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Collective Behavior of Polar Impurities in Ionic Crystals

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The purpose of this work is to construct a theory which will explain recent low-temperature measurements of the dielectric properties of KCl crystals containing substitutional hydroxyl ions. The Onsager theory of polar liquids, as extended by Pirenne to allow for the possibility of spontaneous polarization, is modified in order to take into account the strong short-range interactions that are important in solids. The theory leads to two simultaneous transcendental equations, which are solved numerically to obtain the dielectric constant for small applied fields and the spontaneous polarization as a function of temperature. The agreement with experiment is good except in the neighborhood of the Curie temperature, where the discrepancies are such as one might expect to arise from the nonuniform distribution of hydroxyl ions in the experimental samples. Theoretical results are also given for the dielectric constant measured in a large steady field or by means of a small alternating field in the presence of a large steady bias.

I. INTRODUCTION

THIS paper contains an account of the beginning of a theoretical investigation which is motivated by the recent experimental results of Känzig, Hart, and Roberts.[1] These investigators studied the dielectric behavior of KCl cyrstals in which roughly 1 in 10^3 Cl^- ions was replaced by a polar $(OH)^-$ radical. Measurements of the dielectric constant and loss angle were carried out on a number of samples containing different $(OH)^-$ concentrations, at temperatures in the range 0.3–90°K and frequencies in the range 10^2–10^4 cps. It was observed that the dielectric constant increased with decreasing temperature until it reached a maximum value after which it began to decrease. The temperature corresponding to the maximum dielectric constant increased with increasing $(OH)^-$ concentration but was almost independent of frequency, indicating that the dielectric behavior was determined primarily by interaction between the dipoles rather than by relaxation effects associated with the hindered motion of individual dipoles.

More recently,[2] measurements of the dielectric constant as a function of temperature have been carried out in the presence of a strong dc bias. Preliminary results indicate that the bias field has the effect of reducing the dielectric constant over the entire temperature range within which the effect of the dipoles is noticeable. The significance of these measurements lies in the light they shed on the nature of the collective ordering which one may reasonably assume to be responsible for the decrease in dielectric constant at temperatures below that corresponding to its peak value. If this ordering were antiferroelectric it would presumably be inhibited by a dc field and one would therefore expect a bias field to cause an increase in the dielectric constant on the low-temperature side of the peak. Since this is contrary to the behavior observed, one may conclude that the ordering is ferroelectric. The argument used here has been made quantitative by Takagi[3] for a simple model.

Independently of the dielectric measurements on KCl $(OH)^-$, Kuhn and Lüty[4] have studied the ultraviolet (uv) absorption of this material in the presence of a strong electric field. The theoretical explanation which they developed for the observed temperature and crystal-orientation-dependent electric dichroism indicated that the $(OH)^-$ dipoles can orient themselves only along the six [100] axes of the fcc KCl lattice, and yielded a value for the electric dipole moment.

An exact theoretical treatment of KCl $(OH)^-$ would involve a solution of the statistical-mechanical problem of an ionic lattice containing a number of substitutional polar ions on random lattice sites, taking into account the short-range forces, the long-range electrostatic interactions, and an external field. If one considers the difficulties that arise when one attempts to find a solution for the very much simpler Ising model, one must conclude that this rigorous approach is unlikely to yield meaningful results. The literature does, however, contain some solutions for much simpler problems involving dipoles on lattice sites, and it is of interest to discuss these briefly.

Sauer[5] has discussed the energetics of a three-dimensional lattice of dipoles, each of which can have an orientation either parallel or antiparallel to some given direction. The only forces considered were the long-range dipole-dipole interactions. The calculations were actually carried out for the case of magnetic dipoles, but the results can be applied to electric dipoles provided one keeps in mind that in the latter case there is no analog of the demagnetizing field since the dielectric material is always assumed to be between the plates of a capacitor.[6] Thus, the applicable results are those for long thin needles of magnetic material. A

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[1] W. Känzig, H. R. Hart, Jr., and S. Roberts, Phys. Rev. Letters **13**, 543 (1964).

[2] H. R. Hart, Jr. (private communication).

[3] Y. Takagi, Phys. Rev. **85**, 315 (1952).

[4] U. Kuhn and F. Lüty, Solid State Commun. **2**, 281 (1964).

[5] J. A. Sauer, Phys. Rev. **57**, 142 (1940).

[6] For further discussion of this point as well as a good general introduction to dielectric properties see C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., Chap. 7.

number of intuitively chosen lattices at zero temperature were considered and the interaction energy was calculated. It was concluded that for a simple cubic lattice an antiferroelectric arrangement gives the lowest energy, but for a face-centered or body-centered lattice a ferroelectric arrangement gives the lowest energy.

A more powerful method for computing the interaction energy of any dipole lattice at zero temperature was introduced by Luttinger and Tisza[7]; their results substantiated the conclusions reached by Sauer.

The calculations of Takagi[3] have been referred to already. They deal with a simple cubic lattice of freely rotating dipoles which contains, in addition, a polarizable ion at each body site. The temperature is not assumed to be zero. These calculations are not exact, however. A two sublattice model is used in order to allow for the possibility of an antiferroelectric array, and the field acting on a dipole at a particular site is calculated by supposing that every other dipole has just the average orientation taken over the specified lattice to which it belongs. With this simplification, it was possible to show that as long as the polarizability of the central ion is below a certain value, the lattice becomes antiferroelectric below a critical temperature, a result consistent with the results of Refs. 5 and 7. However, if the polarizability of the central ions is larger, the lattice becomes ferroelectric.

A different approach to the problem of dipoles on a lattice at a finite temperature was taken by Lax[8] who employed the spherical model.[9] It was concluded that a cubic lattice of permanent dipoles should undergo an antiferroelectric transition, a result consistent with those described above. Toupin and Lax[10] have also applied the spherical model to the case of a lattice of dipoles which are polarizable in addition to having a permanent moment.

If one turns now to the situation of experimental interest, i.e., dipoles on random-lattice sites in a polarizable medium, one notes that it seems quite possible that an exact theory would show that the state of lowest energy of a random array would be ferroelectric at zero temperature even if the polarizability of the medium were zero. The fact that the polarizability of the medium is not zero makes it more likely that an exact theory would predict a transition to a ferroelectric state at some critical temperature, and this is in fact the most natural explanation of the experimental results.

In view of the difficulties that arise when one attempts a rigorous analysis of the problem, one is naturally led to consider the possibilities of the simplest method for calculating the dielectric properties of condensed materials, i.e., the method of the "local field." In materials that have at least cubic symmetry,[6] one simply considers a typical ion and calculates the electric field acting on it with the assumption that the rest of the material may be considered to be homogeneous. For *nonpolar* materials this method leads in the well-known way to the local field of Lorentz and to the Clausius-Mossotti (or Lorenz-Lorentz) equation for the dielectric constant. The derivation of the Lorentz local field depends on the fact that all *induced* dipoles are oriented parallel to each other, a point which is made more explicitly in the argument leading to Eq. (9) of the next section. Accordingly, the Clausius-Mossotti equation does not apply to materials containing permanent dipoles.[11] This point was recognized by Onsager[12] who proceeded to develop the first qualitatively successful theory of polar liquids.

The principal shortcoming of the Onsager theory,[13] and one which is of particular importance if one wishes to apply it to solids, is that it takes no account of the short-range forces between polar molecules. However, the present paper is concerned only with solids containing polar ions as widely separated impurities so that only the long-range dipole-dipole interactions are important. There are, to be sure, short-range interactions between polar and nonpolar ions but, following the work of Kuhn and Lüty,[4] one may hope that these forces are adequately taken into account by treating them as steric hindrances which restrict the orientation of the dipoles to certain directions in the lattice.

The original Onsager model predicted a dielectric constant increasing continuously as the temperature is lowered; the theory did not predict the existence of a state of spontaneous polarization at any temperature. However, Pirenne[14] pointed out that this result arose only because it was assumed from the beginning that the polarization in the material was proportional to the externally applied field. Pirenne showed that if the possibility of spontaneous polarization was considered in setting up the equations for the model, then, for an ensemble of freely rotating permanent dipoles, the Onsager approximation did, in fact, predict the occurrence of a first-order phase transition to a ferroelectric state at a Curie point T_c given by

$$kT_c/N\mu^2 \cong 0.31\,, \qquad (1)$$

where N is the number of permanent dipoles of moment μ per cm^3.

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[7] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[8] M. Lax, J. Chem. Phys. **20**, 1351 (1952).

[9] T. H. Berlin and J. L. Thomsen, J. Chem. Phys. **20**, 1368 (1952).

[10] R. A. Toupin and M. Lax, J. Chem. Phys. **27**, 458 (1957).

[11] This invalidates the derivation of the dipole moment for (OH)$^-$ in KCl contained in Ref. 4. See Sec. III for the corrected value.

[12] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

[13] For discussions of the Onsager theory and subsequent elaborations see, for instance, A. R. Von Hippel, *Dielectrics and Waves* (John Wiley & Sons, Inc., New York, 1954), pp. 178 and 266; R. H. Cole, in *Progress in Dielectrics*, edited by J. B. Birks and J. Hart (John Wiley & Sons, Inc., New York, 1961), Vol. 3, p. 47; W. F. Brown, Jr., in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 17, pp. 53–59; P. W. Forsbergh, Jr., *ibid.*, pp. 370–372; G. P. Mikhailov and L. L. Burshtein, Usp. Fiz. Nauk **74**, 3 (1961) [English transl.: Soviet Phys.—Usp. **4**, 389 (1961)].

[14] J. Pirenne, Helv. Phys. Acta **22**, 479 (1949).

In the preliminary phases of the present work, the author generalized the calculations of Pirenne in order to investigate the effect of assuming that the dipoles are polarizable in addition to having a permanent dipole moment. This can be done by incorporating into the theory a quantity ϵ_m which is defined as the dielectric constant of the material which one would calculate (from the Clausius-Mossotti equation) if all the permanent moments were equal to zero. Pirenne's calculations were verified for $\epsilon_m=1$. It was found that, for $\epsilon_m=4.3$, the Curie temperature was not changed and moreover neither was the ratio $P_0(T)/P_0(0)$, where $P_0(T)$ is the spontaneous polarization at a temperature $T<T_c$. For the spontaneous polarization at absolute zero, the generalized model yields

$$P_0(0)=\tfrac{1}{3}(\epsilon_m+2)N\mu\,, \tag{2}$$

showing the effect of the local fields due to the aligned array in increasing the moment of each dipole. The dielectric constant predicted by the model increases in the manner calculated by Onsager as the temperature is decreased down to T_c. At this point it drops abruptly to a value of about 1.8 ϵ_m and then decreases to reach ϵ_m at absolute zero. The nature of the effects due to steric hindrances was also investigated by assuming that each dipole can be oriented only along $\pm x$, $\pm y$, or $\pm z$; this leads to the introduction of a modified Langevin function as explained in the next section. This modification has no effect on the high-temperature behavior or on the spontaneous polarization at absolute zero; the Curie temperature, however, is now given by

$$kT_c/N\mu^2\cong 0.62\,. \tag{3}$$

The above results have been quoted without proof because they are probably of interest only from a formal point of view; as has already been pointed out, the importance of short-range interactions in pure polar solids makes the applicability of a local-field theory very doubtful.[15] A detailed account of the theory for polar impurities in ionic crystals, where the physical assumptions make more sense, is given in the next section.

II. THEORETICAL ANALYSIS

One considers a material which consists of a mixture of N molecules/cm^3 having a permanent dipole moment μ, and N_α molecules/cm^3 having a scalar polarizability α.

A block of this material of height d and essentially infinite breadth and width is supposed to be between the plates of a capacitor connected to the source of a time-dependent voltage $V(t)$. The electric field $E(t)=V(t)/d$ will be referred to as the *applied field*. The voltage $V(t)$ is supposed to be changing sufficiently slowly so that all relaxation times associated with molecular motions within the material may be ignored.

The macroscopic properties of the material are characterized by a dielectric constant ϵ and a spontaneous polarization P_0. Both these quantities are, in general, functions of the temperature T; the spontaneous polarization may be zero. Using the method of Onsager as modified by Pirenne, the *local field* $F(t)$ acting on a typical molecule of each kind is calculated in terms of the applied field and the macroscopic material parameters. This permits one to calculate the average polarization of each kind of molecule and hence the average polarization per unit volume which, in turn, determines both ϵ and P_0. Clearly, one is dealing here with a method of *self-consistent parameters.* The procedure yields two simultaneous transcendental equations which are readily solved numerically.

A. Induced Dipoles

In the Onsager model, a typical dipole is considered, located at the center of an otherwise empty spherical cavity whose radius a is determined by the volume associated with each polarizable molecule. Thus, one has

$$\tfrac{4}{3}\pi a^3=N_\alpha^{-1}. \tag{4}$$

The material outside the cavity is considered to be homogeneous. The local field F in the cavity is the sum of two parts:

(i) The "cavity field" which is obtained by solving the electrostatic problem for the empty cavity. Denoting the induced polarization by $\mathbf{P}$, one has

$$\mathbf{F}_C=\mathbf{E}+[4\pi/(2\epsilon+1)](\mathbf{P}+\mathbf{P}_0)\,. \tag{5}$$

(ii) The "reaction field" which is the field in the cavity due to the polarization in the surrounding medium induced by a dipole of moment $\mathbf{m}$ at the cavity center

$$\mathbf{F}_R=(2/a^3)((\epsilon-1)/(2\epsilon+1))\mathbf{m}=g\mathbf{m}\,. \tag{6}$$

The polarizability of the molecules is denoted by α, so one has

$$\mathbf{m}=\alpha\mathbf{F}\,, \tag{7}$$

where

$$\mathbf{F}=\mathbf{F}_C+\mathbf{F}_R\,. \tag{8}$$

At this point one can make the connection with the well-known local field of Lorentz. For a material which contains no permanent dipoles, the average value of $\mathbf{m}$ is clearly equal to $\mathbf{m}$ since all the induced dipoles point in the same direction. Consequently, the macroscopic polarization is equal to $\mathbf{m}/(\frac{4}{3}\pi a^3)$ and, assuming the spontaneous polarization to be zero, one obtains

$$\begin{aligned}\mathbf{F}&=\mathbf{E}+\frac{4\pi}{2\epsilon+1}\mathbf{P}+\frac{8\pi(\epsilon-1)}{3(2\epsilon+1)}\mathbf{P}\,,\\&=\mathbf{E}+(4\pi/3)\mathbf{P}\,,\end{aligned} \tag{9}$$

which is the usual result. One notes that it is valid only in the absence of permanent dipoles.

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[15] For a discussion of phase transitions in the solid hydrogen halides, see J. G. Powles, Trans. Faraday Soc. 48, 430 (1952).

One now defines a quantity ϵ_m which is the dielectric constant of the material which one would calculate if one set all the permanent moments equal to zero; as a consequence of (9), it is given by the Clausius-Mossotti equation

$$(\epsilon_m-1)/(\epsilon_m+2)=(4\pi/3)N_\alpha\alpha. \quad (10)$$

If one uses Eqs. (5)–(8) together with the usual relation for the induced polarization, $4\pi P=(\epsilon-1)E$, one obtains for the average dipole moment per unit volume

$$P_\alpha=N_\alpha\alpha\left(\frac{3\epsilon}{2\epsilon+1}E+\frac{4\pi}{2\epsilon+1}P_0\right)\bigg/(1-\alpha g). \quad (11)$$

One easily evaluates $N_\alpha\alpha$ and αg by means of Eqs. (4) and (10), and obtains

$$P_\alpha=\frac{(\epsilon_m-1)}{4\pi(2\epsilon+\epsilon_m)}(3\epsilon E+4\pi P_0). \quad (12)$$

In the absence of spontaneous polarization ($P_0=0$) and of permanent dipoles ($\epsilon=\epsilon_m$), Eq. (12) gives $4\pi P_\alpha=(\epsilon_m-1)E$ as it should.

B. Permanent Dipoles

Just as in the case of the induced dipoles, one calculates the local field by considering a typical dipole of permanent moment $\boldsymbol{\mu}$ at the center of an otherwise empty spherical cavity. Equations (4), (5), and (6) remain valid provided N_α is replaced by N, but Eq. (7) must be replaced by

$$\mathbf{m}=\boldsymbol{\mu}. \quad (13)$$

One has now to calculate the mean dipole moment. Classically, the potential energy of a dipole of moment $\boldsymbol{\mu}$ oriented at an angle θ to the field $\mathbf{F}$ is given by

$$V=-\mathbf{F}\cdot\boldsymbol{\mu}=-\left(\frac{3\epsilon E}{2\epsilon+1}+\frac{4\pi P_0}{2\epsilon+1}\right)\mu\cos\theta-g\mu^2. \quad (14)$$

It has been assumed here that if a spontaneous polarization exists it is oriented along the applied field. This is, of course, not necessarily the case in a crystal for which a preferred direction of spontaneous polarization exists, unless the applied field is directed along this preferred direction.

For freely rotating dipoles, Eq. (14) leads in the usual way to a mean dipole moment

$$\bar{\mu}=\mu L\left[\frac{(3\epsilon E+4\pi P_0)\mu}{(2\epsilon+1)kT}\right], \quad (15)$$

where $L(x)$ is the Langevin function

$$L(x)=\coth x-1/x. \quad (16)$$

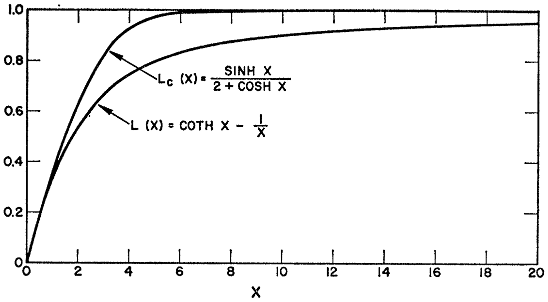

FIG. 1. The Langevin function $L(x)$ and the modified function $L_c(x)$.

In a crystal, dipoles cannot generally rotate freely because of steric hindrances. In a crystal of cubic symmetry, it is in fact more reasonable to assume[4] that a substitutional ionic dipole can be oriented only along one of the (100) axes, i.e., along $\pm x$, $\pm y$, or $\pm z$. The applied field is supposed to be along the z axis so the allowed values of $\cos\theta$ are 1, −1, 0, 0, 0, 0. This model implies that, in Eq. (15), one should use a modified Langevin function

$$L_c(x)=\frac{e^x-e^{-x}}{e^x+e^{-x}+4}=\frac{\sinh x}{\cosh x+2}. \quad (17)$$

One notes that for $x\ll 1$, $L_c(x)\cong L(x)\cong x/3$. A plot of $L_c(x)$ and $L(x)$ is given in Fig. 1.

The dipole moment per unit volume is thus given by[16]

$$P_d=N\mu L_c\left[\frac{(3\epsilon E+4\pi P_0)\mu}{(2\epsilon+1)kT}\right]. \quad (18)$$

C. Total Polarization and Dielectric Constant

The total polarization is found by adding Eqs. (12) and (18).

$$P=P_\alpha+P_d$$
$$=4\pi\frac{(\epsilon_m-1)}{(2\epsilon+\epsilon_m)}[3\epsilon E+4\pi P_0]+N\mu L_c\left[\frac{(3\epsilon E+4\pi P_0)\mu}{(2\epsilon+1)kT}\right]. \quad (19)$$

One now considers the dielectric constant that one would measure by using an infinitesimally small applied field (the dielectric constant for finite applied fields will

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[16] It might be of interest to comment briefly on the validity of the classical derivation leading to Eq. (18). It is well known [see, for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), Chap. 7] that for freely rotating dipoles the Langevin function can also be obtained quantum mechanically provided that the zero-field splitting between the ground and the first excited states is less than kT. It is reasonable to assume that a similar result holds for a dipole rotating in a potential of cubic symmetry. It has been determined experimentally (see Ref. 1) that the zero-field splitting is in fact less that 0.3°K so that quantum-mechanical corrections to $L_c(x)$ should not be large at temperatures above this value.

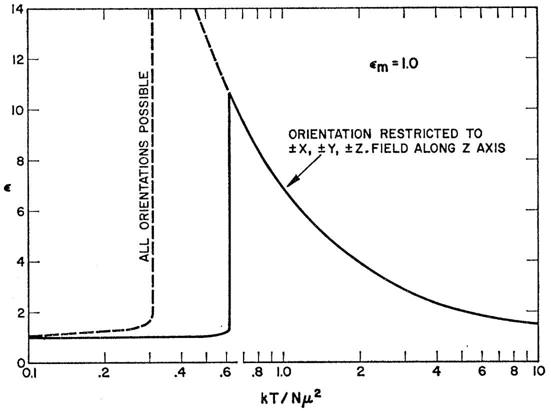

FIG. 2. Differential dielectric constant for $\epsilon_m = 1.0$.

be considered in Sec. II D). Thus, one has by definition

$$\epsilon \equiv 1+4\pi(\partial P/\partial E)_{E=0}$$

$$= 1+\frac{3(\epsilon_m-1)\epsilon}{2\epsilon+\epsilon_m}+\frac{12\pi N\mu^2\epsilon}{kT(2\epsilon+1)}M_c\left[\frac{4\pi P_0\mu}{(2\epsilon+1)kT}\right], \qquad (20)$$

where $M_c(x)$ is the derivative of $L_c(x)$,

$$M_c(x) = (1+2\cosh x)/(2+\cosh x)^2. \qquad (21)$$

It is convenient to introduce the dimensionless variables

$$\bar{T} = kT/N\mu^2, \qquad (22)$$

$$\bar{P}_0 = P_0\mu/kT. \qquad (23)$$

One thus obtains the following two simultaneous transcendental equations for the unknown quantities ϵ and $\bar{P}_0$

$$\bar{P}_0 - \frac{2\epsilon+\epsilon_m}{\bar{T}(2\epsilon+1)}L_c\left[\frac{4\pi\bar{P}_0}{2\epsilon+1}\right] = 0, \qquad (24)$$

$$\epsilon - 1 - \frac{3\epsilon(\epsilon_m-1)}{2\epsilon+\epsilon_m} - \frac{12\pi\epsilon}{\bar{T}(2\epsilon+1)}M_c\left[\frac{4\pi\bar{P}_0}{2\epsilon+1}\right] = 0. \qquad (25)$$

One notes immediately that, since $L_c(0)=0$ and $M_c(0)=\frac{1}{3}$, one *possible* solution of these equations is

$$P_0 = 0, \qquad (26)$$

$$\epsilon - 1 - \frac{3\epsilon(\epsilon_m-1)}{2\epsilon+\epsilon_m} - \frac{4\pi\epsilon}{\bar{T}(2\epsilon+1)} = 0. \qquad (27)$$

This is, in fact, the only possible solution at sufficiently high temperatures. Equation (27) is a cubic equation for ϵ and is essentially the Onsager solution for a mixture of polar and nonpolar liquids. The slight difference in appearance between Eqs. (27) and (35) of Ref. 12 arises because ϵ_m is defined as the dielectric constant that would be calculated if all polar molecules were replaced by void, whereas Onsager's n^2 is defined as the dielectric constant that would be calculated if all polar molecules were replaced by nonpolar molecules. The inclusion of steric hindrances makes no difference in this limit, since $M_c(x)$ goes to the same limiting value of $\frac{1}{3}$ as the derivative of the Langevin function when x goes to zero. In the high-temperature limit, the last term in Eq. (24) may be dropped and the resulting quadratic equation yields simply $\epsilon = \epsilon_m$ which is expected, since the permanent dipoles can make no contribution to the dielectric constant at high temperatures. In order to find an approximate solution at somewhat lower temperatures, one may substitute $\epsilon = \epsilon_m + \Delta$ in Eq. (27) and solve to first order in Δ assuming that $\bar{T} \gg 1$. One obtains

$$\epsilon \cong \epsilon_m + (12\pi\epsilon_m^2/(1+2\epsilon_m)^2\bar{T}), \quad \bar{T} \gg 1. \qquad (28)$$

At low temperatures, ϵ becomes large and the second and third terms of Eq. (27) become small compared to the fourth term. In this limit, therefore,

$$\epsilon \cong 2\pi/\bar{T}, \quad T \ll 1. \qquad (29)$$

It is easy to show that, in general, Eq. (27) has only one positive root and that ϵ therefore varies smoothly between the limits given by Eqs. (28) and (29), provided that $\bar{P}_0 = 0$.

At low temperatures, one may anticipate that a possible solution of Eqs. (24) and (25) exists for which $\bar{P}_0 \neq 0$. In this case, one easily finds that as $\bar{T} \to 0$, $(\bar{T})^{-1}M_c(\bar{P}_0) \to 0$ and therefore Eq. (25) yields

$$\epsilon \to \epsilon_m, \quad \bar{T} \to 0. \qquad (30)$$

This is to be expected since at absolute zero the dipoles become frozen in position and cannot contribute to the dielectric constant. In the same limit, since $L_c(\bar{P}_0) \to 1$, one finds from Eq. (24) that

$$P_0 \to P_0^{\max} = (3\epsilon_m/(2\epsilon_m+1))N\mu, \quad \bar{T} \to 0. \qquad (31)$$

For $\epsilon_m = 1$, this result simply means that all the permanent dipoles are lined up parallel to each other at absolute zero. For $\epsilon_m > 1$, Eq. (31) shows that the polarizable molecules also contribute to the spontaneous

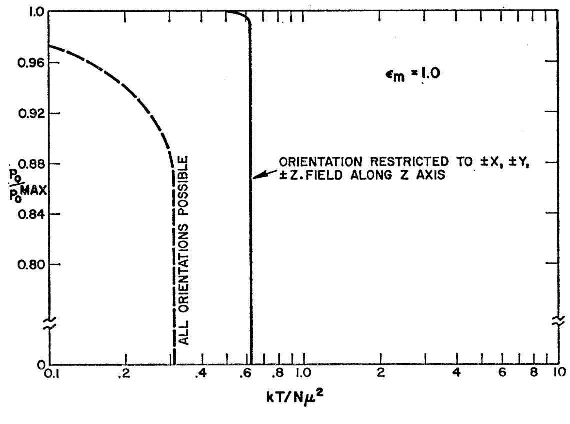

FIG. 3. Spontaneous polarization for $\epsilon_m = 1.0$.

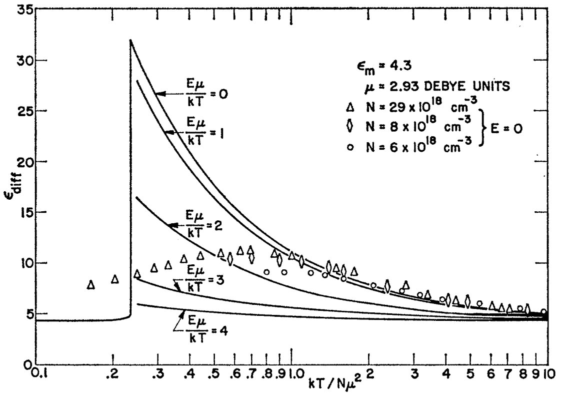

FIG. 4. Differential dielectric constant for $\epsilon_m = 4.3$ and for several values of dc bias.

polarization—they are polarized by the local field due to the permanent dipoles.

An exact solution of Eqs. (24) and (25) may be readily obtained by means of a suitable numerical iterative procedure. The Newton-Raphson method[17] was found to be convenient; the equations were programmed in FORTRAN for the RCA 601 computer at RCA Laboratories.

The numerical calculations require an initial guess for ϵ and $\bar{P}_0$. It is convenient to carry out preliminary computations using for guesses the known zero-temperature results $\epsilon = \epsilon_m$ and $\bar{P}_0 = 3\epsilon_m/(2\epsilon_m+1)\bar{T}$, in order to find the approximate Curie temperature T_c below which a nonzero $\bar{P}_0$ can exist. Then, by extrapolating the calculated low-temperature values of ϵ and $\bar{P}_0$, one may obtain improved guesses in order to obtain the precise value of T_c. Some care is necessary, since $\bar{P}_0 = 0$ is always a possible solution and if poor initial guesses are put into the program the numerical iteration may lead to this solution, or to a nonphysical solution with $\epsilon < 0$, even though the equations actually admit a solution with $P_0 > 0$ and $\epsilon > \epsilon_m$.

The results of computations for $\epsilon_m = 1$, i.e., a system consisting only of permanent dipoles, are shown in Figs. 2 and 3. In order to investigate the effect of steric hindrances, calculations were also carried out for freely rotating dipoles, i.e., using the usual Langevin function instead of $L_c(x)$. In either case, one notes that ϵ follows the Onsager result, Eq. (27), for temperatures down to a Curie temperature T_c, at which point it drops abruptly to a value only slightly larger than 1. The effect of including steric hindrances in the calculation is to increase T_c by roughly a factor of 2, a reasonable result since if it is hard for the dipoles to rotate one would expect to be able to freeze them into fixed positions at a higher temperature. The spontaneous polarization decreases only slightly from its saturation value as the temperature is raised from 0°K to T_c, at which point it drops abruptly to zero. The result shown in Fig. 3 for freely rotating dipoles was previously obtained by Pirenne.[14]

The results of computations for $\epsilon_m = 4.3$, an approximate value for KCl at low temperatures, are shown in Figs. 4 and 5. The results are qualitatively similar to those for $\epsilon_m = 1$ but the Curie point is lower by roughly a factor of 3. This last result may be qualitatively understood by noting that at the Curie temperature the thermal energy of a typical dipole must be approximately equal to its potential energy in the field of the other dipoles taking into account the screening effect of the polarizable medium in which the dipoles are embedded. Thus, one expects

$$kT_c \cong N\mu^2/\epsilon_m, \qquad (32)$$

in agreement with the exact calculations.

D. Calculations for Finite Applied Fields

In the following, $\epsilon(E,T)$ is used to denote the dielectric constant which one would infer from a measurement of the electric polarization resulting from the application of a finite field E at a temperature T. Thus, one has by definition

$$\epsilon(E,T) \equiv 1 + 4\pi \left\{ \frac{P(T,E) - P_0(T)}{E} \right\}, \qquad (33)$$

which should be compared with Eq. (20). The method of calculating $P_0(T)$ has already been given so that it will now be considered simply as a known number. The quantity $P(T,E)$ is given by Eq. (19), it being now understood that ϵ is a function of E as well as T. Thus, Eq. (33) yields a transcendental equation for $\epsilon(E,T)$. It is convenient to introduce the dimensionless variable

$$\bar{E} = E\mu/kT, \qquad (34)$$

and Eq. (33) can now be written as

$$\epsilon - 1 - \frac{3\epsilon(\epsilon_m - 1)}{2\epsilon + \epsilon_m} + \frac{4\pi\bar{P}_0(2\epsilon+1)}{\bar{E}(2\epsilon+\epsilon_m)} - \frac{4\pi}{\bar{E}\bar{T}} L_c\left[\frac{3\epsilon\bar{E} + 4\pi\bar{P}_0}{(2\epsilon+1)}\right] = 0. \qquad (35)$$

One notes that if, in Eq. (35), one assumes $\bar{E}$ to be small, expands the modified Langevin function to first order in $\bar{E}$, and uses Eq. (24), one obtains again Eq. (25). Equation (35) can be readily solved numerically by means of the Newton-Raphson method.[17] A convenient initial guess for $\epsilon(\bar{E},\bar{T})$ is $\epsilon(0,\bar{T})$. Having found $\epsilon(\bar{E},\bar{T})$, the dimensionless displacement vector $\bar{D}(\bar{E},\bar{T}) = D\mu/kT$ can be calculated from

$$\bar{D}(\bar{E},\bar{T}) = \epsilon(\bar{E},\bar{T})\bar{E} + 4\pi\bar{P}_0(\bar{T}). \qquad (36)$$

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[17] See, for instance, J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, 1962), 5th ed., Chap. 10.

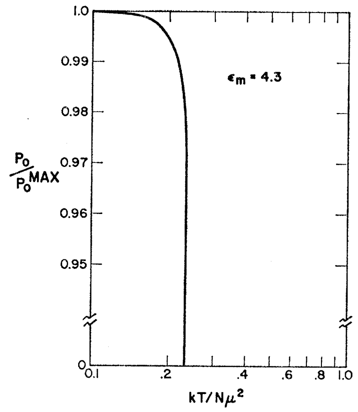

FIG. 5. Spontaneous polarization for $\epsilon_m=4.3$.

It should be recalled at this point that Eqs. (35) and (36) are based on the assumption that E is parallel to P_0. If one wished to calculate hysteresis loops, one would also have to carry out the computations for E antiparallel to P_0 in which case one would simply replace E by $-E$.

Another quantity that is of interest is the dielectric constant that one would measure by determining the polarization induced by an infinitesimally small field in the presence of a large bias field. This is the dielectric constant that one would infer if, in an experiment of the usual type in which one measures the resonant frequency of a circuit containing a capacitor filled with the material under study, one were to add a large dc bias. Roughly speaking, "large" means that $\bar{E}=E\mu/kT$ is comparable to unity. The dielectric constant determined in this way may be referred to as the "differential dielectric constant at bias E" and is given by

$$\epsilon_{\mathrm{diff}}(\bar{E},\bar{T})=\left(\frac{\partial \bar{D}}{\partial \bar{E}}\right)_{\bar{E}}=\epsilon(\bar{E},\bar{T})+\frac{\partial\epsilon(\bar{E},\bar{T})}{\partial \bar{E}}\bar{E}. \qquad (37)$$

The quantity $\partial\epsilon(\bar{E},\bar{T})/\partial\bar{E}$ is readily evaluated using Eq. (35), which gives a somewhat complicated but straightforward expression for $\epsilon_{\mathrm{diff}}(\bar{E},\bar{T})$ in terms of $\epsilon(\bar{E},\bar{T})$. In Fig. 4, results for $\epsilon_{\mathrm{diff}}(\bar{E},\bar{T})$ are shown as a function of $\bar{T}$, for several values of $\bar{E}$. One notes that the calculated effect of a bias such that $\bar{E}=1$ is quite small, whereas for $\bar{E}=4$ one has almost complete saturation, i.e., $\epsilon=\epsilon_m$ at all temperatures, indicating that the dipoles are almost completely aligned by the dc bias so that they can contribute hardly at all to the differential dielectric constant.

III. COMPARISON WITH EXPERIMENT

It is important to note, first of all, that the theory developed in the present paper leads to a change in the value of μ to be inferred from the work of Kuhn and Lüty.[4] These authors assumed that the local field tending to orient a typical dipole was given by the Lorentz result $(\epsilon+2)E/3$. However, the theory developed in Sec. II B shows that one should use instead the "cavity field" given by $3\epsilon E/(2\epsilon+1)$; the "reaction field $g\boldsymbol{\mu}$ is always parallel to the dipole and hence, as Onsager pointed out,[12] it has no effect on the orientation. As a result, one finds that for an $(\mathrm{OH})^-$ dipole in KCl

$$\mu=2.93 \text{ Debye units.} \qquad (38)$$

Some experimental results from Ref. 1 are shown in Fig. 4, for comparison with the theoretical curve for zero bias. The values of N that were used were those determined in Ref. 1 by fitting the results to a Clausius-Mossotti formula at high temperatures; this procedure is not quite correct, of course, but it turns out that one gets essentially the same values by fitting the results to the Onsager result, Eq. (27). It is to be noted that the peak value of the oscillating field in all these experiments was only 15 V/cm so that even at $T=0.3$°K, the lowest temperature used, the peak oscillating field corresponds to $E\mu/kT\cong 0.004$. Thus the oscillating field is essentially infinitesimal and Eq. (20) or (37) is applicable.

The agreement between the theory and experiment is evidently rather good down to $kT/N\mu^2\cong 1$. The discrepancy at lower temperatures can be readily understood by recalling that the theory was based on the implicit assumption that the $(\mathrm{OH})^-$ ions are distributed uniformly throughout the crystal. In fact, since the distribution is random, localized regions in the crystal will have concentrations higher or lower than the average so that one would expect the sharp transition predicted by the theory to be somewhat smeared out in practice. To put it another way, below $kT/N\mu^2\cong 1$, one presumably has randomly distributed, locally ferroelectric regions in the crystal, and these regions grow in size and number as the temperature is reduced. This interpretation is in contradiction to the recent suggestion of Brout[18] that one has randomly distributed locally antiferroelectric regions. Further work may be desirable to determine which interpretation is correct, although the argument given in the second paragraph of Sec. I supports the ferroelectric interpretation.

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[18] R. Brout, Phys. Rev. Letters **14**, 175 (1965).