Equation (A7) can then be solved algebraically, and Q_ω substituted into Eq. (A6) to obtain

$$Q(\mathbf{q}) = T \sum_\nu R(\mathbf{q})/[1 - n|u|^2 R(\mathbf{q})], \qquad \text{(A9)}$$

where

$$R(\mathbf{q}) = (2\pi)^{-3} \int d^3p \, \bar{G}_\omega(\mathbf{p}) \bar{G}_{-\omega}(\mathbf{q}-\mathbf{p}). \qquad \text{(A10)}$$

Substituting expression (A3) into (A10), the integrations may be carried out, provided $q \ll p_F$, with the result that

$$R(\mathbf{q}) = (2\pi N(0)/v_F q) \tan^{-1}(v_F q/[2|\omega| + (1/\tau)]). \qquad \text{(A11)}$$

If we only consider those values of q for which $q \ll (v_F/2\pi T)^{-1} + l^{-1}$, where $l = v_F \tau$ is the mean free path, then we can expand the $\tan^{-1}$ and find

$$Q(\mathbf{q}) = N(0)\pi T \sum_\nu \left[|\omega| + \frac{1}{6\tau}\left(\frac{ql}{1+2|\omega|\tau}\right)^2 \right]^{-1}. \qquad \text{(A12)}$$

The divergence in the sum over integers ν can be cured by subtracting $Q(0)$ from both sides; a cutoff is then introduced into $Q(0)$ in the usual way.[15] We thus obtain

$$Q(\mathbf{q}) - Q(0) = N(0)\sum_\nu\{[|2\nu+1| + (ql)^2(6\pi T\tau)^{-1} \times (1+2\pi T\tau|2\nu+1|)^{-2}]^{-1} - |2\nu+1|^{-1}\}, \qquad \text{(A13)}$$

and

$$Q(0) = N(0) \ln 1.14 \theta_D/T. \qquad \text{(A14)}$$

When $2\pi T\tau \ll 1$, the "dirty" limit which is almost always the situation in thin film experiments, the term $2\pi T\tau|2\nu+1|$ may be neglected in (A13), and so finally

$$Q(\mathbf{q}) - Q(0) \cong -N(0)\{\psi[\tfrac{1}{2} + \tfrac{1}{2}(v_F l q^2/6\pi T)] - \psi(\tfrac{1}{2})\}, \qquad \text{(A15)}$$

where ψ is the digamma function.[11] Combining Eqs. (A4), (A5), (A14), and (A15) just reproduces Eqs. (1)–(4) of Sec. II.

High-Temperature Dielectric Constant of Potassium Chloride*

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A dispersion of the dielectric constant of zone-purified potassium chloride has been observed at temperatures above 650°C and in the frequency range between one and ten megacycles/sec. The data are interpreted in terms of the Debye equations and the assumption that the dipoles are vacancy pairs. The activation energy for reorientation of a vacancy pair is found to be $1.04^{\pm 0.05}$ eV and the heat of formation of a vacancy pair is found to be $1.34^{\pm 0.07}$ eV. These quantities have been calculated by Tharmalingam and Lidiard as 1.15 and 1.28 eV, respectively. The dielectric data yield, however, an absolute number of vacancy pairs that is at least a factor of ten larger than is acceptable. Interfacial or Maxwell-Wagner types of polarization are excluded as explanations of the data.

INTRODUCTION

THE dielectric constant of pure potassium chloride at high temperature and in the frequency range between one and ten megacycles/sec exhibits a rather simple behavior. The real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2, are described by the Debye equations[1] and the expected contribution to ϵ_2 of the frequency-independent volume conductivity σ:

$$\epsilon_1 = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + \omega^2\tau^2), \qquad \text{(1)}$$

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

where τ is the relaxation time of the Debye dipoles and

ω is the angular frequency. According to the simple Debye theory, the difference between the low-frequency dielectric constant ϵ_s and the high-frequency dielectric constant ϵ_∞ is given by

$$\epsilon_s - \epsilon_\infty = 4\pi n \, \mu^2/3kT, \qquad \text{(3)}$$

where n is the number of dipoles per unit volume and μ is the dipole moment.

EXPERIMENTAL PROCEDURE

The potassium chloride crystals were prepared from reagent grade powder by zone refining in an atmosphere of chlorine.[2] Twenty or more zones were passed through the salt which was contained in an open silica crucible. The zone speed was approximately 1 in./h. The dc conductivity of the zone-refined salt is illustrated in Fig.

[1] H. Frohlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949), p. 70.

[2] T. M. Srinivasan, Technical Note No. 3, AFOSR Contract 49(638)-529, University of Illinois, 1962 (unpublished).
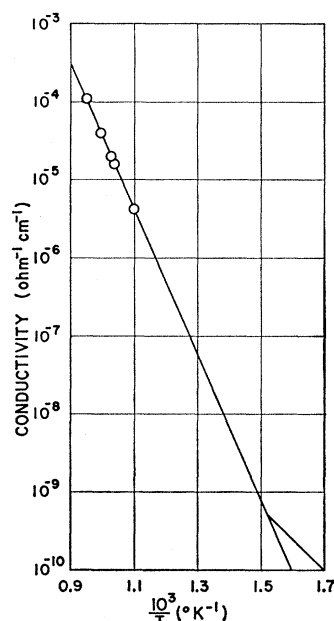
FIG. 1. The ionic conductivity of zone-refined potassium chloride. Solid line measured by dc technique. Circles obtained from high-frequency measurement of imaginary part of dielectric constant.

The real and imaginary parts of the dielectric constant of the crystal were obtained from measurements of the capacitance and conductance of the crystal and coaxial line.[4] These measurements, accurate to within ±10%, were made with a General Radio type 821-A Twin-T bridge that was driven by a General Radio type 1330-A oscillator. The detector was a Collins type 51J receiver.

RESULTS

The frequency dependence of the imaginary part of the dielectric constant is shown in Figs. 2 and 3 for the temperatures of 703 and 740°C. The lowest frequency data fall on the straight line of negative unit slope that represents the contribution to ϵ_2 of the frequency independent-volume conductivity σ as described by the first term of Eq. (2). This conductivity, as determined from the radio-frequency measurements, is

1. Single crystals that were used for the dielectric constant measurements had typical dimensions of 5 mm ×5 mm×1 mm.

The dielectric measurements were made with the crystal terminating a stainless steel coaxial line.[3] Platinum foil electrodes were hard soldered to the stainless steel. To inhibit the formation of oxides, helium was circulated through the line. A platinum-platinum rhodium thermocouple was mounted adjacent to the crystal. A small, manually controlled oven was used to maintain the crystal at the desired temperature. Measurements were made in the temperature range from 650 to 775°C with an accuracy of ±1°C.
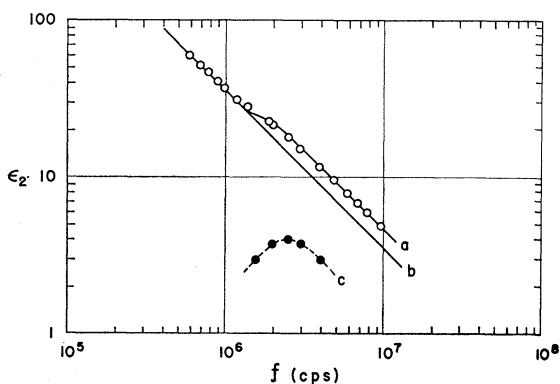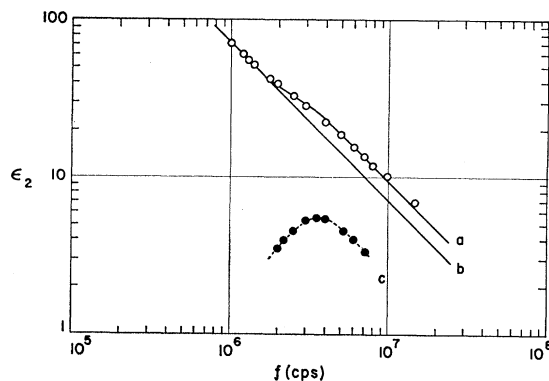

FIG. 3. The imaginary part of the dielectric constant ϵ_2 of potassium chloride as a function of frequency at 740°C. Curve a: experimental data. Curve b: contribution of dc conductivity. Curve c: dipolar contribution.

plotted in Fig. 1 for comparison with the conductivity σ that was measured by dc techniques. The agreement between the radio frequency and dc determination of the conductivity is well within the experimental errors.

Curves c of Figs. 2 and 3 are the result of subtracting from the measured values of ϵ_2 the contribution due to the conductivity. These curves are interpreted as a Debye dipolar contribution to ϵ_2 as described by the second term of Eq. (2). The maximum value of the dipolar contribution to ϵ_2 increases and the frequency at which it occurs increases with increase of temperature.

The dipole relaxation time τ can be obtained from the condition

$$2\pi f_m \tau = 1, \qquad (4)$$

where f_m is the frequency for which the dipolar contribution to ϵ_2 has its maximum value. The relaxation time is shown as a function of temperature in Fig. 4

FIG. 2. The imaginary part of the dielectric constant ϵ_2 of potassium chloride as a function of frequency at 703°C. Curve a: experimental data. Curve b: contribution of dc conductivity. Curve c: dipolar contribution.

[3] G. D. Watkins, Phys. Rev. 113, 91 (1959).

[4] Preliminary measurements were made with a Boonton type 160-A Q-meter. P. V. Sastry, Technical Report No. 6, U. S. Office of Naval Research Contract Nonr 1834(19), University of Illinois, 1963 (unpublished).

and satisfies the equation

$$\tau = \tau_0 \exp(U/kT), \qquad (5)$$

where $\tau_0 = 2.98 \times 10^{-13}$ sec and $U = 1.04 \pm 0.05$ eV.

The number of dipoles per unit volume can be obtained from the maximum value of the dipolar contribution to ϵ_2 with the help of Eqs. (2) and (3). The temperature dependence of the dipole concentration is shown in Fig. 5. These data satisfy the equation

$$n = A \exp(-h/kT), \qquad (6)$$

with $A = 7.4 \times 10^{27}$ cm^{-3} and $h = 1.34 \pm 0.07$ eV. In the calculation of n, the dipole moment μ was taken as ea where e is the electronic charge and a is the cation-anion separation in potassium chloride.

Figure 6 shows the frequency dependence of the real part of the dielectric constant ϵ_1 at 703°C. Curve a is the real part of the dielectric constant as calculated from the measured imaginary part of the dielectric constant by means of Eqs. (1) and (2). The measured ϵ_1 agrees reasonably well with curve a. The high-frequency value of the dielectric constant ϵ_∞ was found to be 5.00 and temperature-independent. von Hippel[5] found $\epsilon_\infty = 5.60$ at 600°C with a small temperature dependence that would have escaped the precision of the present measurements.

DISCUSSION

The interpretation of the unexpected dipolar contribution to the high temperature, high-frequency dielectric constant of potassium chloride is an intriguing, and because of its magnitude, an important problem. Since
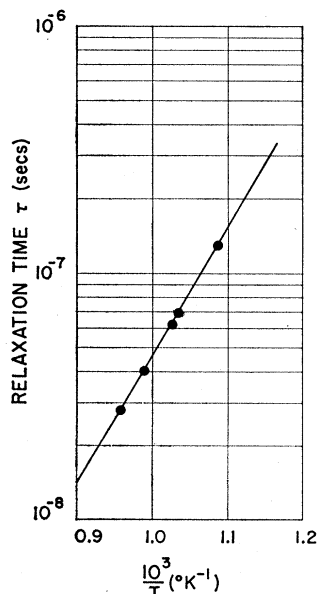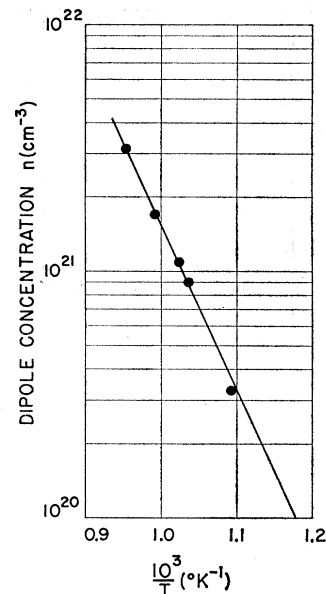

FIG. 5. The dipole concentration n as a function of temperature.

FIG. 4. The relaxation time τ as a function of temperature.

the conductivity σ is known to result from the mobility of Schottky defects, that is, cation and anion vacancies, we have attempted an interpretation in terms of vacancy pairs.[6] The vacancy pair is a cation and an anion vacancy occupying nearest neighbor sites in the crystal. The effective charges of the vacancies give the vacancy pair a dipole moment which should be approximately $\mu = ea$ where e is the electronic charge and a is the cation-anion nearest neighbor separation. These same charges should, by purely electrostatic arguments, lead to a binding energy of the vacancy pair of the order of 1 eV. The reorientation of a pair may occur as the result of either the jump of a neighboring cation into the cation vacancy of the pair or by the jump of a neighboring anion into the anion vacancy of the pair. The relaxation time for reorientation is given by Eq. (5) and the experimental value of τ_0 is of the expected magnitude for vacancy pairs. Tharmalingam and Lidiard[7] have calculated that the activation energy for the jump of an anion into the anion vacancy of a pair in potassium chloride is 1.15 eV. The calculated value of the activation energy for the jump of a cation into the cation vacancy of a pair is 1.30 eV and larger than that of the anion jump. The relaxation time for reorientation of a vacancy pair should be almost completely determined by the mean-jump time of the anion into the anion vacancy of the pair. The agreement between the theoretical value of 1.15 eV for the activation energy of this jump and the experimental value of $U = 1.04$ eV is probably within the errors of the calculation and the experiment.

The theory of vacancy pairs yields Eq. (6) for the

[5] A. R. von Hippel, Tables of Dielectric Materials, U. S. Office of Naval Research, Technical Report No. 119, Massachusetts Institute of Technology, 1957 (unpublished).

[6] N. F. Mott and R. Gurney, Electronic Processes in Ionic Crystals (Clarendon Press, Oxford, 1940), p. 41.

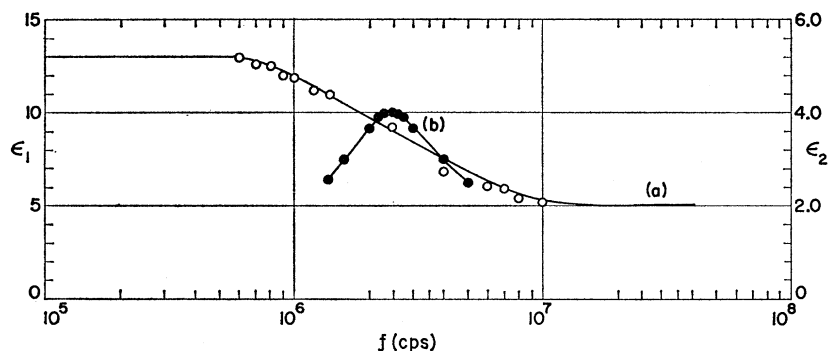[7] K. Tharmalingam and A. B. Lidiard, Phil. Mag. 6, 1157 (1961).

FIG. 6. The real and imaginary parts of the dielectric constant as a function of [frequency] at 703°C. Curve a: the real part of the dielectric constant calculated from the dipolar contribution to the imaginary part. Open circles are the measured real part of the dielectric constant. Curve b: the dipolar contribution to the measured imaginary part of the dielectric constant.

concentration of pairs with the quantity h identified as the heat of formation of a vacancy pair. Tharmalingam and Lidiard have calculated the heat of formation of a vacancy pair in potassium chloride to be 1.28 eV in excellent agreement with the experimental value of 1.34 eV. Furthermore, Tosi and Fumi[8] have independently calculated the binding energy of the vacancy pair to be 0.72 eV. If this number is subtracted from the known heat of formation of Schottky defects in potassium chloride, 2.2 eV, the result is a second estimate of the heat of formation of a vacancy pair of 1.48 eV that is also in good agreement with the result of the present experiments.

According to the theory of vacancy pairs, the pre-exponential factor of Eq. (6) can be written as

$$A = 6N \exp(s/k), \qquad (7)$$

where N is the number of ion pairs per unit volume ($N = 1.6 \times 10^{22}$ cm^{-3} for KCl) and s is the entropy of formation of a vacancy pair.[9] A theoretical calculation of the entropy of formation of a vacancy pair does not exist, but Dreyfus and Nowick[10] have obtained the experimental value, $s = 7.1\ k$, for a Schottky defect in
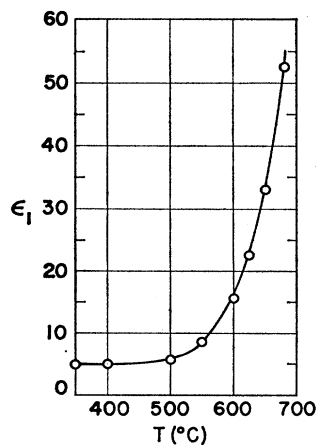

FIG. 7. The real part of the dielectric constant ϵ_1 as a function of temperature at 100 kc/sec.

potassium chloride. The magnitude of s for vacancy pairs is presumably about the same as that for Schottky defects but our value of $A = 7.4 \times 10^{27}$ cm^{-3} yields $s = 11\ k$.

Because of the large value of the constant A, the concentration of pairs given by Eq. (6) is implausibly large. At 775°C, near the melting point, $n = 3.2 \times 10^{21}$ cm^{-3}, or 20% of the concentration of ion pairs. Such a large concentration of vacancy pairs would produce a major anomaly in the specific heat that could not have escaped detection. It is tempting to speculate that either the numerical factor of Eq. (3) is incorrect by a factor of ten or more or that the dipole moment of a vacancy pair is substantially greater than $\mu = ea$. It is noteworthy, however, that Watkins[3] treated his data on the dielectric loss of Mn^{++}-cation vacancy complexes with assumptions similar to those used in the present work and obtained a concentration of complexes that agreed within a factor of two with the concentration obtained from spin resonance measurements. Furthermore, it does not seem appropriate to modify Eq. (3) by the introduction of a local electric field as has been attempted in the past.[11] The reorientation of a pair is the result of a thermally activated exchange of a vacancy and an ion; the process is fundamentally the same as occurs in the drift of Schottky defects in an electric field and it is well known that the introduction of a local field in the treatment of the dc conductivity is incorrect.

The possibility must be considered that the observed behavior of the dielectric constant is due to Schottky defects. Interfacial polarization due to the development of space charge at the crystal-electrode interfaces is an obvious possibility. The theory of MacDonald[12] indicates, however, that interfacial polarization occurs at lower frequencies than those used in the present work. This low-frequency interfacial polarization has been observed by Alnatt and Jacobs[13] and by Bean.[14] The

[8] M. P. Tosi and F. G. Fumi, Nuovo Cimento 7, 95 (1958).
[9] A. B. Lidiard, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20.
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[11] R. G. Breckenridge, in Imperfections in Nearly Perfect Crystals edited by W. Shockley, J. H. Hollomon, R. Maurer, and F. Seitz (John Wiley & Sons, Inc., New York, 1952) p. 219.
[12] J. Ross MacDonald, Phys. Rev. 92, 4 (1953).
[13] A. R. Alnatt and P. W. M. Jacobs, J. Phys. Chem. Solids 19, 281 (1961).
[14] C. P. Bean, thesis, University of Illinois, 1952 (unpublished).

large increase of ϵ_1 with increase in temperature at a frequency of 100 kc/sec that is shown in Fig. 7 is undoubtedly due to interfacial polarization.[15] But we do not believe that the apparent dipolar contribution to ϵ_2 can be interpreted in terms of interfacial polarization for the following reasons. MacDonald's theory predicts that the relaxation time associated with interfacial polarization is proportional to the crystal thickness. Although the crystal thickness was varied by a factor of three, the measured relaxation time τ remained constant. It is also significant that at the lowest frequencies used in the present work, the measured values of ϵ_2 yielded values of σ that agreed with the dc conductivity. This fact indicates, according to MacDonald's theory, that the frequencies were sufficiently large to eliminate the effects of interfacial polarization. Finally, because of the uncontrolled nature of the crystal-electrode interface, it is difficult to obtain reproducible data concerning interfacial polarization but the present data were reproducible from crystal to crystal and independent of the thermal history of the crystals.

A two-phase system in which the phases possess different conductivities and dielectric constants exhibits a Maxwell-Wagner interfacial polarization[16] with characteristics similar to that observed in the present investigation. But the presence of a second phase in our crystals is not only improbable because of the method of preparation but excluded by their optical perfection.

The Debye-Hückel space charge cloud that is formed around each vacancy of a Schottky defect produces a high-frequency dependence of the conductivity. This effect has been considered by Lidiard and is too small to account for the observed behavior of ϵ_2.[17]

Despite the unreasonably large concentration of vacancy pairs that results from the analysis of our data in terms of the Debye theory, we believe that this interpretation is the most plausible. Unfortunately, there is little experimental information concerning the properties of vacancy pairs. The self-diffusion of the chloride ion in sodium chloride and potassium chloride has been interpreted by assuming that the vacancy pair contributes to the diffusion mechanism.[18,19] Laurance obtained an activation energy for translation

of the vacancy pair in NaCl of 1.07 eV in good agreement with the theory of Tharmalingam and Lidiard. Smith[20] has interpreted microwave measurements of the dielectric constant of potassium chloride in terms of a contribution from vacancy pair and obtained a value of 0.9 eV for the reorientation activation energy.

An important test of the vacancy-pair interpretation of the present data may be performed by repeating the present measurements on crystals that have been doped with a suitable divalent impurity such as strontium. The presence of the strontium is known to increase the concentration of cation vacancies and decrease the concentration of anion vacancies. Any contribution of the Schottky defects to the dielectric constant may be expected to be influenced by the strontium impurity. The concentration of vacancy pairs, however, is independent of the presence of the strontium impurity so that if the observed effects are due to these pairs the behavior of the dielectric constant should be uninfluenced by the impurity. Experiments of this type have been initiated.

SUMMARY

A significant dispersion of the dielectric constant of zonepurified potassium chloride has been observed between one and ten megacycles and at temperatures above 650°C. Interpretation of the data in terms of the Debye equations and the assumption that the dipoles are vacancy pairs leads to excellent agreement with the theory of Tharmalingam and Lidiard of the magnitudes of the activation energy for reorientation of a pair and of the heat of formation of a pair. The absolute number of pairs is found to be about fifty times larger than is expected and reasonable. This discrepancy may be due to an underestimate of the dipole moment of a pair. An interpretation of the data in terms of either interfacial polarization or Maxwell-Wagner polarization is excluded by the character of the data and the homogeneity of the crystals.

ACKNOWLEDGMENTS

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