Dielectric Loss of Potassium Chloride*

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The dipolar contribution to the high-temperature dielectric loss of potassium chloride is shown to be unaffected by additions of strontium chloride that cause major changes in the frequency-independent volume conductivity, the cation vacancy concentration, and the anion vacancy concentration. The observations provide additional strong evidence that the dipoles responsible for the loss are vacancy pairs, since their concentration is not dependent on the strontium content of the crystal.

INTRODUCTION

A DISPERSION of the dielectric constant of pure potassium chloride exists at high temperatures in the frequency range between one and ten megacycles.[1] This dispersion can be described by the Debye theory with a single dipole relaxation time.[2] Since the experimental dipole heat of formation and activation energy for reorientation agree with the theoretical properties of vacancy pairs, these imperfections may be the cause of the observed dispersion. It is plausible to assume that a vacancy pair, a cation vacancy and an anion vacancy occupying nearest-neighbor sites in the crystal, has a dipole moment of magnitude $\mu = ea$, where e is the electronic charge and a is the cation-anion nearest-neighbor distance. With this assumption, however, the data yield a concentration of dipoles that is about fifty times larger than the expected concentration of vacancy pairs.

The experiments which are reported in the present paper were designed to test the possibility that the observed dispersion is an unforeseen effect caused by the isolated cation and anion vacancies, or Schottky defects, that are known to be present in the crystals. The concentration of isolated cation vacancies can be increased and the concentration of isolated anion vacancies can be decreased by the addition of a divalent cation like Sr^{++} to potassium chloride.[3] The concentration of vacancy pairs should not be affected by such an impurity.[4] It should be noted, however, that the product of the isolated cation and anion vacancy concentrations is also independent of the concentration of divalent cation impurity.[3] A comparison of the characteristics of the dispersion in KCl and KCl−SrCl₂ crystals should, nevertheless, significantly limit the possible explanations of the effect.

EXPERIMENTAL PROCEDURE

Single crystals were grown by the Kyropoulos method in air. Reagent-grade potassium chloride and strontium

chloride powder was used to form the melt which was contained in a platinum crucible. Measurements were also made on single crystals obtained from the Harshaw Chemical Company.

Measurements were made on crystals whose faces had dimensions of approximately 5×5 mm. Data were obtained from two specimens of crystal I with thicknesses of 1.15 and 2.38 mm and two specimens of crystal II with thicknesses of 1.14 and 2.90 mm. The specimen of crystal III that was used had a thickness of 3.23 mm. The results were independent of crystal thickness. These crystals were mounted in the crystal holder described by Sastry and Srinivasan and the apparatus and measurement techniques of these authors were used.[1] The General Radio type 821 twin T bridge, type 1330A oscillator, and Collins type 51R radio receiver were used to measure the resistance and capacitance of the crystal specimens over the temperature range from 630 to 740°C. It was found helpful to maintain the crystal specimens at approximately 740°C for an hour or more before beginning the measurements to ensure good contact between them and the platinum electrodes.

The dc conductivity of the crystals was measured with an Applied Research Corporation vibrating reed electrometer. Agreement of the dc and rf conductivities is an important criterion for the absence of interfacial polarization.[5] The concentration of strontium in the crystals was estimated by comparing the dc conductivity with similar data of Kelting and Witt on crystals of known strontium content.[6]

RESULTS

The dc conductivity of three crystals is shown in Fig. 1. The strontium concentration in crystal I was approximately 9×10^{-5} mole fraction; that of crystal II was approximately 3×10^{-5} mole fraction. Crystal III was a "pure" Harshaw specimen.

The frequency dependence of the imaginary part of the dielectric constant ϵ_2 of crystal I is shown in Fig. 2 for three temperatures. These data can be described by the equation

$$\epsilon_2 = \frac{4\pi\sigma}{\omega} + \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}, \tag{1}$$

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[2] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1949), p. 70.

[3] A. B. Lidiard in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20.

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where the first term represents the contribution of the frequency-independent volume conductivity σ. The second term of Eq. (1) is the contribution of a Debye dipole relaxation. $(\epsilon_s - \epsilon_\infty)$ is the difference between the static and high-frequency dielectric constants and τ is the dipole relaxation time. The angular frequency is $\omega = 2\pi f$.

The low-frequency data of Fig. 2 fall on straight lines of unit negative slope that are represented by the first term of Eq. (1). The volume conductivity σ determined
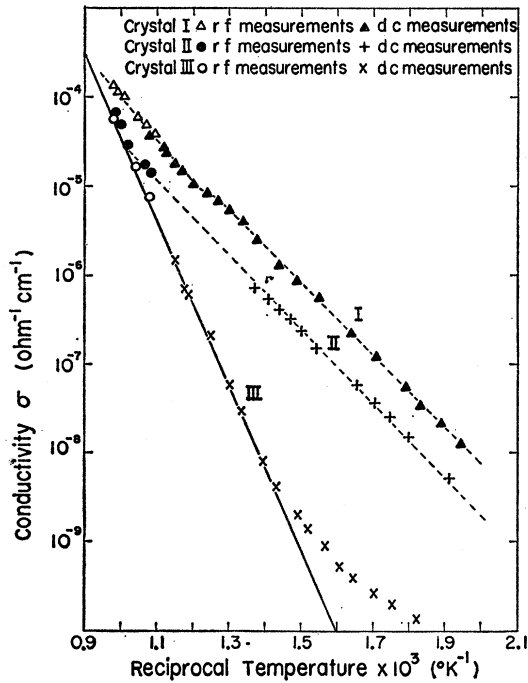

FIG. 1. The ionic conductivity of KCl-SrCl$_2$ crystals as a function of temperature. Crystal I, strontium concentration 9×10^{-5} mole fraction. Crystal II, strontium concentration 3×10^{-5} mole fraction. Crystal III, "pure" Harshaw crystal.

in this manner is plotted in Fig. 1 for comparison with the dc conductivity. The agreement is excellent and shows that the frequencies used were sufficiently high to avoid interfacial polarization. The dipole contribution to the imaginary part of the dielectric constant, the second term of Eq. (1), was obtained by subtracting from the data the contribution of the volume conductivity. The result is shown in Fig. 2 by curves d, e, and f. The dipole contribution to ϵ_2 has its maximum at

$$2\pi f \tau = 1. \qquad (2)$$

The relaxation time τ is obtained in this manner and the concentration of dipoles n can be obtained from the maximum of the dipole contribution to ϵ_2 since, according to simple Debye theory,

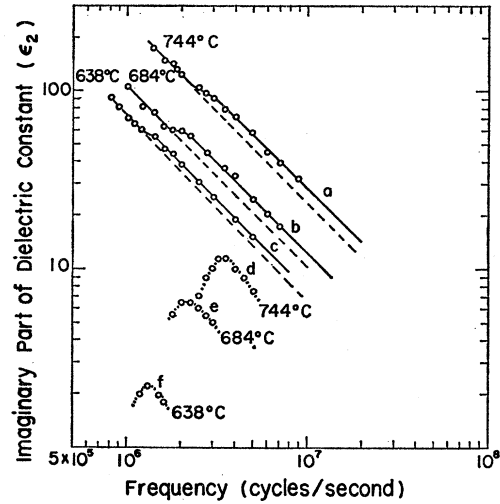$$(\epsilon_s - \epsilon_\infty) = 4\pi n \mu^2 / 3kT. \qquad (3)$$

FIG. 2. The frequency dependence of the imaginary part of the dielectric constant of crystal I for three temperatures (curves a, b, and c). Curves d, e, and f are the dipolar contribution to ϵ_2.

Figure 3 shows the frequency dependence of ϵ_2 for each of the three crystals at the same temperature, 647°C. Although the volume conductivities σ of crystals I and II are seven and three times, respectively, that of crystal III, the dipole contributions to ϵ_2 of the three crystals are the same.

Figure 4 shows the temperature dependence of the dipole concentration n and the relaxation time τ. The straight lines which represent the data are those determined by Sastry and Srinivasan from their measure-
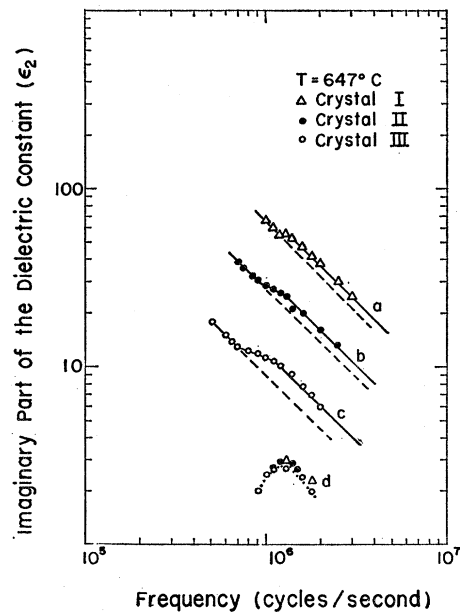

FIG. 3. The frequency dependence of the imaginary part of the dielectric constant of crystals I, II, and III at 647°C (curves a, b, and c). Curve d shows the dipolar contributions to ϵ_2.
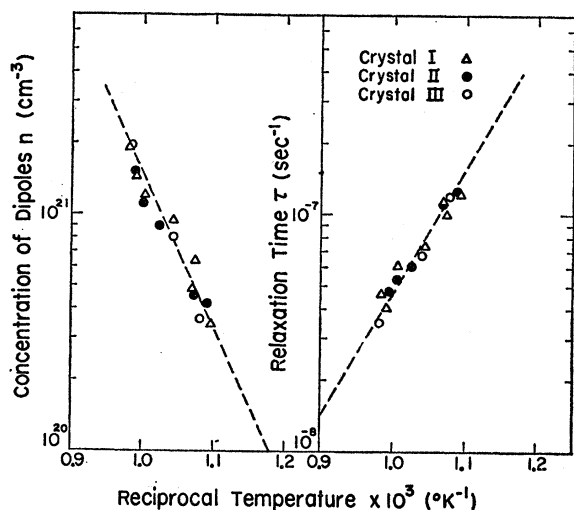
FIG. 4. The temperature dependence of the dipole concentration and relaxation time of crystals I, II, and III. The straight lines represent the results of Sastry and Srinivasan (Ref. 1).

ments on zone refined potassium chloride.[1] As determined by these authors, τ and n are represented by the equations

$$\tau = \tau_0 \exp(U/kT) \tag{4}$$

$$n = A \exp(-h/kT), \tag{5}$$

with $\tau_0 = 2.98 \times 10^{-13}$ sec, $U = 1.04 \pm 0.05$ eV, $A = 7.4 \times 10^{27}$ cm^{-3}, and $h = 1.34 \pm 0.07$ eV. The theoretical values of U and h for vacancy pairs are 1.15 and 1.28 eV, respectively.[7]

DISCUSSION

The data establish unambiguously that the dipolar contribution to the high-temperature dielectric loss of potassium chloride is an intrinsic property which is independent of the concentrations of isolated cation and isolated anion vacancies. Since the ratio of the frequency-independent volume conductivities of crystals I and

III at 647°C was about seven, as is shown in Fig. 3, the cation vacancy concentration of crystal I was approximately seven times larger and its anion vacancy concentration was approximately seven times smaller than those of crystal III at this temperature. This conclusion is derived from the conductivity data because the cation vacancy mobility is much larger than that of the anion vacancy.

Although the addition of strontium to potassium chloride does not change the product of the cation and anion vacancy concentrations, it is extremely unlikely that the observed loss is due to these vacancies in such a manner that its magnitude depends only on this product. The temperature dependence of the cation and anion vacancy concentrations, n_c and n_a, can be written in the form

$$n_c \times n_a = \text{constant} \times \exp(-W/kT), \tag{6}$$

where W, the heat of formation of Schottky defects in potassium chloride, is 2.22 eV.[8] This is very different from the heat of formation of the dipoles, $h = 1.34$ eV, that determines the temperature dependence of the dipole concentration.

The best interpretation of the data which is presently available is that vacancy pairs are responsible for the dipolar contribution to the high-temperature dielectric loss of potassium chloride. Three theoretical properties of vacancy pairs are in agreement with the data: the independence of their concentration of the strontium content of the crystal, their heat of formation, and their activation energy for reorientation. The large discrepancy between the observed concentration of dipoles and the expected concentration of vacancy pairs may result from an incorrect estimate of the dipole moment of a vacancy pair or the failure of the simple Debye theory to properly account for the numerical factors of Eq. (3).

ACKNOWLEDGMENT

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