Dipole interactions among polar defects: A self-consistent theory with application to OH⁻ impurities in KCl

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(Received 22 September 1975)

We consider a set of dipole impurities randomly distributed in a nonpolar medium where the *only* interaction between the impurities is the dipole-dipole interaction. The dipoles are assumed to be oriented in the six equivalent (1,0,0) directions found experimentally to exist when OH⁻ impurities are dissolved in KCl crystals. Effects arising from tunneling between the six equivalent directions are neglected. We set up the expression for the random molecular electric field vector $\vec{E}$ at a particular impurity site and derive self-consistently the probability distribution of $\vec{E}$ for all temperatures and (sufficiently low) impurity concentrations. The thermodynamic properties of the system are then obtained by integrating the thermodynamic variable of a single dipole in a fixed vector field $\vec{E}$ over the distribution of all fields. Evaluating the thermodynamic properties arising from the dipole-dipole interaction we show that the dielectric susceptibility scales with the ratio of the temperature T to the impurity concentration c. Similarly the specific heat per impurity scales with T/c. Even though the experimentally measured $T^{3/2}c^{-1/2}$ dependence of the specific heat is consistent with our "scaling" requirements, indicating that the dipole-dipole interaction is involved in the excess low-temperature specific heat, our theory gives that the specific heat is linear in T and independent of c for very low temperatures. Thus, the dipole-dipole interaction alone, using a molecular-field approximation, *does not explain* the experimentally observed low-T specific heat. A detailed study of the temperature dependence, the concentration dependence, and the scaling properties of the specific heat and the dielectric susceptibility are discussed and compared with experiment.

I. INTRODUCTION

Certain atoms and molecules when dissolved in small concentrations in alkali halides are known to form dipoles with well-defined discrete orientations. The dipole orientations are determined by the directions of the potential minima within the lattice vacancy they occupy, and the dipoles can tunnel among the equivalent potentials in the crystalline lattice. One example of the occurrence of such dipoles is found when OH⁻ impurities are dissolved in KCl. This system was shown by Kuhn and Lüty[1] to have six possible orientations in the six equivalent (1, 0, 0) directions; its properties will be discussed in this paper.

The calculation of the tunneling states for a three-dimensional system with n wells was made by Bauer and Saltzman,[2] and by Gomez, Bowen, and Krumhansl[3] using the ideas developed by Hund[4] and Pauling[5] for the harmonic oscillator. The essential feature of these calculations is that the degeneracy of the multiorientational states is removed by the tunneling matrix element and the levels are split into tunneling states. The tunneling states associated with dipoles dissolved in alkali halides are well understood and the reader is referred to an excellent review article by Narayanamurti and Pohl[6] on the subject. For OH⁻ impurities in KCl the tunnel splitting energy was obtained by Bron and Dreyfus,[7] and Feher et al.,[8] and is believed to be about 0.18 K. In this paper we completely neglect effects arising from tunneling between the equivalent dipole directions.

The effect of the tunneling states on the vibrational absorption is discussed by Lüty[9] and the dynamics of the dipole reorientations were reported on by Kapphan,[10] and Kapphan and Lüty.[11] Since our paper is concerned only with the statics of the dipole system, we shall immediately proceed in this direction, giving the above references for purposes of general interest only.

Electric dipole interactions between impurities dissolved in alkali halides were first reported by Kanzig et al.,[12] who measured the dielectric constant of OH⁻ impurities dissolved in KCl. They[12] found that the dielectric constant of this system exhibits a relatively broad temperature-dependent maximum. This maximum was interpreted as arising from the dipole-dipole interaction and several theoretical treatments discussed this problem.[13-16]

A detailed study of the dipole-dipole interaction of impurities dissolved in alkali halides was done by Fiory.[17] Peressini et al.[18] measured the temperature and concentration dependence of the low-temperature specific heat, and Fiory[17] obtained the remanent polarization, the dielectric constant, and the relaxation time of OH⁻ impurities in KCl (as well as some other systems; here however we are only interested in KCl-OH⁻) and compared these with various theories presented.[13-16] The low-temperature specific heat of relatively concentrated OH⁻¹ impurities (around 1%) in KCl was found to be proportional to[17,18] $T^{3/2}c^{-1/2}$, where T is the tem-

perature and c is the fractional dipole impurity concentration.

The $T^{3/2}$ behavior of the specific heat is reminiscent of the low-temperature specific-heat contribution of spin waves in a ferromagnet and has been interpreted as arising from the excitation of "polarization waves" in the "ordered" ferroelectric system of KCl-OH⁻. A detailed study by Fiory[17] to detect the polarization waves failed to given any evidence for their existence.

The previous theoretical treatments[13-16] have either been qualitative in nature or have not treated the dipole-dipole interaction over the whole temperature range of interest. In this paper we obtain a self-consistent treatment of the dipole-dipole interaction for all temperatures and (low enough) concentrations using the mean-random-molecular-field (MRF) approximation developed previously for dilute alloys.[19] The dipoles are assumed to be "rigid" in the sense that the strength of the dipole moment p does not vary with temperature, with applied electric field, or with the dipole impurity concentration. We consider the dipoles to be randomly distributed throughout the host material and assume that the fractional dipole impurity concentration c is small, with $c = N_d/N$, where N_d is the number of dipoles and N is the number of Cl⁻ sites in the solid. We set up the expression for the random vector molecular field $\vec{E}$ of the dipoles and solve for the probability distribution of $\vec{E}$, $P(\vec{E})$, self-consistently for all temperatures. To obtain the average value of a thermodynamic variable $Q(T)$, we first find the value $Q(\vec{E}, T)$—the thermal average value of the quantity Q in an effective electric field $\vec{E}$ and temperature T—for a single dipole impurity, and then average $Q(\vec{E}, T)$ over the distribution of all internal fields $\vec{E}$. The strength of the dipole moment is the only parameter which enters our calculations. Once this parameter is found from an experimentally measured quantity like, for example, the temperature of the maximum in the dielectric constant, all the thermodynamic quantities can be obtained from our self-consistent theory.

In comparing our result with experiments, we must first put this work into proper perspective. It is known that the effect of tunneling between the dipole orientations separates the states, giving a certain tunnel splitting energy between these states. In order to obtain the contribution to the thermodynamic properties of the system one must be able to separate the contributions due to the tunneling effects alone, due to the dipole-dipole interaction alone, and possibly due to a mixture of these two effects. We consider here the self-consistent treatment of a pure classical dipole system neglecting quantum-mechanical effects (like tunneling) completely.

It is thus our hope that our theoretical results

will help separate the various effects which contribute, for example, to the low-temperature specific heat into their different components. Only the component arising from the dipole-dipole interaction is considered here. We find it encouraging that a number of experimentally observed results are in agreement with our theoretical predictions. We find, for example, that the deviation of the dielectric constant from its Langevin-Debye value at high temperatures is in agreement with experiment.[17] A detailed comparison with experiment is made in Sec. V of the paper.

A brief summary of our theoretical predictions is as follows: The dielectric susceptibility χ_D scales with temperature T and impurity concentration c according to the relation $\chi_D \propto f(T/c)$, and similarly the specific heat C_D scales according to the relation $C_D \propto cg'(T/c)$, where f and g' are only functions of T/c. Furthermore our theory gives a temperature-dependent maximum in χ_D and C_D where the temperature of the maximum is in both cases proportional to the impurity concentration. Similarly we discuss the deviations of χ_D and C_D from their $T = 0$ values. Even though we find that the experimentally observed $T^{3/2}c^{-1/2}$ dependence[17,18] of the specific heat obeys our scaling requirements in the sense that if we assume a $T^{3/2}$ dependence for the specific heat, its concentration dependence should be $c(T/c)^{3/2} = T^{3/2}c^{-1/2}$ as observed, our theory predicts that C_D is in effect proportional to T^1c^0. Thus our theory *does not explain* the experimentally observed low-temperature specific-heat data. The absence of polarization waves,[17] and the agreement of the experimentally observed specific heat with our scaling requirements suggest a coupling term between the tunneling states and the dipole-dipole interaction.

The contents of our paper is as follows. In Sec. II we develop the self-consistent theory for the probability distribution of the random dipole fields. In Sec. III we obtain the dielectric susceptibility and in Sec. IV we obtain the specific heat. Section V is devoted to a comparison of our theoretical predictions with experiment.

II. THEORY

A. Effective dipolar field of rigid dipoles

We consider a set of randomly distributed dipoles in a nondipolar host. We assume that the magnitude of each dipole moment does not change as a function of temperature or applied electric (or stress) field. Let this magnitude be p. Then the vector dipole $\vec{p}$ may be written

$$\vec{p} = p\vec{\mu} , \qquad (2.1)$$

where for convenience we assign $\vec{\mu}$ to have a mag-

nitude of unity. Because the moment of each di-
pole is fixed we shall refer to the dipoles as "rigid."
Let $\vec{p}_i$ be the dipole vector at site i, then

$$\vec{p}_i = p\vec{\mu}_i ,\qquad (2.2)$$

where $\vec{\mu}_i$ is the vector dipole whose orientation is
dictated by the physics of the problem. For ex-
ample OH⁻ impurities dissolved in KCl are found
to have six possible orientations. If we denote the
collection of the six orientations of the vector $\vec{\mu}$
by $\{\vec{\mu}\} = \{\mu_x, \mu_y, \mu_z\}$, the six orientations for OH⁻
in KCl can be written as

$$\{\vec{\mu}\} = (\pm 1, 0, 0),\ (0, \pm 1, 0),\ (0, 0, \pm 1) .\qquad (2.3)$$

The classical dipole-dipole Hamiltonian $\mathcal{H}$ for N_d
dipoles distributed on N sites such that $N_d/N = c$,
where c is the fractional impurity concentration, is

$$\mathcal{H} = \sum_{i=1}^{N_d} \sum_{j=1}^{N_d} \frac{p^3}{\epsilon_m r_{ij}^3} [\vec{\mu}_i \cdot \vec{\mu}_j - 3(\vec{\mu}_i \cdot \hat{r}_{ij})(\vec{\mu}_j \cdot \hat{r}_{ij})] ,\qquad (2.4)$$

where ϵ_m is the dielectric constant of the medium,
r_{ij} is the distance between dipoles located at sites
i and j, respectively, and the unit vector $\hat{r}$ is the
direction of the radius. For purposes of notation
we define

$$v_{ij} = p/\epsilon_m r_{ij}^3 .\qquad (2.5)$$

We next use the molecular-field approximation in
which we consider the Hamiltonian to be

$$\mathcal{H} = \sum_i p\vec{\mu}_i \cdot \vec{E}_i ,\qquad (2.6)$$

where $\vec{E}_i$ is thermal average of the field at site i.
Using the definition Eq. (2.6) and the Hamiltonian
(2.4) we obtain

$$\vec{E}_i = \sum_j v_{ij}[\langle \vec{\mu}_j \rangle - 3(\langle \vec{\mu}_j \rangle \cdot \hat{r}_{ij})\hat{r}_{ij}] ,\qquad (2.7)$$

where $\langle \vec{\mu}_j \rangle$ is the thermodynamic average of the
dipole vector at site j. The dipole at site j experi-
ences a dipolar field from all the other dipoles.
Therefore, we define the quantity

$$\vec{x}_j = \langle \vec{\mu}_j(\vec{E}_j) \rangle = \sum_{\{\vec{\mu}\}} \vec{\mu} e^{\beta p\vec{E}_j \cdot \vec{\mu}} \Big/ \sum_{\{\vec{\mu}\}} e^{\beta p\vec{E}_j \cdot \vec{\mu}} ,\qquad (2.8)$$

where $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann con-
stant and T the temperature. In order to simplify
our notation in Eq. (2.8) we let $\langle \vec{\mu}_j(\vec{E}_j) \rangle = \vec{x}_j$, the
brackets $\langle\ \rangle$ indicate thermal averages, and

$$\vec{E}_j = \sum_k v_{jk}[\vec{x}_k - 3(\vec{x}_k \cdot \hat{r}_{jk})\hat{r}_{jk}] .\qquad (2.9)$$

Equations (2.7)–(2.9) represent a set of equations
for $\vec{E}_i$, the field at site i, in terms of functionals
of the dipole fields at all other sites of the system.

Examining Eq. (2.7) we note that since the di-
poles are randomly distributed, r_{ij} and consequent-

ly v_{ij} are random variables. Therefore $\vec{E}_i$ and $\vec{E}_j$
are also random variables and as a result of this
each of the $\vec{x}_j$'s (which are functions of the $\vec{E}_j$'s)
are also random variables. The purpose of this
section is to obtain self-consistently the probabil-
ity distribution $P(\vec{E})$ of the random dipolar fields
$\vec{E}$ for all temperatures as a function of the dipole
impurity concentration c. Once the probability
distribution of the field $\vec{E}$ has been obtained, vari-
ous thermodynamic quantities are directly obtained
by integration. The idea behind this is as follows.
In order to obtain the average value of thermody-
namic quantity Q for the whole system, we find the
expression of the thermal average value of Q in a
fixed (external or internal) field $\vec{E}$, $Q(\vec{E}, \beta)$, and
average over the probability distribution of all
fields $\vec{E}$. This gives the value of $Q(\beta)$ for a single
impurity. To obtain the contribution for the whole
system we multiply $Q(\beta)$ by $N_d = Nc$. For example,
if we have the polarization of a single dipole in an
effective field $\vec{E}$ at temperature T, $p(\vec{E}, T)$, we
can readily obtain the mean polarization as a func-
tion of T, $p(\vec{T})$, by the relation

$$p(T) = Nc \int_{-\infty}^{\infty} P(\vec{E})p(\vec{E}, T) d\vec{E} ,\qquad (2.10)$$

where $d\vec{E} = \sin\theta\, d\theta\, d\phi\, E^2\, dE$, where θ and ϕ are the
azimuthal and polar angles, respectively, and E
is the magnitude of the field. Similarly, if we have
the dipolar specific heat $C_D(\vec{E}, T)$ of a single dipole
in a field $\vec{E}$, we can approximate the average specif-
ic heat for the system by the relation [the validity
of Eq. (2.11) is discussed in Sec. IV]

$$C_D(T) = Nc \int_{-\infty}^{\infty} P(\vec{E})C_D(\vec{E}, T) d\vec{E} .\qquad (2.11)$$

In our classical mean-field approximation, obtain-
ing the thermodynamics of the system thus reduces
to deriving the probability distribution of the ran-
dom internal dipolar fields. We shall find below
that this can be done self-consistently for all tem-
peratures and (low) dipole-impurity concentrations.

B. Statisitcal formulation of the probability distribution

We consider the N_d dipoles to be randomly and
uniformly distributed throughout the volume of the
solid, each Cl⁻ site being occupied with a dipole
impurity with probability c. The formal expression
for the probability distribution can be written using
the statistical model of Margenau[20] as applied by
Anderson[21] and Klein.[19] Let $P(\vec{E}_0)$ be the probabil-
ity distribution (density) function of the dipole vec-
tor field $\vec{E}_0$ for an impurity which is located at arbi-
trarily chosen origin r_0. Then the formal expres-
sion for the probability distribution is

$$P(\vec{E}_0) = \int_{r_{N_d}} \delta\left(\vec{E}_0 - \sum_{j=1}^{N_d} v_{0j}[x_j - 3(\vec{x}_j \cdot \hat{r}_{0j})\hat{r}_{0j}]\right)$$

$$\times P(r_1, r_2, \ldots, r_{N_d})d^3r_{N_d}, \qquad (2.12)$$

where $\vec{x}_j \equiv \langle \vec{\mu}_j(\vec{E}_j) \rangle$ is the thermodynamic average value of the dipole vector at site j which experiences a vector field $\vec{E}_j$ and is defined by Eqs. (2.8) and (2.9), $P(r_1, r_2, r_3, \ldots, r_{N_d})$ is the N_d-particle distribution function for the coordinates of the impurities, and $d^3r_{N_d}$ is a $3N_d$ dimensional integral over the coordinates of all N_d impurities.

The physical picture of Eq. (2.12) is as follows: The δ function simply takes all values of dipole potentials which contribute to a specific value of $\vec{E}_0$ and multiplies them by unity; the ones that do not contribute to $\vec{E}_0$ it multiplies by zero. Summing over the coordinates of the impurities with the appropriate distribution $P(r_1, r_2, \ldots, r_{N_d})$ gives us the "histogram" of the distribution. We also assume that the concentration is sufficiently low that it is a good approximation to integrate (rather than sum) over all coordinates.

Our development here is similar to a treatment by one of the present authors of the dilute-alloy problem[19]; however it is more complicated since the internal field in Eq. (2.9) is a vector. Rewriting Eq. (2.12) gives

$$P(\vec{E}_0) = (2\pi)^{-3} \int d\vec{\rho}\, e^{i\vec{\rho} \cdot \vec{E}_0} \int_{r_{N_d}} d^3r_{N_d} P(r_1, r_2, \ldots, r_{N_d})$$

$$\times \prod_{j=1}^{N_d-1} \exp\{- iv_{0j}[\vec{\rho} \cdot \vec{x}_j - 3(\vec{\rho} \cdot \hat{r}_{0j})(\hat{r}_{0j} \cdot \vec{x}_j)]\},$$

$$\qquad (2.13)$$

where

$$\vec{x}_j = \vec{x}_j(\vec{E}_j) = \vec{x}_j\left(\sum_k v_{jk}[\vec{x}_k - 3(\vec{x}_k \cdot \hat{r}_{jk})\hat{r}_{jk}]\right). \qquad (2.14)$$

The functional form of $\vec{x}_j$ is obtained from Eq. (2.8) and will depend on the physical assumptions made about the dipole orientations. It is convenient (for reasons which will become clear further on) to rewrite any functional of $\vec{x}_j$ given in Eq. (2.12) as follows:

$$\vec{x}_j(\vec{E}_j) = f(\vec{E}_j) = f\left(\sum_k v_{jk}[\vec{x}_k - 3(\hat{r}_{jk} \cdot \vec{x}_k)\hat{r}_{jk}]\right) = \int_{-\infty}^{\infty} d\vec{E}_j\, \delta\left(\vec{E}_j - \sum v_{jk}[\vec{x}_k - 3(\hat{r}_{jk} \cdot \vec{x}_k)\hat{r}_{jk}]f(\vec{E}_j)\right). \qquad (2.15)$$

Using Eq. (2.15) in Eq. (2.13) gives

$$P(\vec{E}_0) = (2\pi)^{-3} \int d\vec{\rho}\, e^{i\vec{\rho} \cdot \vec{E}_0} \int_{r_{N_d}} d^3r_{N_d} P(r_1, r_2, \ldots, r_{N_d}) \prod_{j=1}^{N_d-1} \int d\vec{E}_j\, \delta\left(\vec{E}_j - \sum_k v_{jk}[\vec{x}_k - 3(\hat{r}_{jk} \cdot \vec{x}_k)\hat{r}_{jk}]\right)$$

$$\times \exp(- iv_{0j}\{\vec{\rho} \cdot \vec{x}_j(\vec{E}_j) - 3(\vec{\rho} \cdot \hat{r}_{0j})[\hat{r}_{0j} \cdot \vec{x}_j(\vec{E}_j)]\}) . \qquad (2.16)$$

Equations (2.16) and (2.13) are identical as can be seen by integrating over each of the $d\vec{E}_j$ on the right-hand side of Eq. (2.16). [Note the integral over $d\vec{E}_0$ is absent from the right-hand side of Eq. (2.16).]

In Eqs. (2.13) and (2.16) we express the probability distribution of the internal field $\vec{E}_0$ at site 0 in terms of a function of all other potentials v_{0j} and functionals of the internal fields $\vec{E}_j$ at site j, where each $\vec{E}_j$ in itself is a random variable having its own probability distribution $P(\vec{E}_j)$, also to be obtained self-consistently.

The physical meaning of our procedure is as follows. In order to obtain $P(\vec{E}_0)$, the probability distribution of $\vec{E}_0$, we average over an ensemble of dipole systems in which each member of the ensemble has a dipole fixed at the origin of the coordinates but all other dipoles are placed at a frozen-in but random position.

In order to solve our equations we will have to make an approximation. To exhibit clearly the approximation to be made, we define the term

$$D_j = \delta\left(\vec{E}_j - \sum_k v_{jk}[\vec{x}_k - 3(\hat{r}_{jk} \cdot \vec{x}_k)\hat{r}_{jk}]\right) . \qquad (2.17)$$

$\Pi_j D_j$ is contained in Eq. (2.16). Now let us fix the N_d coordinates of the dipoles in some position $r^0_{N_d}$, where $r^0_{N_d}$ stands for the $3N_d$ coordinates of the N_d dipoles. This fixes every member of the $\Pi_j D_j$ in Eq. (2.16). Next we change the position of a single dipole from r^0_1 to r^1_1, where the subscript 1 indicates a single particle and the superscripts 0 and 1 indicates that the single particle is in position 0 and 1, respectively. This change in the position of the single dipole changes all the D_j's and gives them new fixed values. So every time the position of any of the particles is changed all D_j's are likewise changed, but the D_j's are all interdependent once the positions of the N_d dipoles are fixed. To solve the problem we make the approximation that each of the D_j's can take all possible allowable values independent of any of the other D_j's. Thus we "factor" the D_j's (I am grateful to Professor M. Gitterman for helping me

clarify this point) using a kind of "rearrangement" idea that once the D_j's are factored they may take all possible allowable values independently of all other D_j's as the positions of the particles are changed. We call this approximation the mean-random-field (MRF) approximation. In this approximation we replace each D_j by an *average over all random spacial configurations of the system*; thus

$$D_j \overset{\text{MRF}}{\longrightarrow} \int_{r_{N_d}} d^3 r_{N_d} P(r_1, r_2, \ldots, r_{N_d})$$
$$\times \delta\left(\vec{\mathbf{E}}_j - \sum_k v_{jk}[\vec{\mathbf{x}}_k - 3(\vec{\mathbf{x}}_k \cdot \hat{r}_{jk})\hat{r}_{jk}]\right), \quad (2.18)$$

where the arrow with MRF above it means "becomes in the MRF approximation." Comparing Eq. (2.18) with Eq. (2.12) shows that

$$D_j \overset{\text{MRF}}{\longrightarrow} P(\vec{\mathbf{E}}_j). \quad (2.19)$$

Substituting Eq. (2.19) into Eq. (2.15) gives in the MRF approximation

$$P(\vec{\mathbf{E}}_0) = (2\pi)^{-3} \int d\vec{\rho}\, e^{i\vec{\rho} \cdot \vec{\mathbf{E}}_0} \int_{r_{N_d}} d^3 r_{N_d} P(r_1, r_2, \ldots, r_{N_d})$$
$$\times \prod_{j=1}^{N_d} \int P(\vec{\mathbf{E}}_j)\, d\vec{\mathbf{E}}_j \exp\{-i\rho v_{0j}$$
$$\times[\vec{\rho} \cdot \vec{\mathbf{x}}_j - 3(\vec{\rho} \cdot \hat{r}_{0j})(\hat{r}_{0j} \cdot \vec{\mathbf{x}}_j)]\}. \quad (2.20)$$

The meaning of the MRF approximation becomes further clarified by Eq. (2.20). The probability distribution of the field at site 0, $P(\vec{\mathbf{E}}_0)$, is given in terms of functions of the fields at all other sites integrated over the respective probability distributions. Since there is nothing special about any one of the sites of the system, we require as a self-consistency condition that the $P(\vec{\mathbf{E}}_j)$ shall be site independent. We then drop the indices 0 and j, and we have an integral equation for the probability distribution. We will obtain the solution of this integral equation with not too much difficulty.

C. Solution for the probability distribution

We now assume that all particles are *independently* distributed over the volume V of the solid with a probability V^{-1}. Then

$$P(r_1, r_2, \ldots, r_{N_d}) = V^{-N_d}. \quad (2.21)$$

We also require as a self-consistency condition that $P(\vec{\mathbf{E}})$, but not necessarily $\vec{\mathbf{E}}$, be site independent. With these assumptions Eq. (2.20) becomes

$$P(\vec{\mathbf{E}}) = (2\pi)^{-3} \int d\vec{\rho}\, e^{i\vec{\rho} \cdot \vec{\mathbf{E}}} \left(\frac{1}{V} \int P(\vec{\mathbf{E}}) d\vec{\mathbf{E}}\right.$$
$$\times \left.\int d\vec{r} \exp\{-iv(r)[\vec{\rho} \cdot \vec{\mathbf{x}} - 3(\vec{\rho} \cdot \hat{r})(\hat{r} \cdot \vec{\mathbf{x}})]\}\right)^{N_d}. \quad (2.22)$$

Equation (2.22) is an integral equation for the vector-field distribution $P(\vec{\mathbf{E}})$.

Let

$$\frac{1}{V} \int P(\vec{\mathbf{E}})\, d\vec{\mathbf{E}} \int d\vec{r} \exp\{-iv(r)[\vec{\rho} \cdot \vec{\mathbf{x}} - 3(\vec{\rho} \cdot \hat{r})(\vec{\mathbf{x}} \cdot \hat{r})]\}$$
$$\equiv 1 - V'/V, \quad (2.23)$$

where

$$V' = \int P(\vec{\mathbf{E}})\, d\vec{\mathbf{E}}\left(\int_{R_0}^{R_1} r^2\, dr \int_0^\pi \sin\theta\, d\theta\right.$$
$$\times \left.\int_0^{2\pi} d\phi(1 - \exp\{-iv(r)[\vec{\rho} \cdot \vec{\mathbf{x}} - 3(\vec{\rho} \cdot \hat{r})(\vec{\mathbf{x}} \cdot \hat{r})]\})\right), \quad (2.24)$$

where θ and ϕ are the angles in spherical coordinates associated with vector $\vec{r}$. R_0 is the lower cutoff radius. R_0 should be a near-neighbor distance which is the closest approach between two impurities; however, in this paper it will be convenient to set $R_0 = 0$. We find that for our problem this approximation is reasonable. R_1 in Eq. (2.24) is found using the relation

$$\tfrac{4}{3}\pi R_1^3 = V. \quad (2.25)$$

Let ρ be in the z direction, then let

$$\vec{\rho} \cdot \vec{\mathbf{x}} = \rho x \cos\theta', \quad (2.26)$$

where ρ and x are the magnitudes of ρ and thermal average of the dipole vector, respectively, where $x = x(\vec{\mathbf{E}})$.

Let

$$\vec{\mathbf{x}} \cdot \hat{r} = x \cos\theta'', \quad (2.27)$$

since we recall that $\hat{r}$ is a unit vector. Let

$$\vec{\rho} \cdot \hat{r} = \rho \cos\theta. \quad (2.28)$$

Then referring to Fig. 1, we obtain[22]

$$\cos\theta'' = \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi'). \quad (2.29)$$

Substituting Eqs. (2.25)–(2.29) into Eq. (2.24) gives

$$V' = \int P(\vec{\mathbf{E}})\, d\vec{\mathbf{E}} \left\{\int_{R_0}^{R_1} r^2\, dr \int_0^\pi \sin\theta\, d\theta\right.$$
$$\times \left.\int_0^{2\pi} d\phi\left[1 - \exp\left(\frac{-i\rho x p}{\epsilon_m r^3} F(\theta, \theta', \phi - \phi')\right)\right]\right\}, \quad (2.30)$$

where

$$F \equiv F(\theta, \theta', \phi - \phi') = -\tfrac{1}{2}\left[(1 + 3\cos 2\theta)\cos\theta'\right.$$
$$+ 3\sin 2\theta \sin\theta' \cos(\phi - \phi')]. \quad (2.31)$$

Let

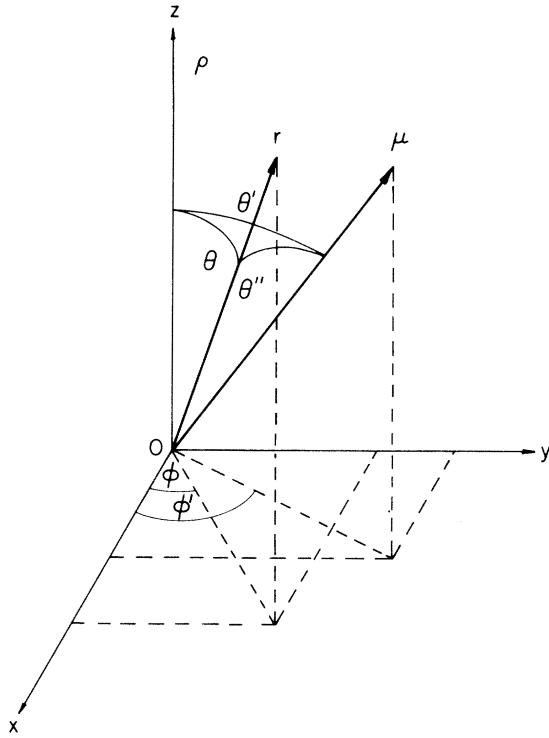$$z = \left|\frac{\rho x p}{\epsilon_m} F(\theta, \theta', \phi - \phi')\right| r^{-3}, \quad (2.32)$$

FIG. 1. Relation between the directions of vectors $\vec{\rho}$, $\vec{\mu}$, and $\vec{r}$ and the angles θ, θ', θ'', ϕ, ϕ' between them.

$$z_0 = \left|\frac{\rho x p}{\epsilon_m} F(\theta, \theta', \phi - \phi')\right| R_0^{-3} , \tag{2.33}$$

$$z_1 = \left|\frac{\rho x p}{\epsilon_m} F(\theta, \theta', \phi - \phi')\right| R_1^{-3} , \tag{2.34}$$

where the vertical brackets | | indicates absolute values. Substituting Eqs. (2.32)–(2.34) into Eq. (2.30) gives

$$V' = \frac{p\rho}{3\epsilon_m} \int P(\vec{E}) \, d\vec{E} \, x(\vec{E}) \int_0^\pi \sin\theta \, d\theta$$

$$\times \int_0^{2\pi} d\phi \left| F(\theta, \theta', \phi - \phi')\right|$$

$$\times \int_{z_1}^{z_0} \left(\frac{1 - \cos z}{z^2} + i \operatorname{sgn} F \frac{\sin z}{z^2}\right) dz , \tag{2.35}$$

$$|\mu| \equiv \int P(\vec{E}) \, d\vec{E} \, x(\vec{E}) f(\theta')$$

$$\equiv \int P(\vec{E}) \, d\vec{E} f(\theta') \left(\frac{(\sinh\beta p E_x)^2 + (\sinh\beta p E_y)^2 + (\sinh\beta p E_z)^2}{(\cosh\beta p E_x + \cosh\beta p E_y + \cosh\beta p E_z)^2}\right)^{1/2} . \tag{2.40}$$

It is important to note that $|\mu|$ is independent of $\vec{E}$ and θ', where θ' is the angle between $\vec{x}$ and ρ. As we integrate over all possible field orientations the direction of $\vec{\rho}$ is immaterial. In principle the integration of $f(\theta')$ over all angles may give a slightly temperature-dependent quantity, since $\vec{E}$ and μ

where sgn$F$ is the sign of F.

So far we have kept the volume of the sample finite. At the end of our calculations we will allow the volume to go to infinity. We shall presently find that the physics of the problem dictates the manner in which we should allow V to approach infinity. We first remark that

$$\langle F \rangle = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \left| F(\theta, \theta', \phi - \phi')\right|$$

$$\times \operatorname{sgn} F(\theta, \theta', \phi - \phi') = 0 . \tag{2.36}$$

Integrating the imaginary part of V' in Eq. (2.35) over r^2 and afterwards over the angles gives

$$\lim_{V_0 \to \infty} \int_{z_1}^{z_0} \frac{\sin z}{z^2} \, dz \to \lim_{V_0 \to \infty} \ln V_0 = \infty . \tag{2.37}$$

On the other hand if we integrate over θ and ϕ first, by Eq. (2.36) Im$V' = 0$. The appropriate order of integration is dictated by the fact that we have a cubic crystal in which the average dipole field is zero. We therefore have to do the angular integration, Eq. (2.36), first. In a noncubic crystal we may get depolarization effects and the imaginary part of V' will not vanish.

Using a computer we have evaluated the magnitude of F, $\langle |F| \rangle$,

$$\langle |F| \rangle = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \left| F(\theta, \theta', \phi - \phi')\right| \equiv 8f(\theta')$$

$$= 8(1 + 0.2963\cos^2\theta' - 0.09597\cos^4\theta') . \tag{2.38}$$

The result of the computer calculation of Eq. (2.38) is shown in Fig. 2. On the same graph we show the function $8f(\theta')$. Substituting Eq. (2.38) into Eq. (2.35) and allowing the volume to go to ∞ and $z_1 \to 0$, we obtain

$$V' = \frac{4\pi}{3} \frac{\rho p}{\epsilon_m} |\mu| . \tag{2.39}$$

Using Eq. (2.8) we obtain

are not necessarily in the same direction.

Substituting Eqs. (2.35)–(2.38) into Eqs. (2.23) and (2.24) and allowing $V \to \infty$, $N_d \to \infty$, we obtain

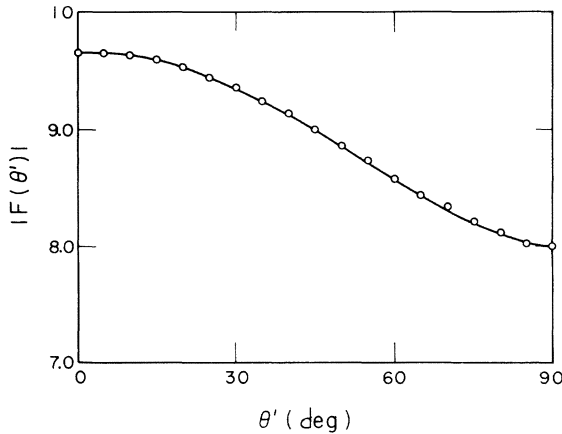$$P(\vec{E}) = (2\pi)^{-3} \int d\vec{\rho} \, e^{i\vec{\rho} \cdot \vec{E}} e^{-\rho\Delta} , \tag{2.41}$$

FIG. 2. Function $F(\theta')$ obtained from computer calculations. The solid curve is a fit of $8f(\theta') = 8(1 + 0.2963 \cos^2\theta' - 0.09597 \cos^4\theta')$. The points are the computer-calculated values for the integral given by Eq. (2.31).

where

$$\Delta = \frac{4\pi}{3} \frac{p}{\epsilon m d^3} n_0 c |\mu| \equiv \Delta_0 |\mu| \; , \qquad (2.42)$$

where d is the lattice constant and n_0 is the number of Cl^- sites per unit volume.

Equation (2.41) can be readily integrated to give

$$P(\vec{E}) = \frac{1}{\pi^2} \frac{\Delta}{[\Delta^2 + (E_x^2 + E_y^2 + E_z^2)]^2} \; . \qquad (2.43)$$

Equation (2.43) coupled with Eqs. (2.42) and (2.40) gives a self-consistent integral equation for the probability distribution for all temperatures and (low) impurity concentrations; it is the central result of this section.

For $T = 0$, $|\mu|$ becomes $\langle f(\theta') \rangle$, which is a constant, and Eq. (2.43) takes a relatively simple form. For T low but not zero, $|\mu|$ is a very slowly varying function of T, and its value will be given in Sec. II D.

D. Temperature dependence of $P(E)$

The expression for $P(\vec{E})$ for all temperatures is given by Eq. (2.43) with the value of Δ given by Eqs. (2.42) and (2.40). In order to obtain $|\mu(T)|$ we have to solve Eq. (2.40) for all T. Rather than solving directly for $|\mu(T)|$ as a function of T it is more convenient to solve for $|\mu(T)|$ as a function of parameters u and u_0 defined by

$$u(T) = k_B T / [p\Delta(T = 0) |\mu|]$$

$$\equiv \frac{u_0}{|\mu|} = \left(\frac{k_B T}{p\Delta_0}\right) \frac{1}{|\mu|} \; , \qquad (2.44)$$

where $\Delta_0 \equiv \Delta(T = 0)$ is the width of the distribution function at $T = 0$. Δ_0 is temperature independent.

We next approximate $f(\theta')$ in Eq. (2.40) by its

average value and take this value to be unity [since $f(\theta') \approx 1$ for all θ']. Effectively $f(\theta')$ may slightly modify the strength of the effective dipole-dipole interaction which enters our calculation as a parameter; thus all our results are insensitive to slight errors in the average of $f(\theta')$.

Next we change variables as follows: $\beta p E_x = x$, $\beta p E_y = y$, $\beta p E_z = z$. We then obtain

$$|\mu| = \frac{u_0^3}{|\mu|^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz$$

$$\times \frac{f_1(x, y, z)}{[1 + (u_0/|\mu|)^2 (x^2 + y^2 + z^2)]^2}$$

$$\equiv F_1(u_0/|\mu|) \; , \qquad (2.45)$$

where

$$f_1(x, y, z) = \frac{(\sinh^2 x + \sinh^2 y + \sinh^2 z)^{1/2}}{\cosh x + \cosh y + \cosh z} \; . \qquad (2.46)$$

Multiplying Eq. (2.45) by $u_0/|\mu|$ gives

$$u_0 = \frac{u_0}{|\mu|} F_1\left(\frac{u_0}{|\mu|}\right) \; . \qquad (2.47)$$

Equation (2.47) gives the solution of $u_0/|\mu|$ as a function of u_0. We note from Eq. (2.47) that the value of $|\mu|$ depends only on the parameter $u_0 = k_B T/(p\Delta_0)$; thus, the value of $|\mu|$ scales with (T/c). Thus, if we have $|\mu|$ for all values of T and for some specific c, we can immediately obtain the value of $|\mu|$ for all c. The expression for $|\mu|$ for low temperatures is calculated in Appendix A and the final results given by Eq. (A17) are

$$|\mu| \approx 1 - 0.598 u_0 - (0.598 u_0)^2, \quad u_0 \ll 1 \; , \qquad (2.48)$$

where Δ_0 is given by Eq. (2.42). The values of $|\mu|$ as a function of u_0 were calculated using a computer and the results are shown in Fig. 3. We find that $|\mu|$ decreases monotonically with increasing u_0. In the insert of Fig. 3 we show the rapid decrease of $|\mu|$ with u_0^{-1} for large u_0. The values of $|\mu|$ obtained are to be used in the calculation of the specific heat and the magnetic susceptibility.

Examining the variation of $|\mu|$ with temperature we find that our solutions make good physical sense. As the temperature becomes high the width of the probability distribution approaches zero quite rapidly. Therefore, at high temperatures practically all fields are concentrated near $\vec{E} = 0$. This is exactly what we expect on physical grounds.

III. CALCULATION OF THE DIELECTRIC SUSCEPTIBILITY

The polarization and susceptibility of a single dipole in a field $\vec{E}$ can be obtained from the single-particle partition function $Z_1(\vec{E}, \beta)$ in a field $\vec{E} = (E_x, E_y, E_z)$ for the six orientational dipoles using Eq. (2.3). We thus have
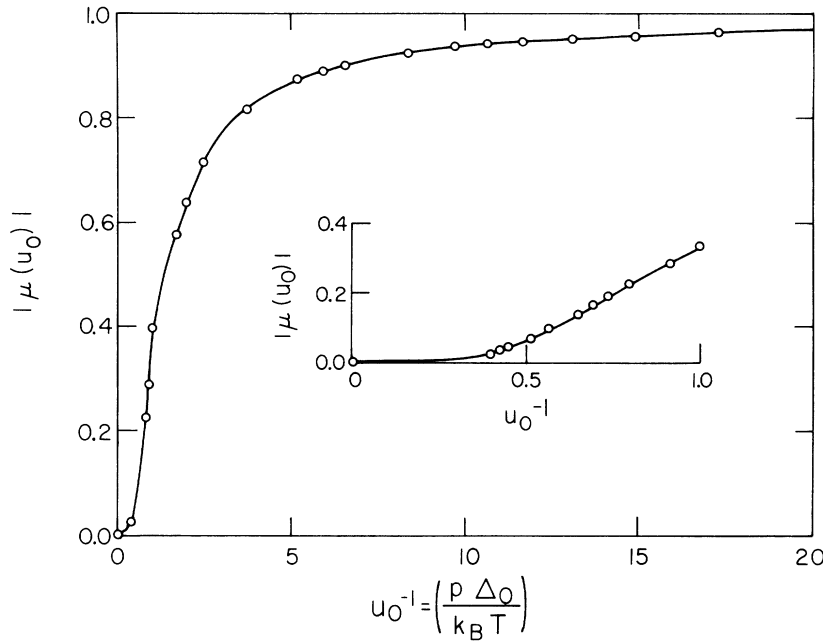
FIG. 3. Values of the parameter $|\mu|$ as a function of u_0, where p is the magnitude of the dipole moment, Δ_0 is the width of the probability distribution at $T = 0$, and T is the temperature.

$$Z_1(\vec{E}, \beta) = \sum_{\{\mu\}} e^{\beta p \vec{\mu} \cdot \vec{E}} = 2(\cosh\beta p E_x$$

$$+ \cosh\beta p E_y + \cosh\beta p E_z)$$

$$\equiv 2D \; . \tag{3.1}$$

The thermal average of the polarization, $M_x(\beta, \vec{E})$, of a single dipole in the x direction is

$$M_x(\vec{E}, \beta) = \lim_{E_{x_0} \to 0} \frac{\partial \ln Z_1(\vec{E}, \beta)}{\partial \beta E_{x_0}} = p \frac{\sinh\beta p E_x}{D} \; , \tag{3.2}$$

where E_{x_0} is the externally applied field in the x direction and

$$\vec{E} = \vec{E}_i + \vec{E}_0 \; , \tag{3.3}$$

where $\vec{E}_i$ is the random internal field and $\vec{E}_0$ is the externally applied field. The average polarization M_x in the x direction in the limit as the externally applied field approaches zero is given by[23]

$$M_x = Ncp \int_{-\infty}^{\infty} dE_x \int_{-\infty}^{\infty} dE_y \int_{-\infty}^{\infty} dE_z P(\vec{E}) \frac{\sinh\beta p E_x}{D} \; 0 \; . \tag{3.4}$$

Since $P(E_x, E_y, E_z)$ is even in E_x, the integral Eq. (4.4) is zero. Thus the net polarization with zero applied field predicted from the theory is zero. The dielectric susceptibility in the x direction χ_x is found by taking the derivative of Eq. (3.4) with respect to E_{x_0} and letting E_{x_0} approach zero. This gives

$$\chi_x = \frac{Nc\beta p^2}{\pi^2} \int_{-\infty}^{\infty} dE_x \int_{-\infty}^{\infty} dE_y \int_{-\infty}^{\infty} dE_z \frac{\Delta}{[\Delta^2 + (E_x^2 + E_y^2 + E_z^2)]^2}$$

$$\times [1 + \cosh\beta p E_x(\cosh\beta p E_y + \cosh\beta p E_z)]D^{-2} \; . \tag{3.5}$$

Since the function $P(\vec{E})$ is even in $\vec{E}$ its derivative with respect to the external field vanishes in the limit as $E_{x_0} \to 0$.

The average susceptibility χ_D is assumed to be $\chi_D = \frac{1}{3}(\chi_x + \chi_y + \chi_z)$. The relationship between the dielectric constant ϵ and the dielectric susceptibility χ_D is (neglecting local-field effects)

$$\epsilon = 1 + 4\pi(\chi_D + \chi_h)$$

$$= \epsilon_D + \epsilon_h \; , \tag{3.6}$$

where the subscripts D and h refer to the dipoles and the host material, respectively.

For general values of β Eq. (3.5) can be solved only using a computer. However, an analytical solution can be obtain for some specific values of T.

A. Very-low-temperature susceptibility

In the limit as $T \to 0$, Eq. (3.5) is solved in Appendix B. The result given by Eq. (B3) is

$$\lim_{T \to 0} \chi_D = 0.352 \frac{Ncp^2}{p\Delta_0 |\mu|} \; , \tag{3.7}$$

where $|\mu|$ is given in Eqs. (2.45) and (2.48). Since Δ_0 is proportional to c, c/Δ_0 is independent of c. The theory thus predicts that the very-low-temperature susceptibility approaches a concentration-independent constant in the limit as $T \to 0$. As we increase T, χ increases, because of the decrease of $|\mu|$ with T. χ undergoes a maximum and then decreases again.

The behavior of χ_D as a function of u_0 was calculated using a computer and the results are shown
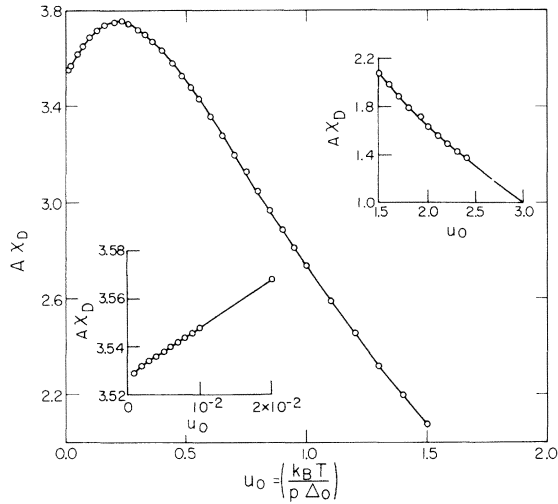
FIG. 4. Variation of the predicted susceptibility as a function of the parameter u_0, where $A^{-1} = p\Delta_0/Ncp^2$.

in Fig. 4. A in the figure is

$$A = p\Delta_0/Ncp^2 . \tag{3.8}$$

In Fig. 4 we also exhibit two inserts; one shows the low-T region the other the high-T region. We find that the deviation of χ_D from its $T = 0$ value, $\Delta\chi_D = \chi_D(T) - \chi_D(T = 0)$, is proportional to u_0 for low T. Thus $\Delta\chi_D$ is proportional to the temperature and is inversely proportional to the impurity concentration for low T.

B. High-temperature susceptibility

The high-temperature susceptibility can be directly obtained by letting β be small in Eq. (3.5). We obtain for high T

$$\chi_D \approx \frac{Ncp^2}{k_B T} \left(1 - B \frac{\Delta_0 |\mu|}{T} \right) , \tag{3.9}$$

where B is a constant of order unity. Our theory thus predicts that the susceptibility (and therefore the dielectric constant) of the dipoles at high T will have a term proportional to T^{-1}. This term in χ_D is the well-known Langevin-Debye contribution and will be referred to as χ_{LD}. The deviation of χ_D from the Langevin-Debye value at high T is from our theory proportional to c^2/T^2 for T just above T_{max}, the temperature of the maximum in χ_D.

In Fig. 5 we show the values of $\chi - \chi_{LD}$ obtained by solving Eq. (3.5) with a computer. These values are plotted on a log-log graph. We find that for T just above T_{max}, the slope of $\chi - \chi_{LD}$ versus u_0 is -2, showing the c^2/T^2 dependence. This result is in agreement with Fiory's[17] experiment of OH$^-$ impurities dissolved in KCl, as is seen from Fig. 10 of Fiory's paper.

For higher temperatures, $|\mu|$ in Eq. (3.9) decreases rapidly with increasing T and the slope of

$\chi - \chi_{LD}$ versus u_0 decreases faster than -2. This again is shown in Fig. 5.

The maximum in the susceptibility occurs at $u_0 = 0.23 = k_B T_{max}/p\Delta_0$. We thus have

$$p\Delta_0 = k_B T_{max}/0.23 . \tag{3.10}$$

From Kanzig's[12] experiments we find that for a dipole concentration of $N_d = 72.5 \times 10^{18}/cm^3$ ($c = 0.45\%$), $T_{max} = 4$ K. Using the value[24] of 1.984 for the specific gravity of KCl and 74.55 for its atomic weight we obtain $p\Delta_0/k_B = 17$ K for $c = 0.45\%$. This gives

$$p\Delta_0/k_B = 38 \text{ K/(each percent of OH}^- \text{ impurity)} . \tag{3.11}$$

Using Eq. (2.42) for the expression of Δ_0 and $\epsilon_m = 4.5$, where ϵ_m is the dielectric constant of pure KCl, we obtain $p = 1.36 \times 10^{-18}$ electrostatic units. Equation (3.11) gives the single constant necessary for our self-consistent solution.

Finally, we remark that we can obtain the scaling properties of the susceptibility by writing Eq. (3.5) in the form

$$\chi_D = \frac{8Np^2c}{\pi^2\beta^2(p\Delta)^3} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \left[1 + u^{-2}(x^2 + y^2 + z^2) \right]^{-2}$$

$$\times \frac{1 + \cosh x(\cosh y + \cosh z)}{(\cosh x + \cosh y + \cosh z)^2} , \tag{3.12}$$

$$\chi_D \propto \left(\frac{c}{\Delta} \right) g(u) = \frac{c}{\Delta_0 |\mu|} g\left(\frac{u_0}{|\mu|} \right) ,$$
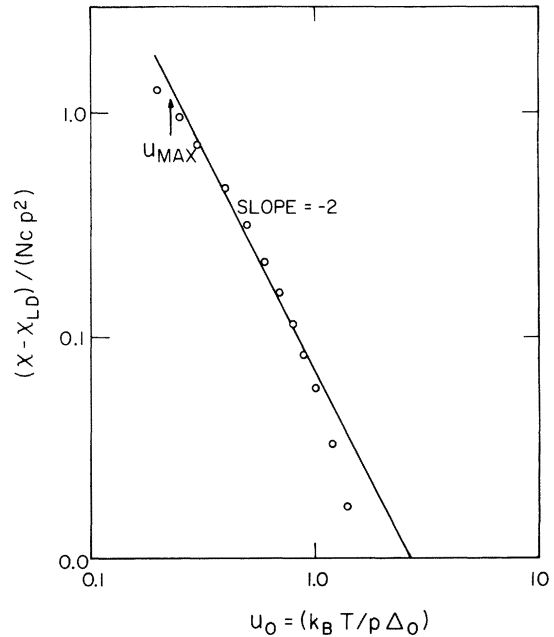

FIG. 5. Deviation of the susceptibility χ_D from its Langevin-Debye value χ_{LD} at T above the temperature of the maximum in the susceptibility. The temperature of the maximum is indicated by the arrow.

where $u_0 = k_B T/p\Delta_0$ and $u = u_0/|\mu|$. Thus we find that all properties of the susceptibility scale with u_0 and it is therefore a function of c/T only. From the above scaling law we find that the value of χ at its maximum is predicted to be independent of the impurity concentration for very low c. This is so since c/Δ_0 in Eq. (3.12) is independent of c. Clearly the predicted $T_{max} \propto c$ as is found in Eq. (3.10).

IV. LOW-TEMPERATURE SPECIFIC HEAT FOR SIX ORIENTATIONAL DIPOLES

The low-temperature specific heat C_D of the six orientational dipoles is obtained from the thermodynamic relation[25]

$$C_D = T\left(\frac{\partial S}{\partial T}\right)_{\vec{E}} , \qquad (4.1)$$

where S is the entropy for the system in an internal dipolar field $\vec{E}$, and

$$S = Nc\int P(\vec{E}, T)S_1(\vec{E}, T)\,d\vec{E} , \qquad (4.2)$$

where

$$S_1(\vec{E}, \beta) = k_B\left(\ln Z_1(\vec{E}, \beta) - \beta \frac{\partial \ln Z_1(\vec{E}, \beta)}{\partial \beta}\right) \qquad (4.3)$$

is the single-dipole entropy in an internal dipole field E and temperature $(k_B T)^{-1}$.

It is shown in Appendix C that to a very good approximation the low-temperature specific heat of the dipoles is given by Eq. (2.11), where the dipolar specific heat for a single impurity in an effective field $\vec{E}$, for the six orientational dipoles, is

$$C_D(\vec{E}, T) = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z_1(\vec{E})}{\partial\beta^2} = \frac{D^{-2}p^2}{2k_B T^2}[2(E_x^2 + E_y^2 + E_z^2) + (E_x - E_y)^2 \cosh\beta p(E_x + E_y) + (E_x + E_y)^2 \cosh\beta p(E_x - E_y)$$

$$+ (E_x - E_z)^2 \cosh\beta p(E_x + E_z) + (E_x + E_z)^2 \cosh\beta p(E_x - E_z)$$

$$+ (E_y - E_z)^2 \cosh\beta p(E_y + E_z) + (E_y + E_z)^2 \cosh\beta p(E_y - E_z)] , \qquad (4.4)$$

where $Z_1(E)$ and D are given by Eq. (3.1).

Using the symmetry of the single-particle specific heat with respect to E_x, E_y, and E_z, and letting $\beta p E_x = x$, $\beta p E_y = y$, $\beta p E_z = z$, the specific heat for the whole system, $C_D(T)$, becomes

$$C_D(T) = \frac{3Nck_B}{2}\left(\frac{k_B T}{p\Delta}\right)^3 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left[1 + \left(\frac{k_B T}{p\Delta}\right)^2(x^2 + y^2 + z^2)\right]^{-2}$$

$$\times [2z^2 + (x-y)^2 \cosh(x+y) + (x+y)^2 \cosh(x-y)]D^{-2} \qquad (4.5)$$

The following scaling property of the specific heat is immediately exhibited by Eq. (4.5):

$$C_D(T) = cg\left(\frac{k_B T}{p\Delta}\right) = cg'\left(\frac{T}{c|\mu(T/c)|}\right) . \qquad (4.6)$$

Thus the specific heat *per impurity* is only a function of c/T. The theory therefore predicts that if the specific heat of a system with fixed impurity concentration is known for all T, we have immediately the behavior for another impurity concentration using the property given in Eq. (4.6).

For very low temperatures we obtain the specific heat in Appendix D. The final result, given by Eq. (D5), is

$$\lim_{T \to 0} C_D = 1.74\left(\frac{k_B T}{p\Delta_0}\right)\frac{Nc}{|\mu|}k_B . \qquad (4.7)$$

We thus find that the very-low-temperature specific heat is approximately linear in T. Thus the dipole-dipole interaction *does not explain* the $T^{3/2}c^{-1/2}$ dependence of the specific heat measured by Peressini *et al.*[18] and Fiory.[17] However, we note that according to Eq. (4.6), *if* the temperature dependence of the specific heat is proportional to $T^{3/2}$

the concentration dependence should be

$$C_D \propto c(T/c)^{3/2} = T^{3/2}c^{-1/2} . \qquad (4.8)$$

Thus the experimentally measured specific heat scales according to the relationship given by the $1/r^3$-dependent dipole-dipole interaction. The fact that our scaling properties are obeyed suggests that the $T^{3/2}$ dependence of C_D is connected to the dipole-dipole interaction. It may, for example, arise from an interaction between a pair of dipoles at low fields which are coupled to the tunneling states of a single dipole. This suggestion is clearly speculative in nature.

The theoretically predicted very-low-temperature specific heat is approximately independent of the impurity concentration. This can be seen from Eq. (4.7), where we find that

$$C_D \propto T(c/\Delta) \propto T^1 c^0 . \qquad (4.9)$$

We find that there is a maximum in the specific heat C_D as a function of T, and the temperature of the maximum is proportional to c. The value of the specific heat at its maximum is also predicted to be proportional to c. This can be seen from
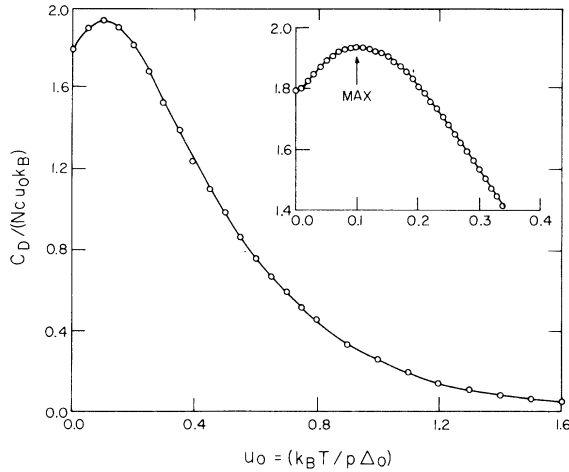
FIG. 6. Specific heat per impurity divided by the parameter u_0. The specific heat at very low T is predicted to be proportional to T and independent of c.

Eq. (4.6), where we find that g' is multiplied by c. The value of the specific heat divided by u_0 is shown in Fig. 6. We find that c_D/T also has a maximum as a function of T. The temperature of the maximum is proportional to the impurity concentration.

V. CONCLUSION AND COMPARISON WITH EXPERIMENT

We obtain the thermodynamic properties of the six-orientational-dipoles system in the molecular-field approximation for all temperatures and (sufficiently) low impurity concentrations for the case when the sole interaction is the dipole-dipole interaction. We thus neglect all quantum-mechanical effects, like tunneling for example, between the dipoles. Therefore, the most one can hope for from our results is that they will be able to separate the contributions as those arising from:
(a) the dipole-dipole interaction alone; (b) all other effects. We summarize our results and indicate where there is agreement with experiment.

A. Dielectric susceptibility

Our results predict that as $c \to 0$, the susceptibility has the following properties: (i) In the limit as $T \to 0$, χ_D approaches a concentration-independent constant; (ii) the deviation of χ_D from its $T \to 0$ value is proportional to T/c; (iii) χ_D has a maximum as a function of T and $T_{max} \propto c$; (iv) $\chi(T_{max})$ is independent of c; (v) the deviation of χ_D from its Langevin-Debye value is proportional to $(c/T)^2$ for $T > T_{max}$; (vi) χ_D scales with T/c.

Properties (iii) and (v) are found to be in agreement with experiments on KCl-OH$^-$ as discussed in Fiory's paper.[17] Property (iv) is approximately valid for low concentrations, as was found by Kan-

zig *et al.*[12] Until further experiments are available we cannot say whether properties (i) and (ii) agree with experiment or not.

B. Specific heat

The most important remark to make about the specific heat is that even though the experimentally measured specific heat scales according to our scaling predictions, in the sense that if C_D is assumed to be proportional to $T^{3/2}$ then its concentration dependence should be $c(T/c)^{3/2} = T^{3/2}c^{-1/2}$, which is observed experimentally, our theory does not predict the $T^{3/2}$ dependence and thus disagrees with experiment. Further properties we obtain are: (vii) The specific heat per impurity scales with T/c; (viii) the value of C_D at its maximum is proportional to c; (ix) last, near $T = 0$, $C_D \propto T$ and is independent of c. Finally we remark that the very-low-temperature specific heat predicted for the vector dipoles is very much like the behavior of dilute alloys found previously.[26,19]

APPENDIX A: EVALUATION OF $|\mu(u)|$ FOR LOW TEMPERATURES

Let $s(x) = \sinh\beta p E_x$ and $c(x) = \cosh\beta p E_x$; we then have

$$| \mu | = \int d\vec{E}\, P(\vec{E}) \left(\frac{s^2(x) + s^2(y) + s^2(z)}{D^2} \right)^{1/2} \qquad (A1)$$

$$= \int P(\vec{E})\, d\vec{E}[1 - v(x, y, z)]^{1/2} , \qquad (A2)$$

where

$$D = c(x) + c(y) + c(z) \qquad (A3)$$

and

$$v \equiv v(x, y, z) \equiv \{3 + 2c(x)\,[c(y) + c(z)]$$
$$+ 2c(y)[c(x) + c(z)] + 2c(z)[c(x) + c(y)]\}/D^2 . \qquad (A4)$$

For low temperatures we have

$$| \mu | = \int P(\vec{E})\, d\vec{E} \left(1 - \frac{X}{2} - \frac{X^2}{8} - \frac{X^3}{16} - \frac{5}{128} X^4 + \cdots + \right) , \qquad (A5)$$

where

$$X = 3\{1 + 2c(x)[c(y) + c(z)]\}/D^2 . \qquad (A6)$$

Equation (A6) is valid because of the symmetry of $P(\vec{E})$. Transforming Eq. (A6) into spherical polar coordinates using the relations

$$pE_x = r \sin\theta \cos\phi \equiv t_1 , \qquad (A7a)$$

$$pE_y = r \sin\theta \sin\phi \equiv t_2 , \qquad (A7b)$$

$$pE_z \equiv r \cos\theta \equiv t_3 , \qquad (A7c)$$

and substituting Eq. (A7) into Eq. (A6) gives

$$X = \frac{\frac{3}{2}\{2e^{-\beta(t_1+t_2)} + (1 + e^{-2\beta t_2})[1 + e^{-2\beta t_1} + e^{\beta(t_3-t_1)}(1 + e^{-2\beta t_3})]\}}{D^2(r\beta, \theta, \phi)} , \quad \text{(A8)}$$

where

$$D(r\beta, \theta, \phi) = \cosh[\beta(t_1 - t_2)/2] + \frac{1}{2}e^{\beta[t_3-(t_1+t_2)/2]}(1 + e^{-2\beta t_3}) + \frac{1}{2}(e^{-\beta(3t_1+t_2)/2} + (e^{-\beta(3t_2+t_3)/2}) . \quad \text{(A9)}$$

From symmetry considerations we find that the integral in Eq. (A5) can be performed between the limits $0 \le \theta \le \pi/2$, $0 \le \phi \le \pi/2$, and $0 \le r \le \infty$, and then we multiply the integral by a factor of 8. Examining the expression for X in the limit as $\beta \to \infty$, we find that for θ and ϕ in the first quadrant

$$\lim_{\beta \to \infty} X = \lim_{\beta \to \infty} \frac{\frac{3}{2}(1 + e^{\beta(t_3-t_1)})}{\{\cosh[\beta(t_2 - t_1)/2] + e^{\beta[t_3-(t_1+t_2)/2]}\}^2} ; \quad \text{(A10)}$$

all other terms are exponentially small. For large values of β, X approaches zero except for the values

$$\tan\theta > \sqrt{2} + \delta , \quad \text{(A11a)}$$

$$\phi = \pi/4 \pm \epsilon , \quad \text{(A11b)}$$

where in the limit as $\beta \to \infty$, $\delta \to 0$, and ϵ becomes as small as we like. When the condition in Eq. (A11) is satisfied, Eq. (A10) becomes

$$\lim_{\beta \to \infty} X = \lim_{\beta \to \infty} \frac{3}{2\cosh^2(\beta r/\sqrt{2})\sin\theta\sin\epsilon} . \quad \text{(A12)}$$

Let $\langle X^n \rangle$ be the value of X^n averaged over the probability distribution of the dipole fields; then for large β

$$\langle X^n \rangle = \frac{8}{\pi^2}\left(\frac{3}{2}\right)^n \int_0^\infty \frac{\Delta r^2 dr}{(\Delta^2 + r^2)^2}$$

$$\times \int_{\tan^{-1}\sqrt{2}}^{\pi/2} \sin\theta d\theta \int_{-\pi/4}^{\pi/4} \frac{d\epsilon}{\cosh^{2n}[(\beta r/\sqrt{2})\sin\theta\sin\epsilon]} . \quad \text{(A13)}$$

Using the table of integrals,[27] we obtain

$$I_n = \lim_{\beta \to \infty} \int_{-\pi/4}^{\pi/4} \frac{d\epsilon}{\cosh^{2n}(\beta r/\sqrt{2})\sin\theta\sin\epsilon}$$

$$= \lim_{\beta \to \infty} \frac{2\sqrt{2}}{\beta r \sin\theta} \frac{4^{n-1}[(n-1)!]^2}{(2n-1)!} . \quad \text{(A14)}$$

Substituting Eq. (A14) into Eq. (A13) gives

$$\langle X^n \rangle = \frac{\sqrt{2}(\pi/2 - \tan^{-1}\sqrt{2})}{\pi^2}\left(\frac{6^n[(n-1)!]^2}{(2n-1)!}\right)\left(\frac{k_B T}{p\Delta_0|\mu|}\right) . \quad \text{(A15)}$$

Substituting Eq. (A15) into Eq. (A5),

$$|\mu| \approx 1 - \frac{k_B T}{p\Delta_0|\mu|}(0.598). \quad \text{(A16)}$$

Solving for $|\mu|$ gives

$$|\mu| \approx 1 - 0.598u_0 - (0.598u_0)^2 , \quad \text{(A17)}$$

where

$$u_0 = \frac{k_B T}{p\Delta(T=0)} = \frac{k_B T}{p\Delta_0} .$$

APPENDIX B: EVALUATION OF THE LOW-TEMPERATURE SUSCEPTIBILITY

The expression for the susceptibility is given in Eq. (3.5) of the text. Transforming Eq. (3.5) into spherical polar coordinates using the definitions given in Eq. (A7) of Appendix A, we obtain

$$\chi_D = \frac{8\beta Ncp^2}{\pi^2} \int_0^\infty \frac{r^2 dr \Delta}{(\Delta^2 + r^2)^2}$$

$$\times \int_0^{\pi/2} \sin\theta d\theta \int_0^{\pi/2} d\phi \frac{N'(\beta r, \theta, \phi)}{D^2(\beta r, \theta, \phi)} , \quad \text{(B1)}$$

where

$$4N'(\beta r, \theta, \phi) = 4e^{-\beta(t_1+t_2)} + (1 + e^{-2\beta t_1})$$

$$\times[1 + e^{-2\beta t_2} + e^{\beta(t_3-t_1-t_2)}(1 + e^{-2\beta t_3})] , \quad \text{(B2)}$$

where $D(\beta r, \theta, \phi)$ is given by Eq. (A9).

We get a contribution to χ_D only when the conditions given in Eq. (A11) of Appendix A is satisfied; for all other values $D^2(\beta r, \theta, \phi)$ goes to infinity as $\beta \to \infty$ and the contribution to χ_D vanishes. We have

$$\chi_D \approx \frac{8\beta Ncp^2}{2} \int_0^\infty \frac{\Delta r^2 dr}{(\Delta^2 + r^2)^2} \int_{\tan^{-1}\sqrt{2}}^{\pi/2} \sin\theta d\theta$$

$$\times \int_{-\pi/4}^{\pi/4} \frac{d\epsilon}{4\cosh^2[(\beta r/\sqrt{2})\sin\theta\sin\epsilon]} , \quad \text{(B3)}$$

$$\lim_{\beta \to \infty} \chi_D \approx \frac{4\sqrt{2} Ncp^2}{\pi^2\Delta_0|\mu|}\left(\frac{\pi}{2} - \tan^{-1}\sqrt{2}\right)$$

$$= 0.352 Ncp^2/\Delta_0|\mu| ,$$

where Δ_0 is given in Eq. (2.42), and the expression for $|\mu|$ is found in Eq. (2.40) and its dependence on u_0 is shown in Fig. 3.

APPENDIX C: APPROXIMATION OF SPECIFIC HEAT BY EQ. (2.11)

In this appendix we show that to a very good approximation the specific heat of the dipoles is given by Eq. (2.11).

Using Eq. (4.1) and (4.2) we have (assuming that the entropy is an additive quantity)

$$C_D = TNc \int d\vec{E}\left[\left(\frac{\partial S}{\partial T}\right)P(\vec{E}) + S\frac{\partial P(\vec{E})}{\partial T}\right] . \quad \text{(C1)}$$

Using Eq. (4.3) we obtain

$$T\left(\frac{\partial S}{\partial T}\right)_{\vec{E}} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z_1(\beta, \vec{E})}{\partial \beta^2} ,$$ (C2)

where $Z_1(\vec{E}, \beta)$ is the single-dipole partition function in field $\vec{E}$.

Substituting Eq. (C2) into Eq. (C1) we find that the first term in the integral is exactly the term given by Eq. (4.4). This term is evaluated in Eqs. (4.5)–(4.7) in the text, and is shown in Fig. 6.

We have evaluated the second term in Eq. (C1) using a computer and we find that for all values of $u_0 = k_B T/p\Delta_0$ the second term is negligible compared to the first. We now prove this for very low temperatures, where it is crucial to ascertain whether the $T^{3/2}$ dependence of the specific heat is a result of the dipole-dipole interaction. Using the expression for $P(\vec{E})$ given in Eq. (2.43) we obtain

$$\frac{dP(E)}{dT} = \frac{-1}{\pi^2|\mu|} \frac{d|\mu|}{dT}\left(\frac{4\Delta^3}{(\Delta^2+E^2)^3} - \frac{\Delta}{(\Delta^2+E^2)^2}\right).$$ (C3)

Using the fact that $d|\mu|/dT$ is always negative, we obtain for the second term in Eq. (C1), C_{D2},

$$C_{D2} = \frac{8Nc}{\pi^2}\left|\frac{d|\mu|}{du_0}\right| u^4 \int_0^\infty r^2\, dr\, f(r)$$

$$\times \left(\frac{4}{(1+u^2r^2)^3} - \frac{1}{(1+u^2r^2)^2}\right),$$ (C4)

where $u_0 = k_B T/p\Delta_0$, $u = u_0/|\mu|$, and

$$f(r) = \int_0^{\pi/2} \sin\theta\, d\theta \int_0^{\pi/2} dS(r, \theta, \phi),$$ (C5)

where $S(r, \theta, \phi)$ is the value of S given in Eq. (4.3) in spherical polar coordinates with $r = \beta|E|$. The values of $f(r)$ versus r were calculated and the re-
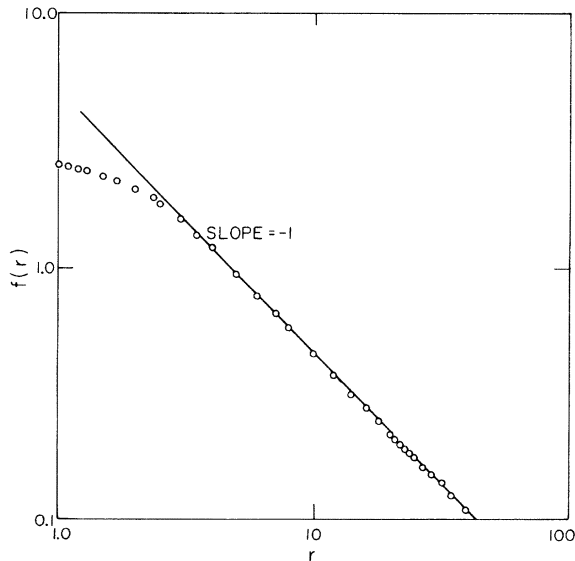

FIG. 7. Function $f(r)$ versus r obtained by the computer calculation. Note the r^{-1} dependence for large r.

sults are shown in Fig. 7. We find that for $r \geq 2$, $f(r)$ can be well approximated by $f(r) = 4.5/r$. We note that Eq. (C4) has a factor of T^4 multiplying the integral. Thus for low T we can neglect the value of the integral from 0 to 2 and we make a very small error in replacing $f(r)$ from 0 to ∞ by its asymptotic value [note $r^2 f(r)$ converges for $r \to 0$]. We can now perform the integral and we obtain

$$C_{D2} \approx \frac{8Nc}{\pi^2}\left|\frac{d|\mu|}{du_0}\right| u^2 .$$ (C6)

Using Eq. (2.48) gives for low temperatures $d|\mu|/du_0 \approx 0.598$ and we find that C_{D2} is proportional to u^2. C_D on the other hand is found from Eq. (4.7) to be proportional to u at low T. Thus for low T, C_{D2} is negligible compared to C_D. A detailed computer calculation has confirmed these results and has shown that C_{D2} is small compared to C_D over the whole temperature range.

APPENDIX D: EVALUATION OF THE LOW-TEMPERATURE SPECIFIC HEAT

The expression for the low-temperature specific heat is given by Eq. (4.5) of the text. Transforming into spherical polar coordinates using the definition given in Eq. (A7) of Appendix A, and using the symmetry of the functions, allows us to integrate fields only over the first quadrant; we obtain

$$C_D(T) = \frac{24Ncp^2}{\pi^2 k_B T^2} \int_0^\infty \frac{\Delta r^4\, dr}{(\Delta^2 + r^2)^2}$$

$$\times \int_0^{\pi/2} \sin^3\theta\, d\theta \int_0^{\pi/2} d\phi\, \frac{N(r, \theta, \phi)}{D^2(r, \theta, \phi)} ,$$ (D1)

where

$$4N(r, \theta, \phi) = 4\cot^2\theta\, e^{-\beta(t_1+t_2)} + (1 - \sin2\phi)(1 + e^{-2\beta(t_1+t_2)})$$

$$+ (1 + \sin2\phi)(e^{-2\beta t_2} + e^{-2\beta t_1})$$ (D2)

and D^2 is given by Eq. (A9) of Appendix A. Examining the expression $N(r, \theta, \phi)/D^2(r, \theta, \phi)$ for large β, we find that we get a contribution only when Eq. (A11) is satisfied. For large β we have

$$\lim_{\beta \to \infty} N(r, \theta, \phi) \to (1 - \sin2\phi) .$$ (D3)

Using the fact that we get contributions only from $\phi = \pi/4 + \epsilon$, $1 - \sin2\phi$ becomes $1 - \cos^2 2\epsilon$. Substituting these values into Eq. (D1) we obtain for very large β,

$$C_D(T) = \frac{24Ncp^2}{4\pi^2 k_B T^2} \int_0^\infty \frac{\Delta r^4\, dr}{(\Delta^2 + r^2)^2}$$

$$\times \int_0^{\pi/2} \sin^3\theta\, d\theta \int_{-\pi/4}^{\pi/4} \frac{2\epsilon^2\, d\epsilon}{\cosh^2[(\beta r/\sqrt{2})\sin\theta\sin\epsilon]} .$$ (D4)

Using the table of integrals, Ref. 27, we obtain

$$\int_0^\infty \frac{\epsilon^2 \, d\epsilon}{\cosh^2(\beta\gamma\sin\theta\epsilon/\sqrt{2})} = \frac{\pi^2\sqrt{2}}{6\beta^3\gamma^3\sin^3\theta} \ .$$

$$= 1.74 k_B \left(\frac{k_B T}{p\Delta_0}\right) \frac{Nc}{|\mu|} = 1.74 k_B \frac{u_0 Nc}{|\mu|} \ . \qquad (D5)$$

Substituting this result into Eq. (D4) gives

$$\lim_{\beta\to\infty} C_D = \frac{4Nc\sqrt{2} \, k_B^2 T}{p} \int_0^\infty \frac{\Delta\gamma \, d\gamma}{(\Delta^2 + \gamma^2)^2} \int_{\tan^{-1}\sqrt{2}}^{\pi/2} d\theta$$

ACKNOWLEDGMENT

*Part of this work supported by USAFOR under Contract No. 73-2430.

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