PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Thermodynamic properties of pure and dilute alkali cyanides: Short-range-order effects

Belita Koiller and Maria A. Davidovich
Departmento de Física, Pontifícia Universidade Católica do Rio de Janeiro, Caixa Postal 38071, 22452 Rio de Janeiro, Brazil

Fritz Lüty
Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 1 October 1984)

We study the alkali cyanides NaCN and KCN, both pure and mixed in alkali halides, in the low-temperature orthorhombic phases (paraelectric and antiferroelectric). Experimental results on the dielectric properties of these systems indicate that short-range-order effects are important. We investigate these effects using the Kikuchi method in the limit of the pair-correlation approximation (Bethe approximation). Our results for the temperature dependence of the dielectric constant for the pure systems are adjusted to the available experimental data to obtain the three relevant parameters of the model: coordination number, coupling interaction, and electric dipole moment of the CN^- molecular ion. This parametrization is used in the study of the dielectric constants of the mixed systems and the critical temperature as a function of the CN^- dipole concentration is obtained. Our results are in good qualitative agreement with the experimental ones.

I. INTRODUCTION

The study of molecular dipole order and phase transitions in alkali cyanides includes an extensive experimental investigation of ionic solids of the type $M^+(CN^-)_x[X^-]_{1-x}$. These are the mixed alkali-cyanide—alkali-halide systems, where M stands for an alkali metal (e.g., Na, K), X is a halogen atom, and x is the concentration of cyanide molecular ions in the anionic sites.

Pure alkali cyanides KCN and NaCN present two phase transitions. The first is associated with ferroelastic ordering of the CN^- elastic dipoles, leading to a lattice distortion from cubic to orthorhombic structure. The second, at lower temperatures, corresponds to an antiferroelectric ordering of the CN^- electric dipoles. An interesting feature of the mixed systems is the existence of critical cyanide concentrations below which one or both phase transitions are not observed.[1-4]

In this paper we are concerned with the low-temperature phases (orthorhombic paraelectric and antiferroelectric) of the pure and dipole-dilute materials. Experimental results for the temperature dependence of the dielectric constant of the pure materials indicate that correlation effects play an important role in these systems.[5] We consider pair correlations in the Bethe approximation, and show that several experimental features of the pure and mixed materials can be understood within this scheme. The specific heat is also studied in the Bethe approximation, and our results are in good qualitative agreement with experiment.

II. THE BETHE APPROXIMATION FOR A DIPOLE-DILUTE ANTIFERROELECTRIC SYSTEM

We consider a lattice in which each anion site is in one of three possible states: A and B stand for a site occupied by a dipole oriented, respectively, up and down along an anisotropy axis, while C represents a halide ion with no permanent dipole moment. We consider the halides to be distributed *randomly* in the lattice.

For an antiferroelectric system the lattice is divided into two equivalent sublattices, α and β, so that the pure ordered system corresponds to all α (β) sites in state A (B). The site probabilities are

$$p_A^\alpha, p_B^\alpha, p_C^\alpha=(1-x)\ ,\quad p_A^\beta, p_B^\beta, p_C^\beta=(1-x)\ , \tag{1}$$

where p_K^ν is the probability of having a K species in a ν site and x is the dipole concentration in the lattice. Within mean field (MF), only these probabilities are considered. In the Bethe approximation,[6] pair correlations are also taken into account; we call $p_{KL}^{\alpha\beta}$ the probability of finding a K-L *nearest-neighbor pair* in α-β sites, where $K,L=A$, B, or C. In the present model C sites are uncorrelated; therefore

$$p_{KC}^{\alpha\beta}=(1-x)p_K^\alpha\ ,\quad p_{CK}^{\alpha\beta}=(1-x)p_K^\beta\ ,\quad p_{CC}^{\alpha\beta}=(1-x)^2\ . \tag{2}$$

Normalization requirements[5] yield

$$p_K^\alpha=\frac{(p_{KA}^{\alpha\beta}+p_{KB}^{\alpha\beta})}{x}\ ,\quad p_K^\beta=\frac{(p_{AK}^{\alpha\beta}+p_{BK}^{\alpha\beta})}{x}\ ,$$
$$\sum_{K,L=A,B} p_{KL}^{\alpha\beta}=x^2\ . \tag{3}$$

We describe an antiferroelectric system by an effective Hamiltonian which takes into account only nearest-neighbor coupling between sites in different sublattices and a uniform external probe field ϵ:

$$H=J\sum_{\langle ij\rangle_{\rm NN}}\sigma_i\sigma_j-\epsilon\sum_i\sigma_i\ , \tag{4}$$

where $\sigma_i=+1$, -1, or 0 according to whether site i is in state A, B, or C, respectively, and $J>0$. In terms of the parameters defined above, the internal energy per unit volume is written as

$$E=\frac{zN}{2}J(p_{AA}^{\alpha\beta}+p_{BB}^{\alpha\beta}-p_{AB}^{\alpha\beta}-p_{BA}^{\alpha\beta})-\epsilon N\frac{p_{AA}^{\alpha\beta}-p_{BB}^{\alpha\beta}}{x}$$

$$=\frac{zN}{2}J\eta-\frac{\epsilon N}{x}(p_{AA}^{\alpha\beta}-p_{BB}^{\alpha\beta})\ , \tag{5}$$

where z is the coordination number and N is the density of sites in the crystal. In Eq. (5) we define for convenience the short-range-order (SRO) parameter η. In the Bethe approximation the entropy for the pure system ($x=1$) is given by[7,8]

$$S=Nk_B\left[\frac{(z-1)}{2}\sum_{\nu=\alpha,\beta}\sum_{K=A,B}p_K^{\nu}\ln p_K^{\nu}\right.$$

$$\left.-\tfrac{1}{2}z\sum_{K,L=A,B}p_{KL}^{\alpha\beta}\ln p_{KL}^{\alpha\beta}\right]\ . \tag{6}$$

Minimization of the free energy $F=E-TS$ yields the following analytic results in the zero-field limit ($\epsilon\to 0$):

(i) The critical temperature[7]

$$T_c^0=\frac{2J/k_B}{\ln[z/(z-2)]}\ . \tag{7}$$

(ii) The SRO parameter[7] for $T\geq T_c^0$

$$\eta^0=-\tanh(J/k_BT)\ . \tag{8}$$

(iii) The static susceptibility for $T\geq T_c^0$

$$\chi^0(T)=\frac{np^2}{k_BT}\frac{1-|\eta^0|}{1+(z-1)|\eta^0|}\ , \tag{9}$$

where n is the density of "active" dipoles, i.e., dipoles which are aligned with the probe field, therefore $n=N/3$ and p is the individual dipole moment.

The pair probabilities and therefore the SRO parameter η and the long-range-order (LRO) parameters

$$P_\alpha=p_A^\alpha-p_B^\alpha\ ,\quad P_\beta=p_B^\beta-p_A^\beta \tag{10}$$

are easily obtained numerically for all temperatures and concentrations by the natural iteration method introduced by Kikuchi.[8] The specific heat $C_V(x,T)=\partial E/\partial T$ is also calculated numerically from Eq. (5). Similarly, the static susceptibility is calculated from the relation

$$\chi(x,T)=np^2\left.\frac{d(P_\alpha-P_\beta)}{d\epsilon}\right|_{\epsilon=0}$$

$$=\lim_{\epsilon\to 0}\frac{np^2}{\epsilon x}\{[p_{AA}^{\alpha\beta}(\epsilon)-p_{BB}^{\alpha\beta}(\epsilon)]$$

$$-[p_{AA}^{\alpha\beta}(0)-p_{BB}^{\alpha\beta}(0)]\}\ . \tag{11}$$

III. THE PURE AND DIPOLE-DILUTE CYANIDES

Experimental results on the temperature behavior of the dielectric constant of KCN and NaCN (Refs. 1–3) show it to decay very slowly with increasing T in the paraelectric orthorhombic phase. Moreover, the maximum of the integrated dielectric loss in KCN is found[1,3] to occur at $T^*=89$ K which is higher than $T_c^0=83$ K, the antiferroelectric ordering temperature.[9] These features cannot be understood in a simple mean-field scheme. We therefore include correlations between dipole pairs in the Bethe approximation.[10]

TABLE I. Experimental data for the pure cyanides: T_c, the critical temperature, is taken from specific-heat measurements, T^* is the temperature for which the static susceptibility χ^0 is maximum which, for NaCN, coincides with T_c, $\chi^0_{\max}$ is the value of χ^0 at T^* and n is the density of "active" dipoles which is $N/3$.

	T_c (K)	T^* (K)	$\chi^0_{\max}$	n (cm^{-3})
KCN	83[a]	89[c]	0.05[d]	0.50×10^{22}
NaCN	172[b]	172[d]	0.04[d]	0.68×10^{22}

[a] Reference 9.
[b] Reference 11.
[c] Reference 1.
[d] Reference 3.

To apply the formalism in Sec. II to the antiferroelectric cyanides, we adjust the parameters in the model by requiring the theoretical predictions to reproduce the experimental data for the *pure* cyanides given in Table I.

For KCN, T_c^0, T^*, and $\chi^0_{\max}$ in Table I are obtained from Eqs. (7), (8), and (9) for the parameters given in Table II. For NaCN, since no maximum is observed in χ^0 for $T>T_c$, we have one less experimental datum to fit the parameters. Therefore we take the same value of p obtained for KCN and fit T_c^0 and $\chi^0_{\max}$ to obtain J and z, which are given in Table II.

Our results for the static susceptibility versus temperature for pure KCN and NaCN are given in Fig. 1. For $T>T_c$ we also give the MF result (dashed line):[9]

$$\chi^0_{\mathrm{MF}}(T>T_c^0)=\frac{2C}{T+T_c^0} \tag{12}$$

with T_c^0 given in Table I and C fitted to reproduce $\chi(T_c^0)$ in each system. A fully quantitative comparison with the measured behavior is difficult for two reasons. First, the measured data are not static but dynamic ones in the 10^1–10^5 Hz. Secondly, the measured dielectric constant $\epsilon(T)$ does not contain only the dipolar susceptibility $\chi(T)$, but also the very large $\epsilon(T)$ background of the host material. As the latter is very strongly decreasing towards low temperatures, a *weak* increase of χ_{dip} under cooling at $T>T_c$ is often not recognizable as a "maximum" in the composite $\epsilon(T)$ curve. A full analysis of the newest and

TABLE II. Values of the parameters calculated to fit data in Table I: electric dipole moment p, coupling interaction J, and coordination number z.

	p (eÅ)	J (meV)	z
KCN	0.13	3.1	3.4
NaCN	0.13	5.0	4.1

best experimental data[3] is underway and will be published soon. Qualitatively, however, all experimental curves in Refs. 1—3 show, in comparison to Fig. 1, that several features not predicted in MF theory are obtained in the Bethe approximation and are therefore due to short-range-order effects:[10]

(i) χ^0 increases very slowly under cooling for $T > T_c^0$ [often not visible in composite $\epsilon(T)$ curves].

(ii) $\chi^0(T)$ is maximum at $T^* > T_c^0$ for KCN.

(iii) The kink at $T = T_c$ of $\chi^0(T)$ is smoother in KCN than in NaCN.

Results for the temperature dependence of the specific heat $C_v^0(T)$ of the pure system are given in Fig. 2. The calculated values go slowly to zero for $T > T_c^0$, which is due to correlation: in the mean-field (MF) treatment we would expect $C_V^0(T > T_c^0) = 0$. The calculated discontinuity at the specific-heat anomaly at T_c^0 reproduces within 30% accuracy the observed ones.[9,11] Note that the fittings in our model do not involve any experimental data for the specific heat.

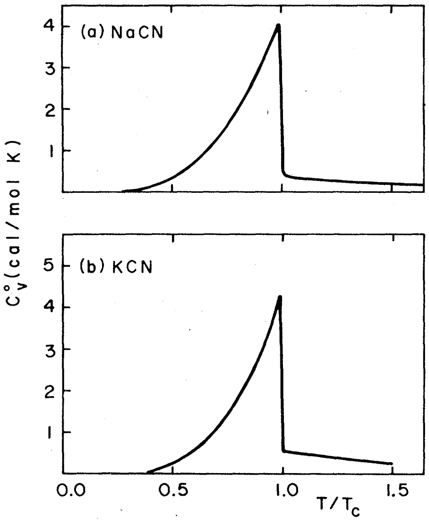

FIG. 2. Specific heat of pure NaCN and KCN calculated in the present model.

The behavior of the mixed systems is studied using the same parameters J, z, and p given in Table II for the pure systems. In Fig. 3 results for the static susceptibility versus temperature are presented for several values of the dipole concentration x. As the dipole concentration is decreased, the maximum in the curve is displaced towards lower temperatures, the susceptibility is lowered in value and becomes a smoother function of the temperature. In the experimental study of the dielectric constant of $K^+(CN^-)_x(Cl^-)_{1-x}$ (Ref. 1) the strong temperature dependence of the host material $\epsilon(T)$ must again be considered and subtracted. After doing this, the above features are observed, namely the existence of a very weak maximum in all curves, which occurs at lower temperatures as x decreases, and the rapid decay of $\chi(x,T)$ as $T \rightarrow 0$.

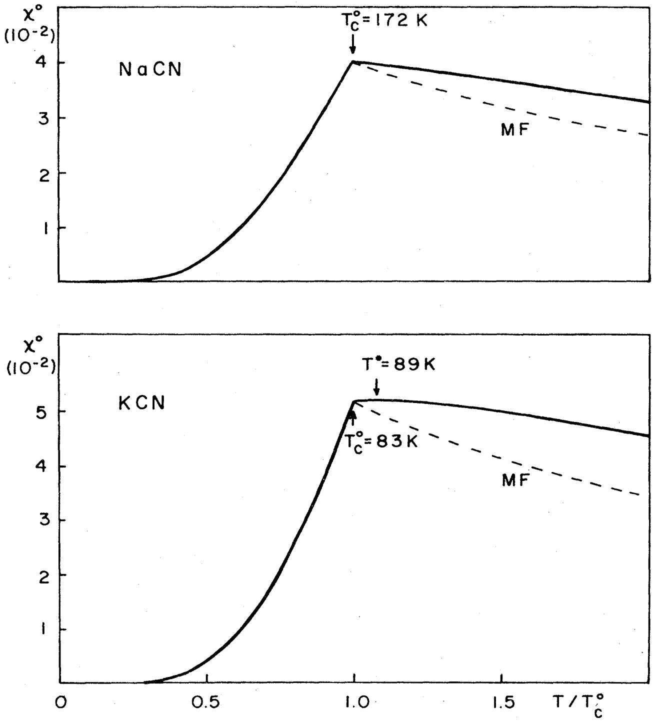

FIG. 1. Static susceptibility of pure NaCN and KCN calculated in the present model. For $T > T_c^0$ the MF results are given by the dashed line.

The critical temperature of the mixed system $T_c(x)$ is determined, for each concentration, as the temperature below which the LRO parameters in (10) become nonzero. The critical temperature corresponding to the susceptibility curves in Fig. 3 is also indicated there. Notice that as x decreases, T_c becomes much lower than the temperature for which χ is maximum.

The decrease of the critical temperature with x as calculated in the present model as well as by MF is presented in Fig. 4. While MF gives a linear decrease of T_c with x, the Bethe approximation predicts a much faster decrease and no LRO below $x_{\min} \sim 0.6$. The critical temperature is determined experimentally from the low-temperature λ-

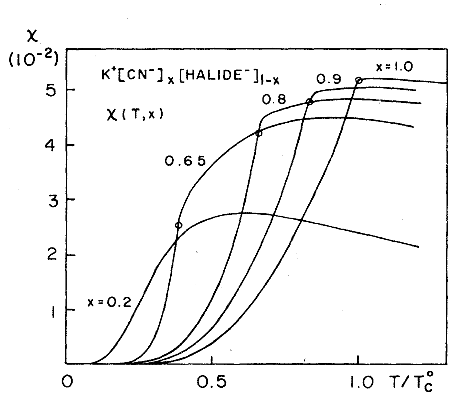

FIG. 3. Static susceptibility for dipole-dilute KCN for the indicated values of the dipole concentration x. The critical temperature for each concentration corresponds to the circle in the curve; no phase transition occurs for $x < 0.59$.

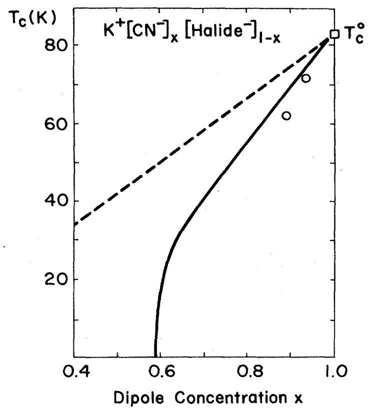

FIG. 4. Critical temperature for dipole-dilute KCN as a function of dipole concentration. The MF result is given by the dashed line. The circles are values measured by Moriya *et al.* (Ref. 12) for the $K^+(CN^-)_x(Br^-)_{1-x}$ system.

like specific-heat anomaly. The fact that T_c decreases with x faster than predicted by MF has been observed in specific-heat measurements in $K^+(CN^-)_x(Cl^-)_{1-x}$ (Ref. 4) and in $K^+(CN^-)_x(Br^-)_{1-x}$ (Ref. 12). For these mixed materials no low-temperature specific-heat anomaly has been observed below a dipole concentration of about 0.9 for the Cl^- mixture and 0.8 for the Br^- mixture.

IV. DISCUSSION AND CONCLUSIONS

The treatment presented in Sec. II for pure and dilute antiferroelectric (or antiferromagnetic) systems is an effective-field theory which improves classical MF by taking into account SRO effects in the disordered regions to the extent of *pair correlations.* The improvement obtained over the MF results as compared to experiments dipole-dilute cyanides shows that correlation effects are relevant and must be taken into account in the study of these materials.

The model Hamiltonian (4) proposed for the cyanides is obviously oversimplified to describe these antiferroelectric systems in which long-range dipolar and elastic interactions are responsible for the electric dipole ordering.[13] Therefore the calculated values of the parameters (Table II) must be regarded as "effective" values and are allowed to be quite different from the corresponding physical quantities in the system. The value of p has only been measured (by Curie Law) for dilute CN^- defects in KCl, yielding[14] $p=0.077\ e\text{Å}$. If the same value holds for pure KCN and NaCN our effective p value is a factor 1.7 too large. Similarly our effective z value is somewhat larger than the expected $z=8$ value.

Our results for the static susceptibility show that the temperature for which it is maximum is not necessarily at the critical temperature. This is because the uniform probe field has a symmetry different from that of the antiferroelectric dipole system. Therefore, the linear-response function χ does not diverge at T_c but is continuous and changes concavity at T_c and may or may not have a maximum at that point. For antiferroelectric systems, the specific-heat anomaly should be used in the measurement of T_c rather than dielectric properties.

In the zero-temperature limit we obtain a different decay rate of χ than the experimentally observed one,[1,3] since freezing effects are not incorporated in our model. At very low temperatures the molecular ions are not able to "jump" over the elastic barriers in the crystal and this effect inhibits the system to fully respond to external probes.

Our model treatment is applicable only for elastically ordered systems, in which all elastic dipole moments are oriented parallel to one anisotropic axis (with the electric dipole moment "up" or "down" along this axis). This is the case for the orthorhombic structure, possessed by pure KCN and NaCN and by the $K^+(CN^-)_x(Cl^-)_{1-x}$ mixed system. Pure RbCN, however, forms an elastically ordered monoclinic structure,[15] in which the CN^- molecules are not oriented all parallel to one axis, but form two subgroups of molecules, oriented parallel to two different axis directions with about 90° angular difference. It is evident that our model treatment does not apply to this case. Dielectric measurements show indeed a very different behavior compared to KCN and NaCN: the dielectric susceptibility raises with Curie-law (T^{-1}) behavior down to the lowest measurable temperature (32 K), showing noninteractive paraelectric behavior without any dipole ordering.[16]

Recent neutron measurements[17] showed for the dipole-dilute $K^+(CN^-)_x(Br^-)_{1-x}$ system a monoclinic structure similar to that of RbCN. For x close to 1 (i.e., close to pure KCN) this mixture is mostly orthorhombic, but with decreasing x it becomes a mixture of orthorhombic and monoclinic structure, with the latter taking over rapidly and becoming the only essential one for $x<0.9$. Dielectric measurements indicate that only the orthorhombic part and not the monoclinic part of the material is showing electric ordering effects. Therefore our model is not valid for this mixed system over a wide x range.

ACKNOWLEDGMENTS

We are grateful to Guilhermo Cabrera, Roberto Osorio, Jean Pierre von der Weid, and Luiz C. S. do Carmo for helpful discussions and suggestions. This research was supported in part by FINEP (Financiadora de Estudos e Projetos), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and CAPES (Coordenaçao de Aperfeiçoamento do Pessoal de Ensino Superior) of Brazil and by National Science Foundation (U. S.) Grants Nos. INT-81-09186 and DMR-81-05532.

---

[1] M Julian and F. Lüty, Ferroelectrics **16**, 201 (1977).

[2] F. Lüty, in *Defects in Insulating Crystals,* edited by V. M. Turkevich and K. K. Shvarts (Springer, Berlin, 1981).

[3] J. Ortiz-Lopez, Ph.D. thesis, University of Utah, 1982.

[4] L. Guivelder, J. P. von der Weid, P. Costa Ribeiro, and C. A. M. Bastos, J. Phys. C (to be published).

[5] M. A. Davidovich, B. Koiller, H. S. Brandi, and F. Lüty, in Proceedings of the Latin American Symposium of the Physics

of Amorphous Systems, Niteroi, 1984 (unpublished).
[6] See, for instance, J. M. Ziman, *Models of Disorder* (Cambridge University Press, London, 1979).
[7] A. M. Stein, G. G. Cabrera, and L. M. Falicov, Phys. Rev. B **23**, 4391 (1981).
[8] R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974).
[9] H. Suga, T. Matsuo, and S. Seki, Bull. Chem. Soc. Jpn. **38**, 1115 (1965).
[10] See, for instance, C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971).
[11] T. Matsuo, H. Suga, and S. Seki, Bull. Chem. Soc. Jpn. **41**, 583 (1968).
[12] K. Moriya, T. Matsuo, H. Suga, and F. Lüty, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984 (unpublished).
[13] B. Koiller, M. A. Davidovich, L. C. S. do Carmo, and F. Lüty, Phys. Rev. B **29**, 3586 (1984).
[14] M. Julian, Ph.D. thesis, University of Utah, 1976.
[15] J. M. Rowe, J. J. Rush, and F. Lüty, Phys. Rev. B **29**, 2168 (1984).
[16] F. Lüty and J. Ortiz-Lopez, Phys. Rev. Lett. **50**, 1289 (1983).
[17] J. M. Rowe, J. J. Rush, and S. Sussman, Phys. Rev. B **28**, 3506 (1983).