating with alternating opaque and transparent strips of equal width. The opaque strips in our rulings consisted of a 1000Å thick deposit on a glass substrate according to the manufacturer, Max Levy Corporation, Philadelphia, Pennsylvania.

[7] I. Nakada, J. Phys. Soc. (Japan) 17, 113 (1962).

[8] J. Jortner, S. Choi, J. L. Katz, and S. A. Rice, Phys. Rev. Letters 11, 323 (1963).

PARAELECTRICITY AND FERROELECTRICITY DUE TO HYDROXYL IONS IN ALKALI HALIDES; PARAELECTRIC COOLING

W. Känzig
Swiss Federal Institute of Technology, Zürich, Switzerland

and

H. R. Hart, Jr., and S. Roberts
General Electric Research Laboratory, Schenectady, New York

(Received 28 September 1964)

In alkali halide crystals, hydroxl ions can be substituted for halide ions. Concentrations up to the order of 10^{19} cm^{-3} can be achieved by adding hydroxide to the melt. Kuhn and Lüty[1] have recently observed by means of optical techniques that the hydroxyl ions can be aligned by an electric field at low temperatures. They concluded that the electric dipole moment has six equilibrium orientations, namely along the [100] axes of the crystal. The externally applied electric field lifts the sixfold orientational degeneracy. The Boltzmann distribution thus corresponds to an alignment of the $(\mathrm{OH})^-$ dipoles. Assuming a Lorentz internal field, Kuhn and Lüty were able to determine the dipole moment as $p_0 = 1.82\times10^{-18}$ cgs units. (Note that their determination does not involve a measurement of the concentration.)

Independently we have studied the dielectric behavior of KCl crystals doped with various concentrations of KOH, in the temperature range from 0.29°K to 90°K at 10^2, 10^3, and 10^4 cps. Whereas the dielectric constant of a zone-refined alkali halide crystal is temperature independent below 15°K, the dielectric constant of hydroxyl-doped KCl increases with decreasing temperature,[2] passes through a maximum, and then decreases again (Fig. 1). The temperature at which the peak occurs is almost independent of the frequency, and it increases with increasing $(\mathrm{OH})^-$ concentration, indicating that the decrease on the low-temperature side is due to interaction between the dipoles and not to relaxation. Presumably, a kind of a ferroelectric state results. The measurement of the dielectric losses seems to support this view. The loss angle δ has a maximum at a temperature which is lower than the temperature of the peak of the dielectric constant, and it does not depend significantly upon the frequency (Fig. 2). This behavior is typical for a ferroelectric.

The dielectric constant on the high-temperature side of the peak was analyzed on the basis of the Clausius-Mossotti expression, according to which the polarizability $N_d\alpha_d$ of the dipole system is given by

$$\tfrac{4}{3}\pi N_d\alpha_d = \frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_m-1}{\epsilon_m+2}.$$

Here N_d is the number of dipoles per cm^3 and α_d is the polarizability attributed to a dipole. The dielectric constants of the doped sample and of a pure (zone-refined) sample are designated by ϵ and ϵ_m, respectively. The quantity $N_d\alpha_d$ was found to be inversely proportional to the temperature at temperatures sufficiently above the peaks of the dielectric constant. For a classical permanent dipole one expects $N_d\alpha_d = N_d p_0^2/3kT$. Using the dipole moment p_0 of Kuhn and Lüty,[1] the concentration N_d can thus be determined from the dielectric behavior. It

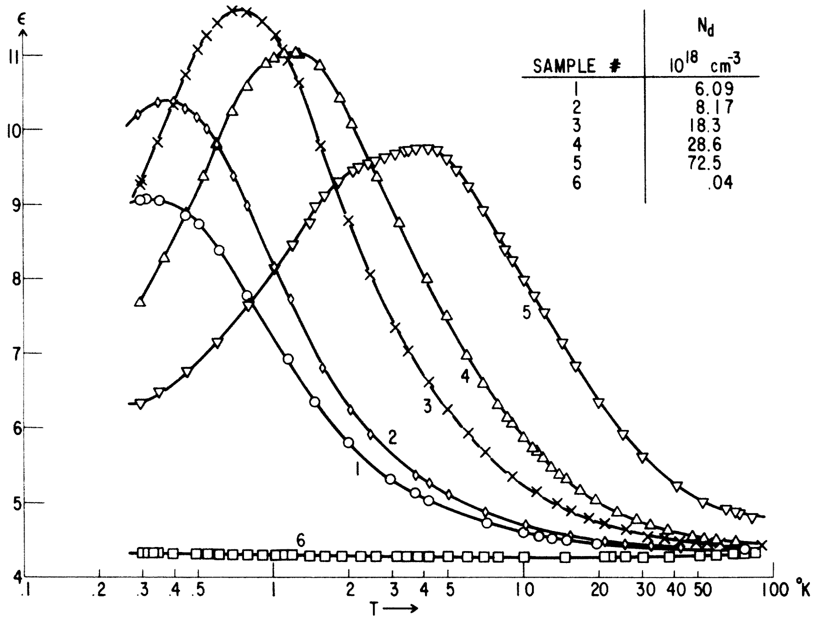

FIG. 1. Temperature dependence of dielectric constant of KCl crystals containing different concentrations N_d of hydroxyl dipoles (measured at 10^3 cps and 15 V/cm).

is interesting to compare this number with the $(OH)^-$ concentration N_{chem} obtained from *p*H measurements. For samples with a very low content of divalent impurities, the agreement is within the experimental error of the chemical concentration measurement (±20%). With increasing content of divalent impurities [such as Ba^{++} and $(CO_3)^{--}$], the ratio N_d/N_{chem} drops, indicating that the random electric fields due to these impurities immobilize a fraction of the $(OH)^-$ dipoles in the temperature range considered (see Table I).

Using the concentration N_d of the "mobile" dipoles as determined from the dielectric measurements and the known dipole moment p_0, a Curie temperature T_c can be calculated on the

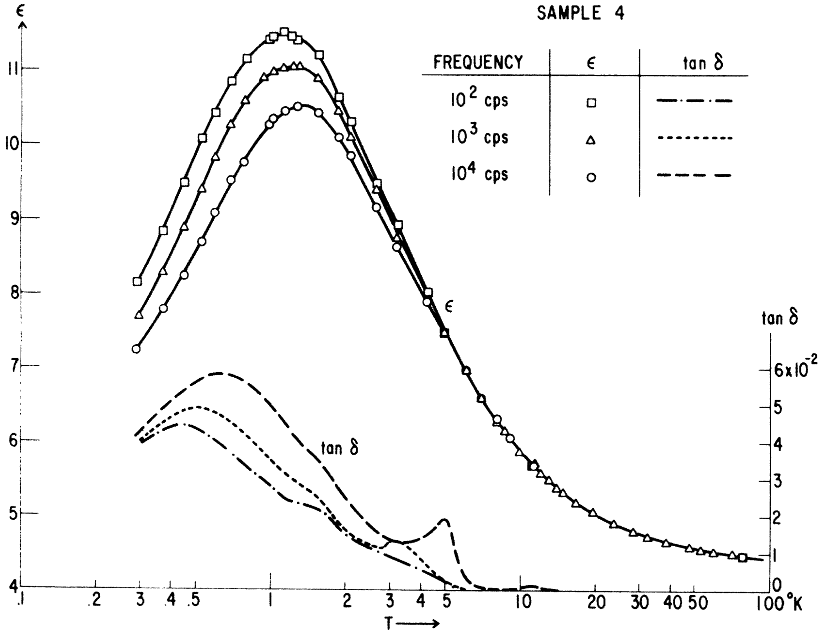

FIG. 2. Dielectric constant and loss angle of sample No. 4 for various frequencies.

Table I. Characteristics of the various samples. The sample numbers correspond with Fig. 1.

Sample No.	Concentration of $(OH)^-$ (10^{18} cm^{-3}) Chemical N_{chem}	Dielectric N_d	Carbonate content (arbitrary units)	Calculated Curie temperature (°K)	Temperature at maximum ϵ
1	5	6.09	<0.001	0.432	0.32
2	11	8.17	0.03	0.580	0.385
3	67	18.3	1.9	1.30	0.74
4	36	28.6	0.13	2.03	1.2
5[a]	140	72.5	0.8	5.15	4
6	undoped (Harshaw)	0.04	···	0.003	<0.29

[a]This sample was doped with $BaCl_2$.

basis of the Clausius-Mossotti approximation. One finds

$$T_c = (4\pi/27)N_d p_0^2(\epsilon_m + 2)/k.$$

There is a systematic correlation between the calculated Curie temperature T_c and the temperature corresponding to the peak of ϵ (Table I). The fact that the calculated Curie temperatures are somewhat higher indicates that the decrease of the dielectric constant toward low temperatures is not due to the electric fields arising from impurities and other imperfections.[3] In contrast to conventional ferroelectrics the hydroxyl-doped alkali halides do not exhibit a sharp Curie point. We believe that this is due to the randomness of the distribution of the dipoles. The width of the transition region on a logarithmic temperature scale is almost independent of the $(OH)^-$ concentration and presumably reflects a property of a random array of interacting dipoles (see Fig. 1; note that sample No. 5 is not typical, since a mole fraction of 2×10^{-4} $BaCl_2$ had been added to the melt in order to study the influence of divalent impurities).

In the paraelectric region the $(OH)^-$-doped alkali halide crystals might be useful for cooling.[1] The relaxation frequency in this region is far above the audio range and seems to be dominated by one-phonon processes.[4] However, the cooperative effects introduce in the vicinity of the Curie temperature a low-frequency component which manifests itself in the audio-frequency range (Fig. 2). Cooling experiments were carried out in the paraelectric region with sample No. 2. The temperature changes observed upon changing the externally applied electric field are reversible and agree with those calculated.

In very dilute ideal samples the zero-field splitting should correspond to the energy difference between the totally symmetric ground state Γ_1 of the proton in the six-well potential and the less symmetric states Γ_{12} and Γ_{15}. A detailed investigation of sample 6 ($N_d = 4\times10^{16}$ cm^{-3}, $T_c = 3\times10^{-3}$ °K) showed that the zero-field splitting is below 0.3°K. Experiments at still lower temperatures are underway.

The authors are indebted to Professor H. Gränicher and D. Itschner for dielectric measurements at the early stages of this work, to Dr. J. S. Nadeau, Dr. W. E. Bron, and Dr. R. W. Dreyfus for supplying samples, and to Dr. R. M. Chrenko and Dr. R. S. McDonald for infrared and ultraviolet analysis of the crystals. Stimulating discussions with Professor M. H. Cohen and Professor Harvey Brooks and with Dr. F. S. Ham are gratefully acknowledged.

---

[1] U. Kuhn and F. Lüty, to be published.

[2] This increase has also been observed by M. C. Robinson and A. C. Hollis Hallett, Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964 (to be published).

[3] Werner Känzig, in Solid State Physics, edited by Frederick Seitz and David Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 1.

[4] Measurements of the dielectric dispersion are in progress at the Swiss Federal Institute of Technology in Zürich.