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Dielectric properties of dilute bcc antiferroelectric systems

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A model is presented for the calculation of the static dielectric properties of pure and dipole-dilute bcc antiferroelectric systems. The real systems display long-range dipolar and elastic interactions, which are simulated in this paper by an effective Hamiltonian with first- and second-neighbor interactions only. The first-neighbor interaction is taken to be antiferroelectric but the second neighbors, although ferroelectrically ordered at $T=0$ K for the pure systems, are allowed to interact via (i) a ferroelectric or (ii) a weak antiferroelectric coupling. The cluster-variation method is used to treat this model. The results show that the dielectric properties are qualitatively different in cases (i) and (ii). We conjecture that in orthorhombic KCN the effective second-neighbor interaction is antiferroelectric. The model is also of interest for other antiferroelectric and antiferromagnetic systems.

I. INTRODUCTION

In a recent study[1] of the thermodynamics of the pure and dilute alkali cyanides NaCN and KCN, the importance of short-range-order effects in the properties of the low-tempertaure orthorhombic phases (paraelectric and antiferroelectric) has been demonstrated. Calculations within the Bethe approximation, in which only nearest-neighbor antiferroelectrically coupled pairs are correlated, are in good qualitative agreement with experiment. This result is somewhat surprising, and must be further investigated since electric interactions are of long-range nature.

As discussed in Ref. 1, the oversimplified model Hamiltonian with only nearest-neighbor coupling proposed there must be regarded as an effective one. In particular, calculated microscopic physical quantities are allowed to be quite different from the corresponding values in the real system. The simplification is justified because short-range-order effects in the specific heat and in the dielectric constant, and particularly deviations from mean field, were being qualitatively investigated there. Such thermodynamic properties are related to energy variations, rather than to total energies for which dipolar lattice sums must be carried out to convergence.[2]

Nevertheless, results presented in Ref. 1 deserve further investigation, not only to incorporate longer-range interactions, but also due to the presence of ferroelectrically ordered pairs. These may contribute differently to the dielectric properties in connection, for example, to frustration effects.

The antiferroelectric structure[3,4] of KCN and NaCN corresponds to a dipolar arrangement of the CN^- permanent dipoles such that in each body-centered *orthorhombic* unit cell the central dipole is antiparallel to the eight dipoles at the corners. In the present work we are concerned with the effect and the nature of the second-neighbor coupling, and for simplicity we assume a body-centered cubic (bcc) unit cell.

We introduce a model for pure and dipole-dilute bcc antiferroelectric systems in which first- and second-neighbor interactions are present. The first-neighbor interaction is taken to be antiferroelectric but the second neighbors, although ferroelectrically ordered at $T=0$ K in the pure system, are allowed to interact via either a ferroelectric or an antiferroelectric coupling. The ratio γ between the values of the second- and the first-neighbor energies must be regarded as an effective parameter rather than the true ratio in real systems where longer-range interactions are present. While in the previous approximation[1] the effective coordination number of the lattice was a fitting parameter, in the present model we have a fixed (bcc) lattice geometry, but γ may be adjusted to reproduce certain features of experimental observations, like the maximum in the paraelectric regime in susceptibility-temperature curves of KCN.

The model we treat is equivalent to a dilute Ising model. We calculate thermodynamic properties through a generalization of Kikuchi's cluster-variation method,[5] formulated in Sec. II, which properly takes into account the dilution. Qualitatively different results for the cases of ferroelectric and antiferroelectric second-neighbor coupling are analyzed in Sec. III, and compared to the previous (Bethe) approximation[1] in Sec. IV. The conclusions of Sec. V summarize the relevance of the present results for the identification of the kind of second-neighbor interactions in similar physical systems.

II. MODEL

We consider a bcc lattice decomposed into the two equivalent sublattices α and β indicated in Fig. 1. Each site corresponds to one of three possible states: States $(+1)$ and (-1) stand for a site occupied by a dipole (a CN^- radical) oriented parallel or antiparallel to an anisotropy axis, while 0 corresponds to a vacancy (a halogen ion). Among the N lattice sites, Np are occupied by di-

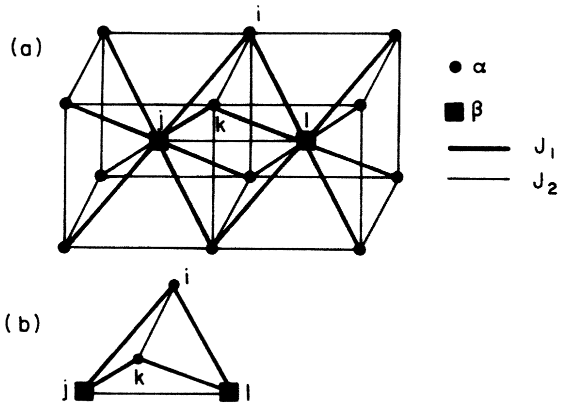

FIG. 1. (a) bcc lattice with first- and second-neighbor interactions: sublattices α and β and the tetrahedron taken as the basic cluster are indicated. (b) Tetrahedron in configuration $\{ijkl\}$.

poles. The pure ($p=1$) ordered system corresponds to all α sites in the ($+1$) state and all β sites in the (-1) state. The nearest-neighbor interaction J_1 is taken to be antiferroelectric (positive) and couples α-β pairs. The second-neighbor interaction J_2 couples α-α and β-β pairs, and may be positive or negative. In the case $J_2>0$ we assume that it is sufficiently weaker than J_1 so that the ground-state structure is determined uniquely by J_1.

We study the thermodynamics of this system within Kikuchi's cluster-variation method (CVM),[5] which approximates the configurational entropy so that correlations among sites within a chosen "basic cluster" in the lattice are fully incorporated. The method is expected to converge to the exact result when the basic cluster is increased.[6] Previous applications of the CVM to site-dilute Ising systems have been done in the pair approximation, equivalent to the Bethe method.[1,7,8]

For the present model, the simplest cluster which preserves the symmetry of the system and includes both first- and second-neighbor pairs is the tetrahedron indicated in Fig. 1. This approximation in the pure bcc lattice has been previously used in the study of binary alloys[9–11] and metamagnetic systems.[12] In the case of first-neighbor antiferromagnetic interactions only,[9] it yields a Néel temperature only 2.2% above the series-expansion result. Here we take parallel dipoles to interact via a first-neighbor repulsion $J_1>0$ and a second-neighbor interaction $J_2=\gamma J_1$, where γ may assume positive or negative values. The energy of a tetrahedron configuration $\{ijkl\}$ [see Fig. 1(b)] is therefore (in units of J_1)

$$\epsilon_{ijkl}=ij+jk+kl+li+\tfrac{3}{2}\gamma(ik+jl)\ , \tag{1}$$

where i,j,k,l may assume values 0 and ±1 according to the state of the site. We define the probabilities of the different possible configurations of the tetrahedron and smaller clusters according to the notation in Table I. Of course, only the tetrahedron configurations are independent parameters; the others are given in terms of appropriate summation rules[5] involving $\{\omega_{ijkl}\}$.

The CVM entropy in the tetrahedron approximation is obtained through a convenient scheme.[13] We incorporate a reduced uniform field $h=H/J_1$, and write the Helmholtz free energy of the system in reduced units as

$$\begin{aligned}\phi_0=(E-TS)/(Nk_BT)=\beta\sum(\epsilon_{ijkl}-hm_{ijkl})\omega_{ijkl}+6\sum\mathscr{L}(\omega_{ijkl})-3\left[\sum\mathscr{L}(u_{ijk})+\sum\mathscr{L}(u_{kli})+\sum\mathscr{L}(\tilde{u}_{jkl})+\sum\mathscr{L}(\tilde{u}_{lij})\right]\\ +\tfrac{3}{2}\left[\sum\mathscr{L}(y_{ik})+\sum\mathscr{L}(\tilde{y}_{jl})\right]+\sum\mathscr{L}(x_{ij})+\sum\mathscr{L}(x_{kj})+\sum\mathscr{L}(x_{kl})+\sum\mathscr{L}(x_{il})\\ -\tfrac{1}{4}\left[\sum\mathscr{L}(p_i)+\sum\mathscr{L}(p_k)+\sum\mathscr{L}(\tilde{p}_j)+\sum\mathscr{L}(\tilde{p}_l)\right]\ ,\end{aligned} \tag{2a}$$

where $m_{ijkl}=(i+j+k+l)/4$ is the polarization per site for the $ijkl$ cluster, $\beta=J_1/(k_BT)$, and the summations are performed over all pertinent indices, which may assume values -1, 0, and $+1$. The operator $\mathscr{L}$ is defined as

$$\mathscr{L}(q)=q(\ln q-1)\ . \tag{2b}$$

TABLE I. Notation for configuration probabilities (see Fig. 1).

Tetrahedron: α-β-α-β	ω_{ijkl}
Triangles: α-β-α	u_{ijk}
Triangles: β-α-β	$\tilde{u}_{jkl}$
Second-neighbor pairs: α-α	y_{ik}
Second-neighbor pairs: β-β	$\tilde{y}_{jl}$
First-neighbor pairs: α-β	x_{ij}
α sites	p_i
β sites	$\tilde{p}_j$

Expression (2) is valid both for the pure ($p=1$) and for the dilute ($p<1$) cases. Yet, in the pure case only one constraint, $\sum\omega_{ijkl}=1$, must be considered in the minimization problem, while in the dilute case additional constraints are needed to specify the distribution of vacancies in the lattice.

We define an "arrangement" as a given distribution of vacancies in the tetrahedron cluster, irrespective of the dipoles orientation. Calling $\hat{i}=|i|$, two configurations $\{i_1j_1k_1l_1\}$ and $\{i_2j_2k_2l_2\}$ belong to the same arrangement when $\hat{i}_1=\hat{i}_2$, $\hat{j}_1=\hat{j}_2$, $\hat{k}_1=\hat{k}_2$, and $\hat{l}_1=\hat{l}_2$. The sum of all tetrahedron configuration probabilities in the same arrangement is equal to the total probability $\psi_{\hat{i}\hat{j}\hat{k}\hat{l}}$ for that arrangement, thus

$$\sum{}'\omega_{ijkl}=\psi_{\hat{i}\hat{j}\hat{k}\hat{l}}\ . \tag{3}$$

In (3), $\sum'$ indicates summation over nonzero indices for all dipolar configurations in the same arrangement. We consider here the case of a quenched random distribution of vacancies, where

$$\psi_{\hat{i}\hat{j}\hat{k}\hat{l}}=p^{\hat{i}+\hat{j}+\hat{k}+\hat{l}}(1-p)^{4-(\hat{i}+\hat{j}+\hat{k}+\hat{l})} . \tag{4}$$

The constraints (3) are incorporated to the free-energy minimization problem through a set of Lagrange multipliers $\lambda_{\hat{i}\hat{j}\hat{k}\hat{l}}$, so that we define

$$\phi=\phi_0+\beta\sum_{\substack{\hat{i}\hat{j}\hat{k}\hat{l}\\ =0,1}}\lambda_{\hat{i}\hat{j}\hat{k}\hat{l}}\left[\psi_{\hat{i}\hat{j}\hat{k}\hat{l}}-\sum{}'\omega_{ijkl}\right] . \tag{5}$$

At a given p, the minimization of ϕ with respect to $\{\omega_{ijkl}\}$ gives

$$\omega_{ijkl}=\exp[\beta(\lambda_{\hat{i}\hat{j}\hat{k}\hat{l}}-\kappa_{ijkl})/6]A_{ijkl} , \tag{6a}$$

where

$$\kappa_{ijkl}=\epsilon_{ijkl}-hm_{ijkl} , \tag{6b}$$

and

$$\begin{aligned}A_{ijkl}={}&(p_i\widetilde{p}_jp_k\widetilde{p}_l)^{1/24}(u_{ijk}u_{kli}\widetilde{u}_{jkl}\widetilde{u}_{lij})^{1/2}\\&\times(y_{ik}\widetilde{y}_{jl})^{-1/4}(x_{ij}x_{il}x_{kj}x_{kl})^{-1/6} .\end{aligned} \tag{6c}$$

This reduces to the Kikuchi-Sato superposition relation[9] in the pure case, where λ_{1111} is the only relevant Lagrange multiplier. We obtain $\lambda_{\hat{i}\hat{j}\hat{k}\hat{l}}$ through Eq. (3), which combined with Eq. (6) yields

$$\exp(\beta\lambda_{\hat{i}\hat{j}\hat{k}\hat{l}}/6)=\left[\sum{}'\exp(-\beta\kappa_{ijkl}/6)A_{ijkl}\right]^{-1}\psi_{\hat{i}\hat{j}\hat{k}\hat{l}} . \tag{7}$$

The system of equations (6)—(7) is solved by the "natural iteration method":[14] initial values are chosen for the set of tetrahedron configuration probabilities $\{\omega_{ijkl}\}$, summation rules (such as $u_{ijk}=\sum_l\omega_{ijkl}$) are used to obtain all Lagrange multipliers, which are then used in Eq. (6a) to yield new values of $\{\omega_{ijkl}\}$. The process is iterated until a convergence criterion is satisfied.

From the converged values of the probabilities, the static susceptibility (in arbitrary units) is calculated numerically through the definition

$$\begin{aligned}\chi(p,T)&=\frac{d(P_\alpha+P_\beta)}{dh}\\&=\lim_{h\to 0}[(p_1-p_{-1})+(\widetilde{p}_1-\widetilde{p}_{-1})]/h ,\end{aligned} \tag{8}$$

where P_ν is the polarization in reduced units of the ν sublattice.

III. RESULTS

A. Pure materials ($p=1$)

The only free parameter in our model is $\gamma=J_2/J_1$. In the bcc lattice with first- and second-neighbor interactions, the ground state is antiferroelectric if

$$\gamma=J_2/J_1<\tfrac{2}{3} . \tag{9}$$

Since our motivation is the antiferroelectric ordering in NaCN and KCN, we restrict γ to that range. A different structure,[15,16] called B32, corresponding to an antiferroelectric arrangement in each of the two sublattices, is stable for $\gamma>\frac{2}{3}$.

Experimental data[1,17] for pure KCN show a maximum in the static susceptibility χ at a temperature T^* which is about 7% higher than $T_{C_0}=83$ K, the ordering temperature, while for NaCN, $T^*=T_{C_0}$. In the present model we get $T^*=T_{C_0}$ for $\gamma\lesssim 0$, i.e., for ferroelectric second-neighbor coupling, and $T^*>T_{C_0}$ for $0\lesssim\gamma<\frac{2}{3}$. This indicates that in KCN the effective second-neighbor interaction is probably antiferroelectric (therefore leading to a frustrated ground state) while for NaCN it is probably ferroelectric.

The effective interactions are not easily calculated from first principles, since the low-temperature ordering of these materials involves a complex elastically dressed electric transition.[2]

B. Dilute materials

We consider initially $\gamma>0$, i.e., antiferroelectric first- and second-neighbor interactions. In Fig. 2, the static susceptibility versus temperature calculated from (8) is presented for several values of the dipole concentration for $\gamma=0.5$. In the pure limit ($p=1$), $T^*=1.05T_{C_0}$, a feature that is not clearly resolved in the figure, and $k_BT_{C_0}=4.6J_1$. Note that at high dipole concentrations, χ increases very slowly as T decreases in the disordered region. At the ordering temperature $T_C(p)$, the susceptibility shows a cusp, which is typical of antiferroelectric systems. In the $T\to 0$ K limit, the susceptibility diverges for any $p<1$, which corresponds to the paraelectric contribution of isolated dipoles. As the dipole concentration de-

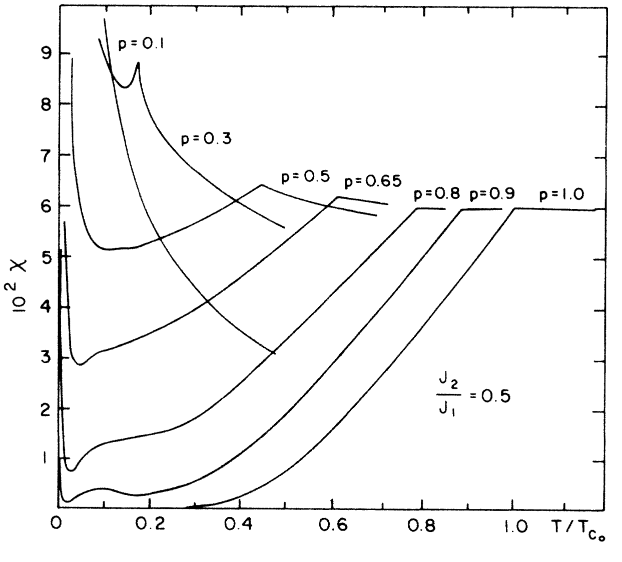

FIG. 2. Static susceptibility of dipole-dilute systems for the indicated dipole concentrations p for $\gamma=0.5$. The pure material transition temperature is $T_{C_0}=4.6J_1/k_B$.

creases, the paraelectric contribution increases both above and below T_C (e.g., the $p=0.3$ curve). For $p \lesssim 0.2$, no ordering transition occurs, and the system shows a simple paraelectric behavior (e.g., the $p=0.1$ curve).

An interesting feature of the susceptibility in the mixed materials is the appearance of a bump around $T/T_{C_0}=0.1$, which we associate to isolated second-neighbor pairs. In the pure ordered materials, second neighbors are frustrated (parallel), but in isolated pairs they may become antiparallel at low T. This anomaly in the χ-versus-T curve corresponds to the partial short-range ordering of second-neighbor clusters, which occurs at a temperature of the order of J_2, independent of p.

In Fig. 3 we present results for ferroelectric second-neighbor interaction with $\gamma=-0.5$; in this case $k_B T_{C_0}=11.2J_1$. Note that the ordering cusp is much more pronounced here than in Fig. 2 due to the faster increase of χ as T decreases in the disordered region. The absence of second-neighbor frustration is clear in this case: the negative second-neighbor interaction in fact reinforces the type of ordering favored by the positive first-neighbor interaction. Thus, no anomaly of the kind described in the preceding paragraph occurs. The paraelectric behavior due to isolated dipoles, i.e., the divergence of χ as $T \to 0$, is also obtained here for any $p<1$. It is not indicated in the figure for $p \geq 0.5$ because the increase occurs for extremely low values of T/T_{C_0}.

IV. COMPARISON WITH THE PAIR-APPROXIMATION RESULTS

The dielectric constant of dipole-dilute antiferroelectric systems has been previously calculated[1] within a simpler scheme in which the basic cluster was taken to be a nearest-neighbor α-β pair. Several features—such as the slow increase of χ under cooling, the maximum of χ at $T^* > T_{C_0}$ for pure KCN—not predicted in mean-field theory, were obtained in that approximation. A semiquantitative fitting with the measured behavior of KCN and NaCN was made by adjusting three parameters of the model. For the effective coordination number (z_{eff}), the fitting yields $z_{\text{eff}}=3.4$ for KCN and $z_{\text{eff}}=4.1$ for NaCN, which is an indication of partial cancellation due to the presence of further-neighbor interactions, since in the real lattice $z=8$. Lower values of z_{eff} are associated with higher values of J_2, which competes with J_1, in the sense that the two interactions do not favor the same ordered structure if they are both positive. Because z_{eff} is smaller for KCN than NaCN, we should expect a higher J_2 for KCN, which is also the conclusion reached in Sec. III A.

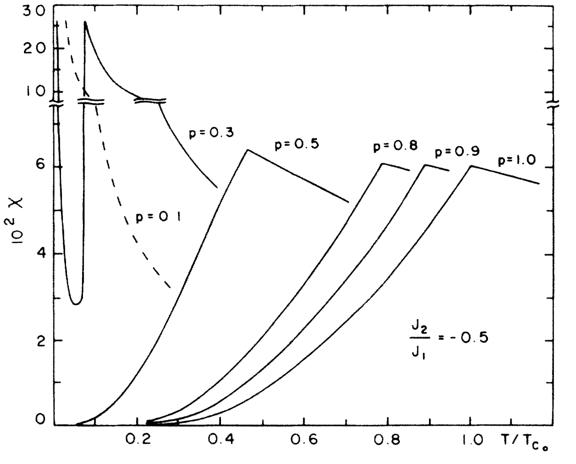

FIG. 3. Same as Fig. 2 for $\gamma=-0.5$. The pure material transition temperature is $T_{C_0}=11.2J_1/k_B$.

Within the range $0<\gamma<\frac{2}{3}$, T^* is at most $\sim 5\%$ higher than T_{C_0}; we do not have the same fitting flexibility for the tetrahedron cluster than for the α-β pair, since the coordination number is fixed in the present model. The measured difference for KCN (about 7%) should be considered approximate because of the experimental difficulties described in Ref. 1. Therefore we do not attempt any quantitative fitting here.

For the dilute materials, the main improvements of the present model over the previous approximation[1] are:

(i) The correct $T \to 0$ limit behavior for $\chi(p \neq 1, T)$; in Ref. 1, χ always goes to zero in this limit instead of diverging, as a consequence of the additional—average coordination number[7]—approximation assumed there. In the notation of Table I, it consists of taking $x_{0i}=p_0\tilde{p}_i$ for any pair containing a vacancy (note $p_0=1-p$). If this condition is relaxed, the correct formal limit is obtained even in the pair approximation.[7] However, because of dipole freezing effects, experimentally χ is actually seen to go to zero at low T for all concentrations in the dilute cyanides,[18] even for very low ($\lesssim 10\%$) dipole concentrations, when the full paraelectric behavior is formally expected. This effect has been discussed in the literature in connection with a dipole-glass phase conjecture.[19]

(ii) The more pronounced cusp in χ in Fig. 2 as p decreases; this is a feature that is also observed in experimental curves,[18] but not obtained in the previous approximation.

(iii) The "signature" of the second-neighbor frustrated interactions, which is not present in the experimental curves, probably due to the freezing effects discussed in (i).

V. CONCLUSIONS

The results of this paper bring about the interesting possibility of the identification of the nature of the second-neighbor interaction from the dielectric properties of dilute antiferroelectric materials, in particular from the dependence of the static susceptibility χ on the temperature T. For example, in the case of antiferroelectric first-neighbor interactions ($J_1>0$), a bump in the ordered regime of the χ-versus-T curve is associated with dilution and with the frustration of second-neighbor antiferroelectric ($J_2>0$) interactions. This anomaly is indeed more likely to be found in similar magnetic systems, where freezing effects do not inhibit the response. Another example is the appearance of a maximum in the χ-versus-T curve of the pure systems in the paraelectric regime in the case $J_1, J_2>0$. Comparison with experimental results leads us to conjecture that $J_2>0$ for KCN, which is consistent with a low value of the effective coordination number in a previous approximation,[1] since J_1 and J_2 favor different ordered structures.

The qualitatively correct predictions of other features of the χ-versus-T curves—the divergence as $T \to 0$ for the dilute case and the cusp at the ordering temperature—indicate that the cluster-variation method (CVM) may become a valuable tool for the study of the general formal problem of site-dilute Ising systems. The CVM has two clear advantages over effective-field (EF) approximations, which are frequently used[20–23] for the thermodynamics of dilute Ising models: (i) while EF results usually depend only on the coordination number of the lattice, the CVM takes into account the geometry of the problem in a more complete way, and (ii) the CVM results are expected to converge to the exact solution when the size of the basic cluster is increased. Therefore, further applications of the CVM to such problems are under investigation.

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