

## Dielectric Properties of Interacting Ion-Impurity Systems in KCl\*

M. E. BAUR†

*Department of Chemistry, University of California, Los Angeles, California 90024*

AND

W. R. SALZMAN

*Department of Chemistry, University of Arizona, Tucson, Arizona 85711*

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The theory of the dielectric properties of assemblies of interacting impurity ions in solids at low temperatures is discussed, with particular reference to KCl:OH<sup>-</sup>, KCl:Li<sup>+</sup>, and KCl:CN<sup>-</sup>. A quantum-mechanical approach in which the effects of zero-field splitting in the motional spectrum of the ions are included is maintained throughout. An analytical study of the properties of an especially simple model with features relevant to the problem of interacting impurity dipoles is presented. The dielectric virial-expansion formalism is introduced, and numerical results for the theoretical second dielectric virial coefficient  $B(T)$  for each of the three species are given. The question of convergence of the virial expansion is considered, and it is shown that convergence fails for the specific case of KCl:OH<sup>-</sup> at impurity densities so far studied. An alternative theory for this system is presented which gives numerical predictions in satisfactory agreement with experiment. The basic notion of this theory is that neighboring impurity ions are locked into coherent ferroelectric pairs. At sufficiently low temperatures, this pairing is partially disrupted by largely antiferroelectric interactions between distinct pairs.

### I. INTRODUCTION

RECENT work on the physical properties of impurity ions in KCl and other alkali-halide species has shown the existence of low-frequency localized modes associated with these impurity species (CN<sup>-</sup>, OH<sup>-</sup>, Li<sup>+</sup>).<sup>1-4</sup> The occurrence of low-temperature features in the heat capacity and dielectric properties of such "paraelectric" crystals have been explained in first approximation by regarding the impurities as isolated from each other and in interaction with the surrounding lattice ions.<sup>5-10</sup> The purpose of this paper is to discuss those features which may arise in the dielectric behavior of these doped crystals when the electrostatic interactions between impurity ions are considered, that is, in crystals at not too low impurity concentration. It has already been noted<sup>3</sup> that in hydroxide doped KCl, a rather significant density-dependent low-temperature anomaly in dielectric behavior occurs, and various theoretical interpretations have been adduced to account for this behavior.<sup>11-15</sup> No such striking anomaly

has yet been noted in other systems studied, but, as we shall discuss, there is reason to believe that similar phenomena may be generally observable in a wide class of such systems at sufficiently high impurity density, when impurity interactions are properly taken into account.

The point of departure for this work is the observation that the relevant experiments on impurity ion species in KCl have been carried out at temperatures sufficiently low so that the motion of a given ion in its lattice cavity cannot in general be considered entirely classical. That is,  $kT$  is less than or on the order of some zero-field splitting parameter  $\Delta$ . This splitting parameter is related to the shift of rotational-librational energy levels of the impurity ion under the lattice crystalline field and may be studied either in strong-coupling (pocket state)<sup>5</sup> or weak-coupling<sup>10</sup> limits. For the purposes of the present study, we shall assume  $\Delta$  to be known, either from experiment or calculation. In particular, we shall also assume that all nonstatic lattice effects<sup>9</sup> can be taken into account through an appropriate choice of  $\Delta$  and that no further attention need be given them. In view of the condition  $\Delta/kT \simeq 1$ , the systems here considered do not fulfill the criterion for classical dipole behavior as set out, e.g., in Van Vleck.<sup>16</sup> Hence they must be considered from a quantum-mechanical standpoint, in which the nonzero value of the zero-field splitting must be rigorously taken into account. Previous treatments of the interaction problem<sup>11-15</sup> have been deficient in this respect, and, as we shall show, there is reason to believe that certain essential physical features of the problem have been omitted thereby.

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† Present address: Institute for Theoretical Physics, Maliesingel 23, Utrecht, the Netherlands.

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The necessity of providing a quantum-mechanical treatment for the problem of interacting impurity ions at low temperatures requires that the approach be made in terms of a *temperature-dependent polarizability* for a given ion. This point of view has already been introduced in a previous paper.<sup>11</sup> It should be understood that the polarizability here referred to is determined only by the *motional* states of the ion in question, and does not include the relatively very tiny polarizabilities associated with electronic (and, in the case of CN<sup>-</sup> and OH<sup>-</sup>, internal vibrational) motions. At high temperatures, for isolated impurity ions, this polarizability takes the familiar Debye form  $m^2/3kT$ ,<sup>16</sup> but we shall here be mainly interested in the region of temperature in which this limit fails to apply.

In introducing the approach, it is convenient to present certain very elementary results derivable by trivial algebraic manipulations for the most simple possible model case, that of two two-level species in interaction through the electrostatic dipole-dipole potential. We believe that this model already discloses most of the physical features relevant to the more general cases of physical interest. It is, moreover, illustrative of certain aspects of the problem of molecular interactions through induced dipole-induced dipole forces not, in our experience, always thoroughly understood. Section II is devoted to the exposition of this model.

The treatment of the general case of interacting impurity ions may be formulated from the standpoint of the dielectric virial expansion<sup>17-19</sup> if the density of impurity ions is sufficiently low. This method is undertaken in Secs. III and IV, with a brief survey of the formalism in Sec. III and a presentation of numerical calculations of  $B(T)$ , the second dielectric virial coefficient, for three species (CN<sup>-</sup>, OH<sup>-</sup>, Li<sup>+</sup> in KCl) in Sec. IV. The question of convergence of the virial expansion is considered, and, in particular, it appears that the expansion does not converge for KCl:OH<sup>-</sup> at the densities so far studied experimentally.

In view of this, we undertake an alternative high-density approach in Sec. V and present numerical calculations for the KCl:OH<sup>-</sup> system. In this approach, the role of nearest-neighbor impurity-ion interactions is emphasized and a criterion developed for transition of the system from a high-temperature situation in which nearest-neighbor impurities form coherent pairs with weak effective interaction between pairs to a low-temperature situation in which longer-range effects eliminate coherence within pairs. Numerical calculations based on this picture lead to results in satisfactory agreement with experiment.

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## II. TREATMENT OF A SIMPLE MODEL

Many of the important physical features present in consideration of the case of interacting impurity ions are disclosed by examining the properties of a model which consists of two identical particles interacting through the Hamiltonian

$$H = H_{01} + H_{02} + r^{-3}[\mathbf{u}_1 \cdot \mathbf{u}_2 - 3r^{-2}(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})], \quad (1)$$

where  $H_0$  is the isolated particle Hamiltonian and  $\mathbf{u}$  is the dipole moment operator, and in which each particle is restricted to possess just two states, separated by the zero-field splitting energy  $\Delta$ . The two states may be labelled  $|0\rangle$  and  $|1\rangle$ , so that  $E_1 - E_0 = \Delta$ , and the transition dipole matrix element between these states is

$$\langle 0 | \mathbf{u} | 1 \rangle = \langle 1 | \mathbf{u} | 0 \rangle = \langle 0 | \mu_z | 1 \rangle \hat{z} = m \hat{z}, \quad (2)$$

where we choose the direction of the dipole moment operator to define the system's  $z$  axis. Further, the isolated particle eigenstates are assumed to have vanishing diagonal elements of  $\mathbf{u}$ , so that at temperatures  $kT \ll \Delta$ , the isolated particles are nonpolar and respond to an applied electric field  $F$  in the  $z$  direction through the zero-temperature polarizability  $\alpha_0(0)$ , where, according to standard second-order perturbation theory,<sup>18</sup>

$$\alpha_0(0) = 2m^2/\Delta. \quad (3)$$

We note that the assumption of a two-state pattern with vanishing diagonal elements of the dipole moment is not entirely consistent with the picture of the particles as embedded in three-dimensional space (the excited state should then be threefold degenerate) but corrections introduced by modifying the model in such a way as to remove this inconsistency are qualitatively unimportant and cumbersome to deal with. Further, the polarizability of the excited state is, on this model, just  $-\alpha_0(0)$ , so that if  $kT \cong \Delta$ , we have in elementary fashion

$$\alpha_0(T) = \alpha_0(0) \left( \frac{1 - \exp(-\Delta/kT)}{1 + \exp(-\Delta/kT)} \right). \quad (4)$$

At high temperatures,  $kT \gg \Delta$ , expansion of the exponentials and use of Eq. (3) leads immediately to

$$\alpha_0(T) = m^2/kT \quad (kT \gg \Delta), \quad (5)$$

which is the usual high-temperature Debye form except for a factor of 3 associated with degeneracy in the excited states of a true three-dimensional model.

In the presence of an electric field  $F$  of arbitrary strength in the  $z$  direction, a term  $\mu F$  is added to the Hamiltonian, and diagonalization of the secular equation

$$\begin{vmatrix} -\frac{1}{2}\Delta - E & mF \\ mF & \frac{1}{2}\Delta - E \end{vmatrix} = 0 \quad (6)$$

## INTERACTING TWO-LEVEL SYSTEMS

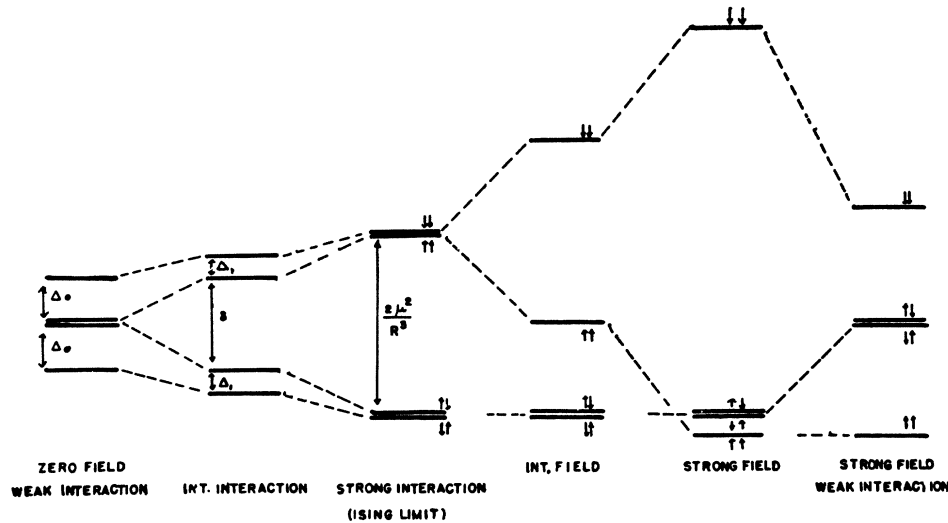


FIG. 1. Schematic diagram of effect of interaction and applied field on energy levels of a pair of two-level particles. Field direction taken perpendicular to interparticle vector. Arrows represent  $(|0\rangle \pm |1\rangle)/\sqrt{2}$ , i.e., states in the limit of complete polarization by either external fields or interaction.

for an isolated particle leads to the energies

$$E_0(F) = -(\frac{1}{4}\Delta^2 + m^2F^2)^{1/2} = -\frac{1}{2}\Delta(1 + 2m^2F^2/\Delta^2 + \dots), \quad (7)$$

$$E_1(F) = (\frac{1}{4}\Delta^2 + m^2F^2)^{1/2} = \frac{1}{2}\Delta(1 + 2m^2F^2/\Delta^2 + \dots).$$

The perturbation-theory result, of course, correctly represents the terms in the expansion on the right in Eqs. (7), which converges if  $mF < \frac{1}{2}\Delta$ . If this criterion is not satisfied,  $mF > \frac{1}{2}\Delta$  (strong field case), we have

$$E_0(F) = -mF(1 + \Delta^2/8m^2F^2 + \dots) \quad (8)$$

and accordingly for  $E_1(F)$ . In this way we see how for the elementary model passage from weak to strong applied fields brings the system from the limit of a polarizable but nonpolar particle to that represented in Eq. (8) in which the system is best considered to have a "permanent" dipole moment  $m$  and the zero-field splitting is represented as a perturbation. In the limit of strong fields, the exact eigenstates of the particle are essentially  $(|0\rangle \pm |1\rangle)2^{-1/2}$ , each of which now has a nonvanishing diagonal element of the dipole moment operator, of magnitude  $m$  and of direction parallel or antiparallel to the field. In this representation, the zero-field Hamiltonian  $H_0$  has only off-diagonal elements. From the general result (7) one finds for the polarizability of the ground and excited states in the presence of a field, using the definition

$$\alpha_j = -\frac{1}{F} \frac{\partial E_j}{\partial F}, \quad (9)$$

$$\alpha_0(F) = +m^2/(\frac{1}{4}\Delta^2 + m^2F^2)^{1/2}, \quad (10)$$

$$\alpha_1(F) = -m^2/(\frac{1}{4}\Delta^2 + m^2F^2)^{1/2}.$$

Thus, as  $F$  becomes large, the polarizability of either ground or excited state tends to zero as  $m/F$ . The

thermal average response to the field is in general given by the temperature and field-dependent polarizability  $\alpha(T, F)$ :

$$\alpha(T, F) = [m^2/(\frac{1}{4}\Delta^2 + m^2F^2)^{1/2}] \times \tanh[(\frac{1}{4}\Delta^2 + m^2F^2)^{1/2}/kT], \quad (11)$$

where we have used Eqs. (7) and (10). In the limit of high temperatures,  $kT \gg \Delta$ ,  $mF$ , we have

$$\alpha(T, F) = m^2/kT - m^2(\frac{1}{4}\Delta^2 + m^2F^2)/3(kT)^3, \quad (12)$$

which is seen to correctly reproduce the standard classical result (5). The second term represents a quantum correction to the classical result<sup>20</sup> for the response of a permanent dipole to a strong field (dielectric saturation), which has as first correction to the Debye term in the response function a term proportional to  $m^4F^2/(kT)^3$ .

Turning to the case of two two-level particles in interaction through the Hamiltonian (1) in the absence of a field, we note that an exact solution for the four states and four energies of the combined system is easily obtained. In this case,  $\mathbf{u} \cdot \mathbf{r} = \mu_z r \cos\theta = \mu_z r s$ , where  $s = \cos\theta$  and  $\theta$  is the angle between  $r$  and the  $z$  axis. The secular equation which must be solved is then

$$\begin{vmatrix} -\Delta - E & D & 0 & 0 \\ D & \Delta - E & 0 & 0 \\ 0 & 0 & -E & D \\ 0 & 0 & D & -E \end{vmatrix} = 0, \quad (13)$$

where  $D = m^2(1 - 3s)/r^3$ . The zero of energy is again chosen so that the energies of the unperturbed isolated particle states are  $\pm \frac{1}{2}\Delta$ . In the secular determinant, the elements in the upper left-hand corner mix the  $|00\rangle$  and  $|11\rangle$  states of the two-particle set, and the elements in

<sup>20</sup> C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Inc., Houston, Texas, 1952), Chap. VI.

the lower right-hand corner mix the  $|01\rangle$  and  $|10\rangle$  states. The solutions of the secular equation are immediately found to be

$$\begin{aligned} E_0 &= -(\Delta^2 + D^2)^{1/2}, \\ E_1 &= -D, \\ E_2 &= D, \\ E_3 &= (\Delta^2 + D^2)^{1/2}. \end{aligned} \quad (14)$$

If one now expands the equation for  $E_0$ , assuming  $D \ll \Delta$ ,

$$\begin{aligned} E_0 &= -\Delta(1 + D^2/2\Delta^2 + \dots) \\ &= -\Delta - m^4(1 - 3s)^2/2r^6\Delta \\ &= -\Delta - \Delta\alpha_0^2(0)(1 - 3s)^2/8r^6. \end{aligned} \quad (15)$$

The correction term to the unperturbed energy on the right-hand side of Eq. (15) is evidently, apart from the geometrical factor  $(1 - 3s)^2$ , just the usual form of induced dipole, or van der Waals, interaction between nonpolar particles.<sup>21</sup> It is seen to be negative, leading to an attractive interaction, for all values of  $s \neq \frac{1}{3}$ . Again, the perturbation-theory result is identical to that obtained in Eq. (15) by expansion of the exact result. This expansion will converge if  $D^2 < 2\Delta^2$  (weak-interaction limit). For orientation, we note that for the case of two helium atoms, taking  $\Delta \simeq 1.6 \times 10^6 \text{ cm}^{-1}$  and  $\simeq 2.4 \text{ D}$ , the critical value of  $r$  below which the series (15) does not converge is about  $0.5 \text{ \AA}$ . On the other hand, for the case of two impurity ions, taking  $\Delta \simeq 1 \text{ cm}^{-1}$  and  $m \simeq 1 \text{ D}$ , the corresponding value of  $r$  is on the order of  $20 \text{ \AA}$ , and it is clear that even for values considerably larger than this, convergence will be slow. Therefore, although the application of perturbation theory is clearly appropriate to the calculation of energies and interaction effects on joint polarizabilities in the case of interacting neutral atoms in the gas phase,<sup>18</sup> it cannot be expected to be satisfactory in general for the case of interacting impurity ions in KCl, where the mean distance between impurities is on the order of  $20\text{--}100 \text{ \AA}$ . In addition, the limit  $D^2 > 2\Delta^2$  (strong-interaction limit) may be treated by perturbation theory, in which  $\Delta$  is regarded as the perturbation, but this limit also is seen not to be applicable in the case of the impurity-ion systems. It is appropriate to note certain points concerning the strong-interaction limit. As  $D$  increases, the separation  $\Delta_1 = E_1 - E_0$  in the interacting system decreases from  $\Delta$  to zero as  $\Delta^2/2D$ , and the separation  $\delta = E_2 - E_1$  rises from zero to a limiting form  $2D$ . This behavior is sketched qualitatively in Fig. 1, drawn specifically for the case  $s=0$ . In the strong-interaction limit, the lower pair of nearly degenerate states may be considered coherent mixtures of configurations in which the individual particles have opposed dipole moments in an essentially classical sense. The upper pair of states

similarly are mixtures of configurations in which the dipole moments are aligned in the same direction, as shown in the figure. It seems appropriate to call this limit in which the interaction completely quenches the zero-field splitting the Ising limit, since here the picture of classical dipolar particles in interaction, with two possible orientations of dipole moment for each particle, becomes applicable. It is important to note that a similar diagram could be drawn for  $s=1$ , i.e., when  $r$  lies along the  $z$  axis. In this case, however, the lower levels in the Ising limit would correspond to the two dipole moments being aligned parallel to one another, along the  $z$  axis, with total dipole moment in either the  $+z$  or  $-z$  direction, and the upper levels would correspond to the two possible antiparallel alignments of the dipoles along the  $z$  axis.

It is possible to write out general expressions for the polarizability of the interacting two-level systems as a function of field and temperature. The solution of the secular equation for the case when a field of arbitrary strength is present unfortunately leads to a quartic equation of general form. The display of the solutions of this equation is cumbersome and unenlightening, and we shall omit it. The general aspect of the behavior of the levels in the presence of an external field along the  $z$  axis is indicated in Fig. 1 for the case  $s=0$ . Here, the effect of the field and of the interaction run opposite to one another, because the field tends to enhance parallel alignment of the dipoles while the effect of the interaction is to enhance antiparallel alignment. One should not, however, push this classical language too hard; for purposes of calculation it is preferable to actually write out the states obtained by exact solution of the secular equation and examine the appropriate dipole moment matrix elements. Not shown in Fig. 1 is the behavior of the interacting system in the presence of a field when  $s=1$ , i.e., when  $r$  is parallel to the  $z$  axis and to the field. In this case, the tendency of the particles to form parallel dipoles along the  $z$  axis in the presence of a field is reinforced by the interaction effect, so that the field strengthens the coherence in effective alignment of the matrix elements of dipole moment. Put another way, if  $s=1$ , in the intermediate or strong-interaction case, one finds two closely spaced levels at the bottom of the manifold of four levels, corresponding to a coherent mixture of up and down dipole configurations. Because of the close spacing of these levels, the lowest of them has an extremely high polarizability and a greatly enhanced response to an applied electric field along the  $z$  axis.

The best manner in which to display the quantitative behavior of a set of two interacting two-level particles is by the plotting of exactly determined temperature-dependent polarizabilities. We have carried out the determination of such polarizabilities for low applied field, using the obvious extension of Eq. (4) and the energies and wave functions obtained by the solution of Eq. (13). The computation was carried out by computer,

<sup>21</sup> See, e.g., M. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), Chap. VIII.

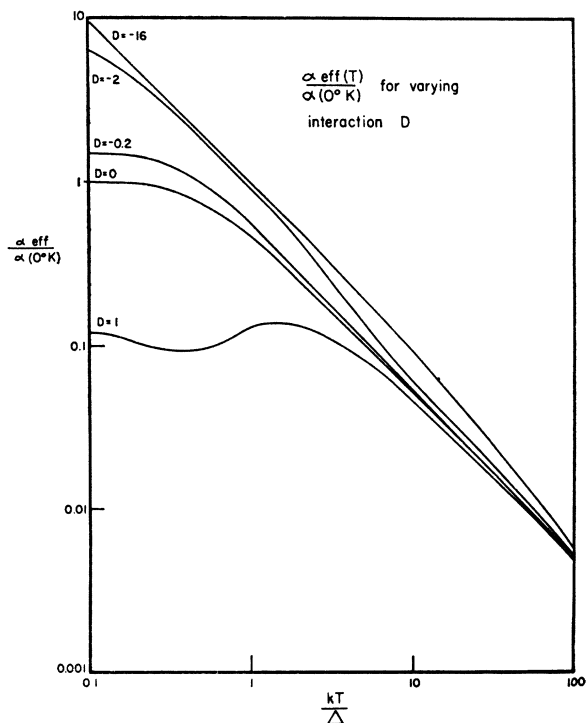


FIG. 2. Reduced effective single-particle polarizability for a pair of interacting two-level particles for selected values of the interaction parameter  $D$ .

and the numerical values of the reduced effective single particle polarizability  $\alpha_{\text{eff}}(T)/\alpha_0(0)$  are presented as a function of the reduced temperature  $kT/\Delta$  in Fig. 2. Here  $\alpha_{\text{eff}}(T)$  is half the total polarizability in the field direction ( $z$  direction) of the set of two two-level particles. The value of  $\alpha_{\text{eff}}(T)$  depends on the magnitude and sign of  $D$  as shown; for clarity we present results for only certain  $D$  values. Positive values of  $D$  correspond to orientations in which the interparticle vector  $\mathbf{r}$  is nearly perpendicular to the applied field, with resultant near compensation of field and interaction effects and consequently a very small value of  $\alpha_{\text{eff}}(T)$ . Negative values of  $D$  correspond to orientations in which  $\mathbf{r}$  is nearly parallel to the applied field, so that field and interaction effects reinforce producing an enhancement of the response to the field and a large  $\alpha_{\text{eff}}(T)$ . At very high temperatures, when  $kT \gg \Delta$ ,  $D$ ,  $\alpha_{\text{eff}}(T)$  assumes the usual  $\mu^2/kT$  form displayed in Eq. (5).

### III. DIELECTRIC VIRIAL FORMALISM

The use of a virial expansion for the calculation of the dielectric properties of dilute nonpolar gases is familiar.<sup>17-19</sup> The same technique is applicable with little change to the case of a dilute assemblage of lattice impurities, if appropriate care is taken with distance and angle weighting factors. The basic notion is that the polarizability of a pair of interacting particles is, in general, different from the sum of the independent

particle polarizabilities,<sup>18</sup> as seen in the case of the special model in Sec. II. For the simple case of an ideal nonpolar gas, we have the Clausius-Mossotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \alpha_0, \quad (16)$$

where  $\epsilon$  is the dielectric constant,  $\rho$  is the particle density, and  $\alpha_0$  is the isolated atom polarizability. More generally, if the specimen of interest is placed in an electric field  $F$  and exhibits a total moment  $M(F)$ , the Clausius-Mossotti function is given by

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\rho}{N_{\text{av}}} \left( \frac{\partial M}{\partial F} \right)_{F=0}. \quad (17)$$

By appropriate manipulation of the thermodynamic average involved in the evaluation of  $M$ , one finds

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \left\langle \frac{\partial \mu_1}{\partial F} \right\rangle_{\text{av}}, \quad (18)$$

where  $\mu_1$  is the component in the field direction of the dipole moment induced in a single member of the assembly by the combination of external field  $F$  and particle interactions. If one now seeks a systematic expansion of the Clausius-Mossotti function in terms of density,

$$\frac{1}{\epsilon + 2} = \rho(A + B\rho + \dots), \quad (19)$$

we find that  $A = \frac{4}{3}\pi\alpha_0(T)$ , where now we explicitly include the possible dependence of  $\alpha_0$  on temperature, and<sup>22</sup>

$$\begin{aligned} B &= \lim_{\rho \rightarrow 0} \frac{1}{\rho} \left( \frac{\epsilon - 1}{\epsilon + 2} - A \right) \\ &= \lim_{\rho \rightarrow 0} \frac{4\pi}{3\rho} \left[ \left\langle \frac{\partial \mu_1}{\partial F} \right\rangle_{\text{av}} - \alpha_0(T) \right]. \end{aligned} \quad (20)$$

We now introduce the distribution function  $\rho g_2(\mathbf{r})$  which gives the probability, given that a particle is present at the origin, that a second particle is present at position  $\mathbf{r}$ . In the general case, we should have to include in  $g_2(\mathbf{r})$  also a dependence on relative angular orientation of the interacting particles. However, for spherical particles or, as in the present application, for particles subject to a local environment of cubic symmetry with the same sense of axes maintained throughout the medium, this inclusion is unnecessary. Hence we arrive at the result

$$B = \frac{4\pi}{3} \int \int \int d^3r \left[ \frac{1}{2} \alpha_{12}(\mathbf{r}, T) - \alpha_0(T) \right] g_2(\mathbf{r}), \quad (21)$$

<sup>22</sup> It should be pointed out that in this derivation we have suppressed certain terms which are only nonvanishing for interacting unlike particles; see Ref. 18.

with the evident identification

$$\frac{1}{2}\alpha_{12} = \frac{\partial\mu_1}{\partial F} = \frac{1}{2} \left( \frac{\partial(\mu_1 + \mu_2)}{\partial F} \right). \quad (22)$$

The formula (21) above for  $B$  differs from that in Ref. 18 by omission of a factor  $N_{av}$ , since we choose to work throughout in terms of number density rather than mole density.

If the interacting particles are immersed in a medium which is sufficiently decoupled from them to be described in terms of its electric properties in terms only of a lattice dielectric constant  $\epsilon_L$ , we have for the Clausius-Mossotti expression for the combined system

$$\frac{\epsilon_x - 1}{\epsilon_x + 2} = \frac{\epsilon_L - 1}{\epsilon_L + 2} + \frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_L - 1}{\epsilon_L + 2} + \rho(A + B\rho + \dots), \quad (23)$$

where  $\rho$  is the density of the interacting particles,  $\epsilon$  is the dielectric constant associated with them, and  $\epsilon_x$  is the experimentally determined total dielectric constant. In the case of interest here, we note that the dielectric constant of alkali-halide lattices is not strongly dependent upon applied field and should hence not be much influenced by the presence of impurities. Equation (23) is the fundamental relation for comparison with experiment in the virial-expansion approach.

#### IV. SECOND DIELECTRIC VIRIAL COEFFICIENT FOR IMPURITY IONS

It is appropriate to summarize the present picture of the nature and splitting of the lowest manifold of motional states of impurity ions in alkali halides before undertaking the application of the formalism of Sec. III to the dielectric effects associated with them. It is believed that these impurities ( $\text{Li}^+$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ) are substitutional in the lattice and hence, in KCl and other alkali-halide crystals, are subject to a crystalline field of octahedral symmetry. Those motions of the  $\text{OH}^-$  and  $\text{CN}^-$  ions which correspond to gas phase rotational modes are strongly affected by this field, and in particular a lowest manifold of states is developed which may be regarded as derived from rotational states. Alternatively, they may be regarded as derived from localized pocket states split by tunnelling. In any case, symmetry requirements fix the degeneracies of the lowest manifold and determine the number of independent energy separations which may be present within it. In the case of  $\text{Li}^+$  in KCl, it is believed that the impurity ion is subject to a crystalline field with off-center minima in the cavity, and hence also develops a lowest manifold (of eight states) which may be regarded as associated with an orbiting motion of the ion around the periphery of the cavity.<sup>23</sup> The KCl:Li system may

then be treated from the same standpoint as the others for our purposes. There is good evidence in each of the three cases considered here that no higher manifold excited motional states lie within energies on the order of  $10\Delta$  of the lowest manifold, where  $\Delta$  represents the average splitting within the lowest manifold. Hence it is a good approximation, for  $kT < 10\Delta$ , to regard the lowest manifold states as an independent system, and this approximation characterizes all interpretations of experimental thermodynamic data at very low temperatures.

The lowest manifold motional states of the impurity ions then must be eigenfunctions of a Hamiltonian of symmetry  $O_h$  (in the absence of applied strains or electric fields) and must correspond to representations of this group. No such state can have a nonvanishing diagonal matrix element of dipole moment, by symmetry, and hence at temperatures low compared with  $\Delta/k$  the impurity ions must be regarded as polarizable, but nonpolar, species with a temperature-dependent polarizability  $\alpha(T)$ . Clearly, at high temperatures  $\alpha(T)$  passes to the classical value  $m^2/3kT$ . (If  $T$  is great enough to make the motions of the ions become classical, it is also high enough for the classical free rotor result to be applicable.) Note that this point of view differs in no way from that applicable to, say, the properties of a dipolar gas at low enough temperature for quantization of molecular rotation to be important. If one were to study the dielectric properties of HCl in the vapor at  $0.1^\circ\text{K}$ , the species would have to be regarded as polarizable but nonpolar. Similarly, if one could study the dielectric properties of H atoms at temperatures sufficiently great so that  $kT$  were comparable to or greater than the  $(1s)-(2p)$  splitting of electronic energy levels, which is in this case the zero-field splitting, the H atoms would have to be considered a polar species. (Obviously under these conditions dissociation would occur, so that the experiment is not feasible.)

The most efficient way of handling the problem of interactions within the impurity system in the quantum limit, then, appears to be to take over the formalism already sketched in Sec. III for the dielectric properties of polarizable, but nonpolar, gases in interaction. One fundamental difference which enters and which should be noted is that the polarizability of most nonpolar gas species is entirely temperature-independent in the range of  $T$  of experimental interest, so that the temperature dependence of the second dielectric virial coefficient arises only from the temperature dependence of the pair distribution function  $g_2(r, T)$ , whereas in the impurity-ion case,  $g_2(r)$  is temperature-independent at the temperatures of interest, and the entire  $T$  dependence of  $B(T)$  comes from the  $T$  dependence of polarizability. It would be interesting to envisage a system in which both  $\alpha$  and  $g_2$  need to be considered  $T$ -dependent, but we are unaware of any physical examples of this. It is clear that the calculation of  $B(T)$  in the impurity-ion case, then, must be undertaken numerically, if recourse is not to be

<sup>23</sup> This picture seems to fail for  $\text{Li}^+$  in KBr, according to recent experimental measurements; see J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. 171, 1037 (1968).

had to perturbation theory or some other approximate method in the construction of the joint two-particle polarizability  $\alpha_{12}(T)$ . As was shown in Sec. II, the introduction of the thermal weighting factors for states of different energy produced unwieldy analytical forms even in the most simple model, and this feature becomes even more severe for the realistic case of impurity ions. For these cases, the total number of states available to an interacting pair is 36 or 64, depending upon whether the lowest manifold of an isolated impurity comprises six or eight states, and the number of distinct eigenenergies becomes correspondingly large. The two central questions from a computational standpoint, then, are the choice of a form for  $g(\mathbf{r})$ , and, concomitant with it, of a procedure for summing over lattice sites; and the method for computing  $\alpha_{12}(T)$  and  $\alpha_0(T)$  exactly. We now discuss these two points in sequence.

The integral defining  $B$  in Eq. (21) should, rigorously, be replaced by a lattice sum in the present problem. The computational problem involved in doing lattice summations here would be intractable. Furthermore, we anticipate that the major contribution to the integral in Eq. (13) will be from interaction distances large compared with the lattice spacing, so that we may treat  $\mathbf{r}$  as a continuous variable. It is only for distances between impurity ions on the order of a few lattice spacings that this approximation will be significantly in error. It should also be noted that work on related classical problems<sup>24</sup> indicates that no very great error from the use of this approximation arises in cases where it might be expected to be even more serious.

In accordance with the assumption of a random distribution of impurities, it is consistent to choose for  $g_2(\mathbf{r})$  a step function, with

$$\begin{aligned} g_2(\mathbf{r}) &= 0 & (\mathbf{r} < \mathbf{r}_{\min}), \\ g_2(\mathbf{r}) &= 1 & (\mathbf{r} \geq \mathbf{r}_{\min}). \end{aligned}$$

Here  $\mathbf{r}_{\min}$  is taken to be the minimum distance between the impurity species in the lattice, i.e., the distance between nearest-neighbor sites of the same charge.

Turning to the calculation of the two-particle polarizability  $\alpha_{12}(\mathbf{r}, T)$  and the isolated particle polarizability  $\alpha_0(T)$ , we note that the calculation of the latter has already been illustrated.<sup>11</sup> In general,

$$\alpha_0(T) = \sum_n \alpha_0(n) \exp\left(\frac{-E_n}{kT}\right) / \sum_n \exp\left(\frac{-E_n}{kT}\right), \quad (24)$$

where the index  $n$  denotes the eigenstates of the isolated impurity,  $E_n$  is their energies, and  $\alpha_0(n)$  is the polarizability of each state, calculated by second-order perturbation theory. It follows from the use of a finite manifold of states that some of these individual state polarizabilities are negative. In the calculation of  $\alpha_{12}(\mathbf{r}, T)$  the fundamental quantum-mechanical problem which must be solved is the diagonalization of the two-

impurity Hamiltonian

$$H_{12} = H_{01} + H_{02} + (\epsilon_L r^3)^{-1} \times [\mathbf{u}_1 \cdot \mathbf{u}_2 - 3r^{-2}(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})], \quad (25)$$

identical with  $H$  in Eq. (1) except for the inclusion of the dielectric constant of the medium intervening between the two particles, in the present case that of the alkali-halide lattice  $\epsilon_L$ . The isolated particle Hamiltonians  $H_{01}$  and  $H_{02}$  are characterized only through the zero-field splitting parameters  $\Delta$ , assumed known. The computation of  $\alpha_{12}(\mathbf{r}, T)$  then proceeds as follows: We calculate the exact eigenstates of the Hamiltonian  $H_{12}$  within the basis set of 36 or 64 states contained within the direct product of the isolated impurity basis states to obtain exact energies  $E_j$  (12) and eigenfunctions  $|j(12, \mathbf{r})\rangle$ . The dielectric properties of  $\text{OH}^-$  in KCl have been measured with the direction of electric field along the  $[100]$  axis, so we have restricted our further calculation of interacting impurity polarizability to the component  $\alpha_{zz, 12}(\mathbf{r}, T)$ . Because of the high symmetry of the octahedral sites in which the impurities reside, there should not be a great dependence of observed dielectric properties upon field direction, and we believe that this calculation is accordingly sufficiently general. We shall in what follows suppress the indices on  $\alpha_{12}(\mathbf{r}, T)$  since only the  $zz$  component is treated. In performing the diagonalization of  $H_{12}$ , it is convenient to work entirely in a matrix formalism in which the operators  $\mathbf{u}$  are written as  $6 \times 6$  or  $8 \times 8$  matrices, with elements  $m$ , the transition dipole matrix elements between states of the isolated impurity manifold. Similarly,  $H_{01}$  and  $H_{02}$  are treated as matrices of like dimension, diagonal within the isolated impurity basis. The matrices  $\mathbf{u}$  have, of course, zero diagonal elements with this choice of basis.

With the exact states for the interacting two-particle system in hand, the joint two-particle polarizability as a function of  $T$  is computed according to

$$\alpha_{12}(\mathbf{r}, T) = \sum_j \alpha_{12j}(\mathbf{r}) \exp\left(\frac{-E_j}{kT}\right) / \sum_j \exp\left(\frac{-E_j}{kT}\right), \quad (26)$$

where  $j$  runs over the 36 (or 64) states of the pair, and  $E_j$  and  $\alpha_{12j}(\mathbf{r})$  are the energy and polarizability of state  $j$ . Explicitly,

$$\alpha_{12j}(\mathbf{r}) = 2 \sum_{i \neq j} \frac{|\langle j(\mathbf{r}) | \mu_{1z} + \mu_{2z} | i(\mathbf{r}) \rangle|^2}{E_j - E_i}, \quad (27)$$

where  $\mu_z$  is the  $z$  component of the dipole moment operator. In carrying out these calculations, the origin of coordinates is taken at the cavity center of one of the impurities and a vector  $\mathbf{r}$  is drawn to the cavity center of the other impurity. The presence of the crystal lattice and the fixed orientations of the impurity eigenstates with respect to the lattice directions dictates our choice of coordinate system. If we were treating the interactions of two molecules in free space, we would be free to choose the  $z$  axis along  $\mathbf{r}$ , which would con-

<sup>24</sup> R. Rosenberg and M. Lax, *J. Chem. Phys.* **21**, 424 (1953).

siderably simplify angle averages. The simplicity in the free-molecule case is due to the fact that the wave functions for a free molecule form the bases of irreducible representations for the full rotation group, whereas our impurity wave functions form bases for irreducible representations only of  $O_h$ . In the present impurity case, we choose a right-hand Cartesian system with axes along the crystalline [100] directions. The question of performing angle averages over  $\mathbf{r}$  with this choice of coordinates must then be examined. Consider a second impurity ion to be placed somewhere on the surface of a sphere of radius  $r$  surrounding the first impurity ion. By symmetry, the angle average of the two-particle polarizability over one octant is equivalent to an average over the entire sphere, so that we may restrict our choices of angle to those within one octant. In principle, it is necessary to diagonalize  $H_{12}$  for all angles in this octant, since the interaction between two impurity ions will depend upon the angle between  $\mathbf{r}$  and the lattice [100] axis. For example, two impurities on the same [100] axis will have a different polarizability than two impurities on the same [111] axis. As an alternative to this impossibly cumbersome procedure, we have selected a set of representative orientation directions such that any terms whose angular dependence would cause them to average to zero with a full spherical averaging will in fact vanish, thus eliminating spurious  $r$  dependences. The [100], [110], and [111] axes provide such a set of orientation directions. Taking full advantage of the symmetry of the problem, it is possible to cover all 26 possible directions with diagonalizations along only these three principal axes.

A computer program<sup>25</sup> was written to diagonalize the Hamiltonian  $H_{12}$  within the combined impurity basis set for the choice of orientations described above and for not less than eight values of  $r$  in the range from  $r_{\min}$  to 500 Å. For each value of  $r$  and orientation, the polarizability was computed using Eqs. (27) and (26), and the result averaged over the sphere for each  $r$  to give  $\alpha_{12}(r, T)$  over the range 0.005–100°K. Graphical inte-

TABLE I. Zero-Field splitting parameters for impurity ions in KCl.

Ion species		Splittings (cm <sup>-1</sup> )
Li <sup>+</sup> <sup>a</sup>	$A_{1g}-T_{1u}$	0.8
	$T_{1u}-T_{2g}$	0.8
	$T_{2g}-A_{2u}$	0.8
CN <sup>-</sup> <sup>a</sup>	$A_{1g}-T_{1u}$	1.4
	$T_{1u}-E_g$	0.7
OH <sup>-</sup> <sup>a</sup>	$A_{1g}-T_{1u}$	0.15 <sup>b</sup> (BS); 0.14 <sup>c</sup> (FSS)
	$T_{1u}-E_g$	0.03 <sup>b</sup> (BS); 0.07 <sup>c</sup> (FSS)

<sup>a</sup> Reference 5.

<sup>b</sup> Reference 11.

<sup>c</sup> G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Letters 16, 500 (1966).

<sup>25</sup> Assistance was obtained from the Health Sciences Computing Facility, UCLA, sponsored by National Institutes of Health Grant No. FR-3.

TABLE II. Magnitude of transition-dipole-moment matrix elements for impurity ions in KCl.<sup>a</sup>

Ion species		Moment (in D)
Li <sup>+</sup>	$A_{1g}-T_{1u}$	1.5
	$T_{1u}-T_{2g}$	1.15 (for symmetry allowed components)
	$A_{2u}-T_{2g}$	1.15
CN <sup>-</sup>	$A_{1g}-T_{1u}$	0.17
	$T_{1u}-E_{2g}(x^2-y^2)$	0.21
	$T_{1u}-E_{2g}(z^2)$	0.12
OH <sup>-</sup>	$A_{1g}-T_{1u}$	0.565 (BS); 1.05 (FSS)
	$T_{1u}-E_{2g}(x^2-y^2)$	0.547 (BS); 1.29 (FSS)
	$T_{1u}-E_{2g}(z^2)$	0.89 (BS); 0.74 (FSS)

<sup>a</sup> We do not here give the detailed breakdown in direction for the matrix elements. For tabulation of these, see W. R. Salzman, Ph.D. dissertation, University of California at Los Angeles, 1967 (unpublished).

gration was carried out over  $r$  in computing  $B(T)$  in accordance with Eq. (21).

### A. Results

We have carried out the calculations described above for three species now sufficiently well characterized so that zero-field splitting parameters and transition dipole matrix elements can be taken with some confidence from available data: Li<sup>+</sup>, CN<sup>-</sup>, and OH<sup>-</sup>, all in KCl. The lattice dielectric constant  $\epsilon_L$  for KCl has been taken throughout as 4.33. The values of the other fundamental parameters assumed are tabulated in Tables I and II. The dipole moment matrix elements given in Table II do not correspond in a simple fashion to the effective classical dipole moment of the species which would be inferred from high-temperature  $1/T$  dependence of the Clausius-Mossotti function. For reference, we give the latter values which are consistent with the above matrix elements: OH<sup>-</sup>, 1.82 D; CN<sup>-</sup>, 0.30 D; Li<sup>+</sup>, 2.00 D.

The isolated particle polarizabilities  $\alpha_0(T)$  which follow from these choices of parameter were calculated by computer and are displayed in Fig. 3. The peak in  $\alpha_0(T)$  for the OH<sup>-</sup> ion at about 0.1°K using the parameters of Ref. 11 should be noted. The parameters were, of course, originally chosen in order to introduce a peak at about this temperature in this species, on the basis of the observation that extrapolation of the peak temperatures in Ref. 3 to zero density appears to give a finite value of about 0.1°K which would accordingly have to be explained as an isolated particle effect.

It was observed in our calculations of  $\frac{1}{2}\alpha_{12}$  that this quantity is smaller than  $\alpha_0$  for configurations in which the angle  $\theta$  between  $\mathbf{r}$  and the  $z$  axis approaches  $\frac{1}{2}\pi$ , and greater than  $\alpha_0$  if  $\theta$  is zero or  $\pi$ . The reason for this is exactly the same as for the similar behavior shown in Fig. 2 in the case of the interacting two-level systems, and qualitatively the behavior indicated there can be taken as representative for the interacting impurity-ion case. In the angle average, the contributions of the  $\theta=0$  or  $\pi$  configurations dominate for all cases at all temperatures, so that the integrand in Eq. (13) is always posi-



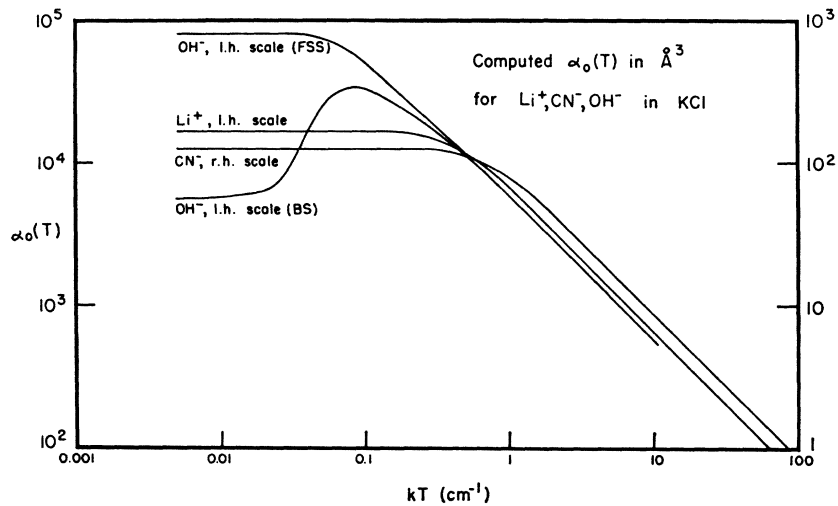


FIG. 3. Isolated particle polarizabilities for  $\text{KCl}:\text{OH}^-$ ,  $\text{KCl}:\text{Li}^+$ , and  $\text{KCl}:\text{CN}^-$  as a function of temperature. Results for both the BS and FSS choices of parameter for  $\text{KCl}:\text{OH}^-$  are shown.

tive after the angle integration has been performed. This behavior is shown in Fig. 4, a plot of the computer-determined values of  $(\frac{1}{2}\alpha_{12} - \alpha_0)r^6\epsilon_L^2$  versus  $(\epsilon_L r^3)^{-1}$  for the case of interacting  $\text{OH}^-$  ions at  $kT = 1.0 \text{ cm}^{-1}$ ,  $T = 1.4^\circ\text{K}$ . The actual computer data are indicated by the points in the plot. Note that if a second-order perturbation-theory calculation of  $\frac{1}{2}\alpha_{12}$  had been adequate in this case,<sup>19</sup> the term  $\frac{1}{2}\alpha_{12} - \alpha_0$  would have exhibited a dependence on  $r$  of the form  $C/r^6$  and the plot in Fig. 4 would have been linear over the whole range up to the cutoff value of  $(\epsilon_L r^3)^{-1}$ . The deviation from this behavior is strong, showing that a perturbation calculation in this case would have been excessively tedious. It appears that the perturbation series contains positive terms in  $r^{-6}$  and  $r^{-9}$  and a negative term in  $r^{-12}$ , and clearly a calculation to at least fourth order would have been required. Figure 4 also shows that the value of the integral defining  $B(T)$  is reasonably insensitive to the exact choice of the cutoff distance and is mainly in-

fluenced by interactions at a distance great enough so that the replacement of a lattice sum by a spherical average should be an excellent approximation. The aspect of these plots for the cases of  $\text{KCl}:\text{CN}^-$  and  $\text{KCl}:\text{Li}^+$  is similar, although in the latter cases the  $r^{-9}$  and  $r^{-12}$  terms, which are uniformly positive and negative, respectively, are smaller relative to the  $r^{-6}$  term than in the case of  $\text{KCl}:\text{OH}^-$  (more so for  $\text{KCl}:\text{CN}^-$ ).

From graphical integration of plots like that shown in Fig. 4, we have determined  $B(T)$  for each of the three systems of interest, and the numerical results are presented in Fig. 5.  $B(T)$  is seen to be everywhere positive for all species; that is, the effect of pair interactions at this level of treatment is to enhance the response of the system to an applied electric field in the  $[100]$  direction. The high-temperature limiting behavior of  $B(T)$  exhibits an interesting variability. As  $kT$  becomes large,  $B(T)$  varies as  $T^{-2}$  in the case of  $\text{Li}^+$ ,  $T^{-2.5}$  in the case of  $\text{OH}^-$ , and  $T^{-4.5}$  in the case of  $\text{CN}^-$ .

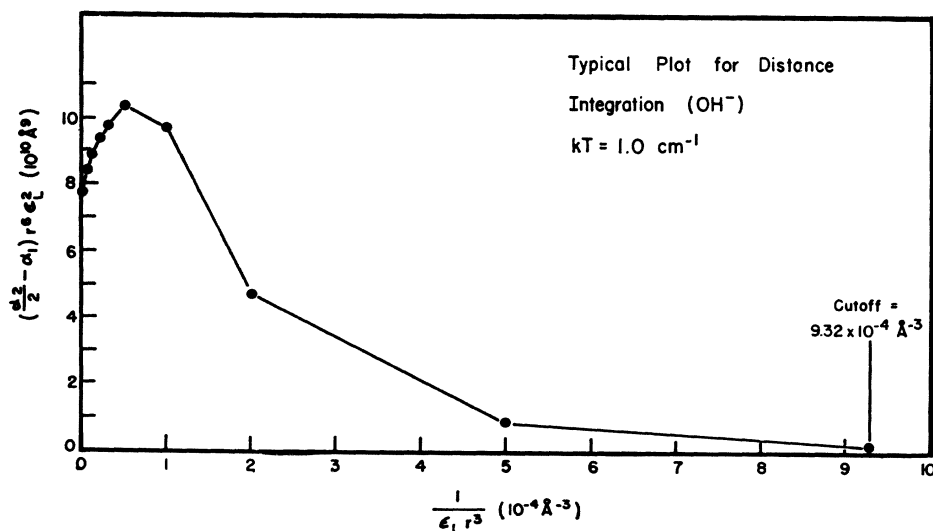


FIG. 4. Computer-determined values of the integrand in the definition of the second dielectric virial coefficient  $B(T)$  as a function of separation distance for  $\text{KCl}:\text{OH}^-$  at  $1.4^\circ\text{K}$ .

There appears to be no simple qualitative argument which can be advanced to account for these dependences. In this connection, we note that calculations in the classical, high-temperature limit for assemblies of dipoles on lattices<sup>24</sup> indicate that the leading term in the deviation from noninteracting dipole behavior there depends on temperature as  $T^{-2}$ . A particularly important feature of our results is that the quantitative behavior of  $B(T)$  appears to be sensitive enough to the numerical values of the isolated particle parameters, so that refined low-temperature measurements of the dielectric constant may be an appropriate technique for deciding among various possible choices of these parameters.

The only one of the systems considered for which a systematic study of concentration dependence of dielectric properties has been carried out is  $\text{KCl}:\text{OH}^{-3}$ . It was originally suggested by the present authors<sup>11</sup> that the peak in the dielectric constant observed in this system might be an essentially single-particle effect, modulated and shifted by interactions. Insertion of the isolated single-particle polarizability  $\alpha_0(T)$  for  $\text{KCl}:\text{OH}^{-}$ , calculated in accordance with the prescriptions of Ref. 11 and displayed in Fig. 3, in the Clausius-Mossotti expression  $\frac{4}{3}\pi\rho\alpha_0(T)$  leads to values of  $\epsilon$  for the system in excess of those experimentally determined. Hence, on the picture originally advanced,  $B(T)$  for this system would be expected to be negative. Since classical calculations<sup>24</sup> do in fact show a reduction in  $\epsilon$  due to interactions, it was originally thought that the same effect might manifest itself in the present problem. Moreover, it appeared that the nonlinear dependence on concentration of the temperature of maximum  $\epsilon$  for  $\text{KCl}:\text{OH}^{-3,11}$  indicated a virial-expansion technique as the logical avenue of approach to the problem. However, as we have just seen,  $B(T)$  for  $\text{OH}^{-}$  is positive at all temperatures of interest for either the BS or FSS choices of parameter; inclusion of a second-order term in impurity density together with the isolated impurity term in Eq. (23) cannot provide an explanation for the observed properties of  $\text{KCl}:\text{OH}^{-}$  in the concentration range so far studied experimentally.

The studies which we have carried out do, however, point to an alternative picture for  $\text{KCl}:\text{OH}^{-}$  which is in reasonable accord with experimental observation and which differs in significant respects from those previously presented.<sup>12-15</sup> We shall consider this picture in detail in Sec. V, and complete the present section with further discussion of the properties of the dielectric virial expansion. Previous work on the dielectric virial expansion for nonpolar gases<sup>17,19</sup> for which quantum effects dominate and the temperature dependence of  $\alpha_{12}$  is unimportant have shown that  $B(T)$  in these cases should be positive. This is in accord with<sup>17</sup> available experimental data<sup>26</sup> except in the anomalous case of He. The reason why the effect of induced dipole-induced

<sup>26</sup> D. R. Johnston, G. J. Oudemans, and R. H. Cole, *J. Chem. Phys.* **33**, 1310 (1960).

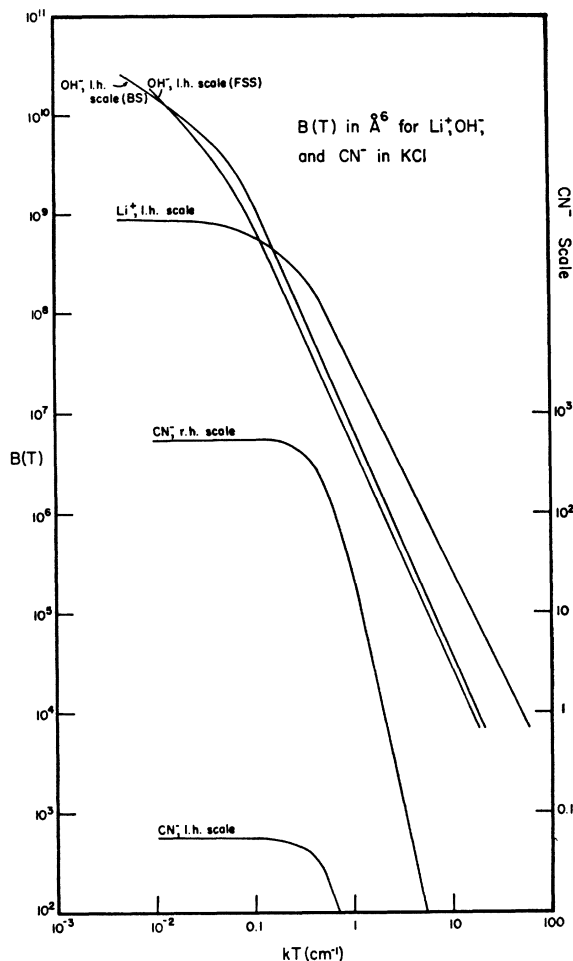


FIG. 5. Computer-determined values of  $B(T)$  as a function of temperature for  $\text{KCl}:\text{OH}^{-}$ ,  $\text{KCl}:\text{Li}^{+}$ , and  $\text{KCl}:\text{CN}^{-}$ . Results for both the BS and FSS choices of parameter for  $\text{KCl}:\text{OH}^{-}$  are shown.

dipole interaction is to enhance the response of the system to an applied electric field in both the gas case and the impurity-ion case is easily seen. If we consider first the isolated particle situation and recall that<sup>27</sup>

$$\left(\frac{\partial\alpha(T)}{\partial T}\right)_V \sim \left(\frac{\partial\epsilon(T)}{\partial T}\right)_V \sim \left(\frac{\partial S}{\partial F}\right)_T, \quad (28)$$

where  $V$  is the volume,  $F$  is the field strength, and  $S$  is the entropy, we see that at sufficiently low temperatures ( $T < \Delta$ ) when the particle is mainly in the ground state, application of a field cannot significantly lower the entropy and hence  $\alpha \sim \text{const}$  independent of  $T$ . Thus in the quantum limit  $\alpha(T)$  deviates negatively from the classical result  $m^2/3kT$ . However, if the particles are in interaction, as we have seen in Sec. II, the splitting  $\Delta$  between the ground state and some at least of the excited states becomes smaller than for isolated particles,

<sup>27</sup> H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1949), Chap. I.

and negative deviation from the  $1/T$  behavior of  $\alpha$  sets in at a lower temperature. Thus the interaction effect tends to counter the quantum effect and make the effective single-particle polarizability more nearly equal to  $m^2/3kT$  than it would otherwise be. This accounts for the positive  $B(T)$ . At very high temperatures when the classical limit applies, the situation is completely different since the density of states available to a given particle is no longer critically dependent on interaction strength. At temperatures  $T > \Delta$ , the isolated particle polarizability for the impurity-ion cases may be shown to take the form

$$\alpha_0(T) = m_e^2/3kT - C/T^2 + \dots, \quad (29)$$

where  $m_e$  is the effective classical value of particle dipole moment and  $C$  is a positive constant.<sup>28</sup> Inclusion of the two-particle effect by addition of the second dielectric virial coefficient adds a term of the form  $+C'\rho/T^n$ , where  $n$  seems always to be  $\geq 2$ . It appears that for the cases considered here, the resulting effective  $\alpha(T)$  for the interacting, nonclassical system is always less than  $m_e^2/3kT$ , so that the net combined effect of quantum corrections and interaction corrections is to give a negative deviation from the classical noninteracting result. It is not clear whether this situation is general or depends critically on the basis set of levels chosen here. In the classical limit, the effective single-particle polarizability of the interacting system would be  $m_e^2/3kT - C''/T^2$ , according to Ref. 24; thus it appears plausible that the exact quantum result, corrected for interactions, joins smoothly onto the classical result, corrected for interactions, at some intermediate temperature. It appears to us that this point merits further investigation.

The virial formalism used here, although taken over from applications to dilute gas systems, is in accordance with the prescriptions given by Brout<sup>29</sup> for density corrections to isolated particle behavior in corresponding magnetic systems. The fact that the impurity ions are fixed in random positions in the lattice affects the nature of the statistical averaging which must be performed, but differences with the case of a dilute gas only show up in the third and higher dielectric virial coefficients. It seems, therefore, as though the calculation of  $B(T)$  as presented here is sound. The reason why application of the virial method fails in the case of the KCl:OH<sup>-</sup> systems studied here is simply seen if one notes that in the temperature range of interest, the quantity  $\frac{4}{3}\pi\rho\alpha_0(T)$  is in the range 0.72–3.2, that is, not small compared with unity. Under these conditions, the isolated particle Clausius-Mossotti result

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\rho\alpha_0(T) \quad (30)$$

is inadequate. *A priori*, there are two possibilities; either

<sup>28</sup> In the special case of a two-level system, the leading correction term is  $O(1/T^2)$ .

<sup>29</sup> R. Brout, Phys. Rev. **115**, 824 (1959).

inclusion of pair interactions via the virial formalism lowers the effective single-particle value of  $\alpha(T)$  sufficiently so that the quantity on the right-hand side of Eq. (30) is less than unity, in which case the virial formalism is appropriate, or it does not, which means that the virial expansion in fact diverges. We see that the latter possibility is the one realized in the KCl:OH<sup>-</sup> system. It is possible, however, to assert that there is a range of temperatures and densities in this system for which convergence of the virial expansion does occur. Evidently, we must have  $\frac{4}{3}\pi\rho\alpha_0(T) \ll 1$ , or, since  $\alpha_0(T)$  is on the order of  $10^4$ – $10^5$  Å<sup>3</sup> at low temperatures, we must have  $\rho < 10^{18}$  cm<sup>-3</sup>. The second virial-coefficient term will then begin to be of importance when  $B\rho \sim \frac{4}{3}\pi\alpha_0(T)$ , or when  $B(T) \sim 2 \times 10^{11}$  Å<sup>6</sup>. Reference to Fig. 5 shows that this occurs at temperatures of about 0.015°K or lower. It would be difficult to perform sufficiently accurate experiments on such dilute samples at these low temperatures, but we note that the conditions are less stringent for the KCl:Li<sup>+</sup> and KCl:CN<sup>-</sup> systems.

There are three simple dimensionless parameters which one may construct for the general case of interacting polarizable particles: the reduced temperature  $T_r = kT/\Delta$ , where  $\Delta$  is a representative zero field splitting, the reduced interaction strength  $D_r = m^2\rho/\Delta\epsilon$ , where  $m$  is a representative dipole moment matrix element, and the ratio  $D_r/T_r = m^2\rho/kT\epsilon$ . A picture of classical orientable dipoles is appropriate in either of the limits  $T_r \gg 1$  or  $D_r \gg 1$ . In the latter case, the interacting particles are strongly correlated, corresponding to the Ising limit in Fig. 1. Neither limit applies well to the impurity species considered here at temperatures on the order of 1°K and densities so far investigated. For KCl:OH,  $T_r$  ranges from 1 to 10 and  $D_r$  from 0.3 to 1.5, for example. The ratio  $D_r/T_r$  in essence determines the convergence of the virial expansion of the Clausius-Mossotti function. If  $D_r/T_r \ll 1$ , convergence may be expected, but if, as in the case of the KCl:OH<sup>-</sup> systems  $D_r/T_r \lesssim 1$ , the virial expansion will not be applicable. Clearly, the question of the convergence of the virial expansion is distinct from that of the applicability of a classical analysis, and convergence or nonconvergence are both possible in either classical ( $T_r \gg 1$  or  $D_r \gg 1$ ) or quantum ( $T_r, D_r < 1$ ) cases.

## V. HIGH-DENSITY CASE

The primary goal of this work is the development of a systematic virial-expansion treatment of the dielectric properties of interacting impurity-ion systems including quantum effects associated with the presence of zero-field splitting. This approach is fundamentally restricted to low impurity-ion densities, in the sense set forth in the Sec. IV, and as such does not apply to the KCl:OH<sup>-</sup> systems so far investigated. It seems appropriate, therefore, to point out that this work also indicates a simple explanation for the main qualitative features observed

in the dielectric behavior of  $\text{KCl:OH}^-$ , although one which falls somewhat outside the framework of the virial expansion.

The basic point of interest here is revealed clearly in Fig. 2, which applies rigorously to the interacting two-level particles but in an approximate fashion also to the interacting impurity-ion cases. Whereas the polarizability of interacting particles in a direction perpendicular to the interparticle vector  $\mathbf{r}$  is reduced relative to that for the noninteracting case,  $\alpha_0$ , the pair polarizability  $\alpha_{12,rr}$  along  $\mathbf{r}$  is very greatly enhanced. Consider a system of impurity ions fixed at random positions in the KCl lattice. Each of the ions will have a well-defined nearest other impurity ion at a position  $\mathbf{r}$  relative to it; the probability that a given ion will have two or more neighbors at the same distance is negligible. As the density of impurities increases, the average distance between nearest-neighbor impurity pairs will diminish as  $\rho^{-1/3}$ . The orientation of  $\mathbf{r}$  taken over all impurities in the lattice is a random variable, but for any given impurity is fixed. Let us then imagine the impurity system to consist of more or less well-defined nearest pairs, with the pair axis  $\mathbf{r}$  randomly oriented with respect to lattice axes. This picture is not entirely unambiguous since a careful specification of what is meant by a nearest pair should be given; however, for most impurities in the lattice it has a clear significance. Such a pair may be characterized by a polarizability ellipsoid, with the long axis of the ellipsoid along  $\mathbf{r}$ . Alternatively, in terms of the effective single-particle polarizability  $\alpha_{\text{eff}} = \frac{1}{2}\alpha_{12}$ , we can say that the components of  $\alpha_{\text{eff}}$  define a polarizability ellipsoid, elongated in the  $\mathbf{r}$  direction and contracted perpendicular to  $\mathbf{r}$  in accordance with the results shown in Fig. 2. Since the effect of pair interaction on polarizability drops off with distance at least as fast as  $r^{-6}$ , the nearest-neighbor effect will dominate the effective single-particle polarizability at least until the polarizability ellipsoids of distinct pairs begin to overlap one another. In a situation in which the pair effect is dominant but ellipsoids of distinct pairs do not overlap, we expect that the principal term in the response of the impurity system to an applied electric field in the lattice  $z$  direction is correctly given by the component along the  $z$  axis of the pair dipole moment induced by the field along the pair axis  $\mathbf{r}$ . This moment is given by

$$2m_r = \alpha_{12,rr} F \cos\theta = 2\alpha_{\text{eff},rr} F \cos\theta, \quad (31)$$

where  $m_r$  is the induced dipole moment per particle of the pair,  $F$  is the field strength, and  $\theta$  is the angle between  $\mathbf{r}$  and the  $z$  axis. The total average polarization of the impurity system along the  $z$  direction is then

$$\begin{aligned} \bar{P}_z &= \rho \langle m_r \cos\theta \rangle_{\text{av}} = \rho \langle \alpha_{\text{eff},rr} \cos^2\theta F \rangle_{\text{av}} \\ &= \frac{1}{3} \rho \bar{\alpha}_{\text{eff},rr} F, \end{aligned} \quad (32)$$

to give for the Clausius-Mossotti function for the im-

purity system

$$\frac{\epsilon_i - 1}{\epsilon_i + 2} = 4\pi\rho \bar{\alpha}_{\text{eff},rr} / 9. \quad (33)$$

We note from Fig. 2 that  $\alpha_{\text{eff},rr}$  increases as  $T$  is decreased. Hence we expect an increase in the Clausius-Mossotti function as  $T$  decreases until  $\bar{\alpha}_{\text{eff},rr}$  reaches a value such that, on the average, the polarizability ellipsoids of distinct pairs begin to overlap. When this overlap begins to occur, the strong coherence between neighbors in a given pair leading to a large value of  $\alpha_{\text{eff},rr}$  is perturbed and the effective single-particle polarizability diminishes except for the improbable case that three or more neighboring impurities happen to lie on a straight line. In order to convert this picture to numerical calculation, we assume that the magnitude of  $\alpha_{\text{eff},rr}$  is the same for all pairs, and may be calculated by setting  $r^{-3} = \rho$ . The condition that the polarizability ellipsoids begin to overlap is then that a "Clausius-Mossotti catastrophe" occurs with  $\alpha_{\text{eff},rr}$  or

$$\begin{aligned} \frac{4}{3}\pi\rho\alpha_{\text{eff},rr} &= 1, \\ \alpha_{\text{eff},rr} &= \frac{3}{4\pi\rho}. \end{aligned} \quad (34)$$

At a temperature  $T_{\text{max}}$  at which condition (34) is satisfied, we should expect a maximum in the dielectric constant. From Eq. (33) we see that at  $T_{\text{max}}$ , on this model,

$$\frac{\epsilon_i - 1}{\epsilon_i + 2} = \frac{1}{3}. \quad (35)$$

Turning to the specific case of  $\text{KCl:OH}^-$ , we remark that the behavior of  $\alpha_{\text{eff},rr}$  for this system is essentially identical with that shown for the interacting two-level systems in Fig. 2, at least for the FSS choice of parameters. The parameter  $D$  appearing in Fig. 2 is, for the two-level particles, just

$$D = (-2m^2/\Delta\epsilon_L)\rho = -\alpha_0(0^\circ\text{K})\rho/\epsilon_L, \quad (36)$$

where we have inserted the lattice dielectric constant  $\epsilon_L$ , replaced  $r^{-3}$  by its approximate average value  $\rho$ , and set  $s = \cos\theta = 1$ , which is the appropriate choice for the calculation of  $\alpha_{\text{eff},rr}$ . Now  $\alpha_0(0^\circ\text{K})$  for the FSS choice of parameters is  $8.0 \times 10^4 \text{ \AA}^3$ , the lattice dielectric constant is known, and the densities of the  $\text{KCl:OH}^-$  systems are available.<sup>3</sup> Hence if we assume that Eq. (36) is applicable to the  $\text{KCl:OH}^-$  system, we can calculate  $D$  for each of the experimental densities studied in Ref. 3. A given value of  $D$  fixes the interparticle distance  $r$ , and from Fig. 2 we can read off for any given value of  $D$  the value of the ratio  $kT/\Delta$  for which the condition (34) is exactly satisfied. The corresponding value of  $T$  should, on this picture, be  $T_{\text{max}}$ . It remains to be decided what value should be taken for  $\Delta$  for the  $\text{OH}^-$  system. The only reasonable and consistent choice seems to be to average the splitting parameters given in Table I for the

TABLE III. Determination of  $T_{\max}$  for KCl:OH<sup>-</sup>.

$\rho$ ( $10^{18}$ cm <sup>-3</sup> )	$-D$	KHR	$T_{\max}$ (°K)		Expt.
			K	BS	
6.07	0.11	0.43	0.20	0.29	0.32
8.17	0.15	0.58	0.27	0.37	0.385
18.3	0.34	1.30	0.60	0.83	0.74
28.6	0.53	2.0	0.94	1.32	1.2

FSS model for OH<sup>-</sup>, taking account of the relative degeneracies of  $T_{1u}$  and  $E_g$  states. This leads to an average effective value  $\Delta=0.17$  cm<sup>-1</sup> for KCl:OH<sup>-</sup>.

We have carried out this simple calculation of  $T_{\max}$  for KCl:OH<sup>-</sup> using the above choices of parameter, the results shown in Fig. 2, and the dielectrically determined densities reported in Ref. 3. In Table III we give the density, value of the  $D$  parameter, experimental  $T_{\max}$  from Ref. 3 (KHR), theoretical  $T_{\max}$  from KHR, theoretical  $T_{\max}$  from Ref. 15 (K), and theoretical  $T_{\max}$  according to the present work (BS). It can be seen that the results of the present work are in reasonable agreement with experiment, at least as good as previous theoretical predictions in spite of the simplifying approximations introduced. Further, we note from Ref. 3 that the experimental ratio

$$\frac{\epsilon_i - 1}{\epsilon_i + 2} = \frac{\epsilon_x - 1}{\epsilon_x + 2} - \frac{\epsilon_L - 1}{\epsilon_L + 2}$$

for the KCl:OH<sup>-</sup> system, where  $\epsilon_L$  and  $\epsilon_x$  are the pure lattice dielectric constant and impurity doped lattice constant, respectively, takes values in the range 0.16–0.26 at  $T_{\max}$ , in order-of-magnitude agreement with the prediction of the present work that this quantity should be 0.33 at  $T_{\max}$  in accordance with Eq. (35). Further, it is clear that the influence of more distant impurity neighbors on a given impurity ion pair, neglected in this work, will be sizeable even before the polarizability ellipsoids begin to overlap, and this effect will tend to make  $(\epsilon_i - 1)(\epsilon_i + 2)$  smaller than  $\frac{1}{3}$  at  $T_{\max}$ , tending to bring the theoretical result into better agreement with experiment. An important feature of the present result is that  $T_{\max}$  is no longer a linear function of the density, as predicted in all previous work on the problem. The curvature in plots of the experimental  $T_{\max}$  versus  $\rho$  is pronounced, and our result is seen to reproduce this curvature, if imperfectly. The curvature arises, on our model, from the fact that in the KCl:OH<sup>-</sup> system we are in a regime of temperature and density such that  $\alpha_{\text{eff}}$  exhibits a complicated dependence on  $T$ , not rigorously representable as a classical  $1/T$  effect. Thus the curvature is a strictly quantal effect which no classical theory would be expected to give. The plot in Fig. 2 for  $D = -2$  shows this effect most markedly, but it is general for all plots.

The generally good agreement with experiment of our results for KCl:OH<sup>-</sup> lends confidence to the belief that we have found the essentials of a correct theoretical treatment of the dielectric properties of this system. A

number of obvious improvements should be carried out, including calculation of  $\alpha_{\text{eff},rr}$  for more realistic representations of the impurity ions than is afforded by the two-level particle result, a more correct averaging over  $r$  than is given by the replacement of  $r^{-3}$  by  $\rho$ , a rigorous specification of the way in which ions may be grouped into coherent nearest pairs, and a treatment of the effect of more distant pairs on a given pair. In connection with the last of these points, one evident device which could be introduced would be an internal or reaction field acting on a given pair due to the remainder of the system, in a way somewhat similar to that presented in Ref. 15. However, in a fixed random system such as the impurity ions in KCl, it seems likely that it would be necessary to take into account the highly nonuniform electrical environment in which any given pair finds itself, that is, the effect of the nearest pair to a given pair. A reaction-field approach, of course, immediately imposes the approximation of a uniform environment for each pair. We hope to return to this point in future work, and will only remark that a virial expansion in terms of interacting *pairs* may be indicated.

A comment is in order on the relation between the method of this section and the straightforward virial expansion discussed in Secs. III and IV. In that approach, we calculate the effective two-particle polarizability in the  $z$  direction averaged over the orientation of  $\mathbf{r}$ . This averaged quantity is much smaller than the polarizability along  $\mathbf{r}$  because of the extreme eccentricity of the two-particle polarizability ellipsoid. This procedure has meaning, and the virial expansion converges only if the largest principal axis of the ellipsoid,  $\alpha_{12,rr}$ , is much smaller than the cube of the average distance between particles, i.e., the reciprocal density. This condition may fail even under conditions such that the computed  $B(T)$  is not very large, and KCl:OH<sup>-</sup> is evidently an example of such a situation. It may readily be checked that this convergence criterion is essentially equivalent to that given in Sec. IV. When  $\alpha_{12,rr}$  is large enough so that the polarizability ellipsoids of distinct pairs overlap, the effects of three and more particle interactions become inseparably mixed with those of pair interactions, and a virial approach is unsuitable. A breakdown in virial expansion generally indicates that a phase transition occurs. In the present case, one might say that the transition is between a high-temperature phase in which particles are locked into coherent pairs, with weak interaction between the pairs, and a low-temperature phase in which coherence within pairs is largely disrupted and replaced by an essentially random collective structure. A parallel could be drawn with the hypothetical case of a gas of dimer particles which condenses at sufficiently low temperature to a liquid in which the dimers are largely disrupted by intermolecular forces.

In summary, our picture of the KCl:OH<sup>-</sup> system at densities so far studied is this: As the temperature is reduced, pairs of near-neighbor impurity ions become

increasingly locked into coherent states with a very large polarizability along the interparticle axis. This has no very great effect on the response of the whole system to an applied electric field since the orientations of the individual pair axes are random with respect to the field, and the Clausius-Mossotti function for the impurity system decreases with temperature faster than  $1/T$  because of quantum effects. It seems appropriate to refer to the coherent pairs as ferroelectrically locked. The interacting particle polarizability, and hence the impurity system dielectric constant, increases with decreasing  $T$  until a temperature  $T_{\max}$  at which distinct pairs begin to interact strongly with each other, partially breaking the coherent ferroelectric coupling between particles within a given pair and reducing the dielectric constant. The dominant effect in the interaction between distinct pairs is primarily antiferroelectric. At sufficiently low temperatures, the impurity-ion system is essentially in a ground state in which both ferroelectric and antiferroelectric effects manifest themselves, and which would appear to exhibit no very clear ordering of any sort. Certainly there appears no reason to expect dramatic manifestations of ordering, i.e., a persistent internal polarization, in  $\text{KCl:OH}^-$  at any  $T$  on this picture, assuming that the system is in equilibrium. If very long relaxation times occur at sufficiently low temperature, of course, a persistent non-equilibrium polarized state might be produced by, e.g., cooling the  $\text{KCl:OH}^-$  system in the presence of a strong applied field, but consideration of this lies outside the scope of this work.

We remark that Figs. 2 and 3 can be used to calculate  $T_{\max}$  for the  $\text{Li}^+$  and  $\text{CN}^-$  systems as well. Since this can immediately be carried out, we give here no detailed predictions for these species, but for orientation comment that for both  $\text{Li}^+$  and  $\text{CN}^-$ , no peak in the dielectric constant would be expected for densities less than about  $2 \times 10^{19} \text{ cm}^{-3}$ .

The discussion above leaves open the question as to whether the BS or FSS model is best for  $\text{KCl:OH}^-$ . In computing  $T_{\max}$ , we have used only the FSS choice, because the low-temperature properties of isolated  $\text{OH}^-$  ions on the BS model are sufficiently complicated for it to be unclear as to what value should be taken for  $\alpha_0(0^\circ\text{K})$  in Eq. (36). Nevertheless, further work is required before a final choice can be made as to which set

of parameters gives the better agreement with available experiment.

#### A. Comparison with Other Work

The other treatments of the dielectric properties of interacting impurity ions in solids extensive enough for a detailed comparison to be given are those of Klein,<sup>14</sup> Lawless,<sup>13</sup> and Zernik.<sup>15</sup> Each of these treatments has been essentially classical, neglecting zero-field splitting effects, and has been restricted to  $\text{KCl:OH}^-$ . Klein makes the serious approximation of truncating the dipole-dipole interaction term in the Hamiltonian to include only  $\mathbf{p}_1 \cdot \mathbf{p}_2 / r^3$ . This guarantees that only antiferroelectric coupling can be present and rules out the ferroelectric coupling between neighboring ions which appears of critical importance. Lawless has kept the entire interaction term and has done a rigorous lattice sum in evaluating the effect of impurity interaction. He also attempts to take quantum effects into account by adding a temperature-dependent polarizability to a classical dipole term for each impurity. This procedure is dubious, and in any case cannot properly account for quantum effects in the interaction between impurity ions except in the limit of weak coupling when second-order perturbation theory can be used. The special properties of impurity pairs do not occur in his work, and his calculated results do not appear to be in good agreement with experiment. The picture of Zernik is similar to that adopted in Sec. V here, although arrived at from a different point of departure. He has emphasized the pair problem, treating an interacting pair of impurities exactly within the classical formulation and taking the remainder of the system into account by reaction-field methods. Zernik's predicted values for  $T_{\max}$  are in nearly as good agreement with experiment as those found here, and his calculated value for  $(\epsilon_s - 1) / (\epsilon_s + 2)$  at  $T_{\max}$  is 0.33, the same value as here. However, his entirely classical theory cannot reproduce the experimentally observed nonlinear dependence of  $T_{\max}$  on  $\rho$ , whereas our quantum result succeeds in accounting in semiquantitative fashion for it. Further, inclusion of interactions between distinct pairs will reduce our value of  $(\epsilon_s - 1) / (\epsilon_s + 2)$  below 0.33, whereas all long-range effects possible in his formulation have already been included by Zernik. Finally, we note that the use of reaction-field methods in this problem may not be entirely sound, as pointed out above.