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Neutron-diffraction study of the phase transition in stannous chloride dihydrate

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The order-disorder phase transition in two-dimensional hydrogen-bonded layers of water molecules in $SnCl_2 \cdot 2D_2O$ is remarkable in several respects. It has been shown that the peak in the specific heat is highly symmetric around the phase-transition temperature, and that the crystallographic symmetry of the system does not change. We present neutron-diffraction results which show that the temperature dependence of the hydrogen-site occupancies is also highly symmetric around the phase-transition temperature. These results are discussed in terms of a lattice statistical model which was proposed and solved by Salinas and Nagle. By means of a comparison with the Rhys F model, this model is shown to account for the experimentally observed symmetry properties, although the model is in quantitative disagreement with the experimental data. This comparison also offers a reason for the existence of the peculiar anomaly in the dielectric constant.

I. INTRODUCTION

Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$ or $SnCl_2 \cdot 2D_2O$; hereafter abbreviated SCD) has attracted attention recently because of its order-disorder phase transition. SCD consists of layers of water molecules alternating with layers of stannous chloride.[1] At room temperature, there is disorder in the positions of hydrogen atoms in the two-dimensional hydrogen-bonded network. At $T_0 = 234$ K (in the case of the deuterated compound), a nearly second-order phase transition is manifested in the specific heat[2,3]; at or near this temperature, there is also a sharp peak in the dielectric response.[4,5] At low temperatures, it appears that the hydrogen positions are ordered.[1]

This paper has two main purposes. One is to report the results of a neutron-diffraction study of the phase transition; the other is to discuss these data, and some of the data mentioned above, in the light of existing exact lattice-statistical results. We will see that while the existing model calculations do not agree quantitatively with the experimental results, the important symmetry properties of the model show up in the experiments.

One peculiarity of SCD is that it is an example of a structural order-disorder system having the same symmetry in the two phases. Frequently, it is possible to characterize an order-disorder system by an "order parameter" having the following properties:

$$\begin{aligned} &\eta = 0, \quad T > T_0 \;, \\ &\eta \geq 0, \quad T \leq T_0 \;. \end{aligned} \tag{1}$$

Typically, η represents the magnitude of some symmetry-breaking distortion or polarization. In SCD, no such quantity has hitherto been defined. While there certainly exist other examples of phase transitions in which the symmetry does not change, such behavior is not typical of order-disorder phase transitions. Moreover, the specific-heat peak is unusually symmetric around T_0, and, as we will show, the temperature dependence of the hydrogen-site occupancies has a related symmetry around T_0. All these features of SCD are features of a dimer model for SCD that was originally proposed and solved by Salinas and Nagle.[6] We will discuss an important connection between their work and that of Baxter[7] on the F model in applied fields. From this connection, one sees that in the dimer model of Salinas and Nagle, the variable

$$t' \equiv \frac{T - T_c}{T} \tag{2}$$

can be thought of as an effective staggered field. From this point of view, all the above-mentioned features of SCD seem quite natural. The character of the specific-heat singularity predicted by this model is known to be wrong[6]; because of this discrepancy, and because the role of ice-rule violations is not yet understood, it cannot be said that the SCD model accuractely describes the behavior of real SCD. Nevertheless, because this is an exactly solvable model which correctly predicts some of the distinctive qualitative features of SCD and because the model is of considerable formal interest in its own right, we have chosen to organize our discussion around this model, rather than try to build up a phenomenological treatment.

The outline of the paper is as follows. In Sec. II, we will describe the structure of SCD, and introduce the Salinas-Nagle model. In Sec. III, we will report our neutron-diffraction results. Then we will discuss our results, together with the specific-heat data and the dielectric measurements.

II. LATTICE-STATISTICAL MODEL OF SCD

A. Dimer model of the hydrogen-bond network

A simplified picture of the hydrogen-bond network is presented[1] in Fig. 1. It is convenient to think of the structure as being made up of clusters, each consisting of four water molecules. In the following, we will refer to these clusters as "cities." The cities are arranged in a rectangular lattice with each city hydrogen bonded to four nearest-neighbor cities. There are two inequivalent water molecules in the structure. Type-I molecules have both hydrogen in the plane of the network, while in Type-II molecules one hydrogen atom is bonded out of the plane. At room temperature, all the in-plane hydrogens are positionally disordered; at low temperatures, the hydrogens are ordered as shown in Fig. 1(a). Each layer orders in the same way. The crystallographic space group is the same ($P2_1/c$) at room temperature as at 77 K, and the translational periodicity does not change.[1]

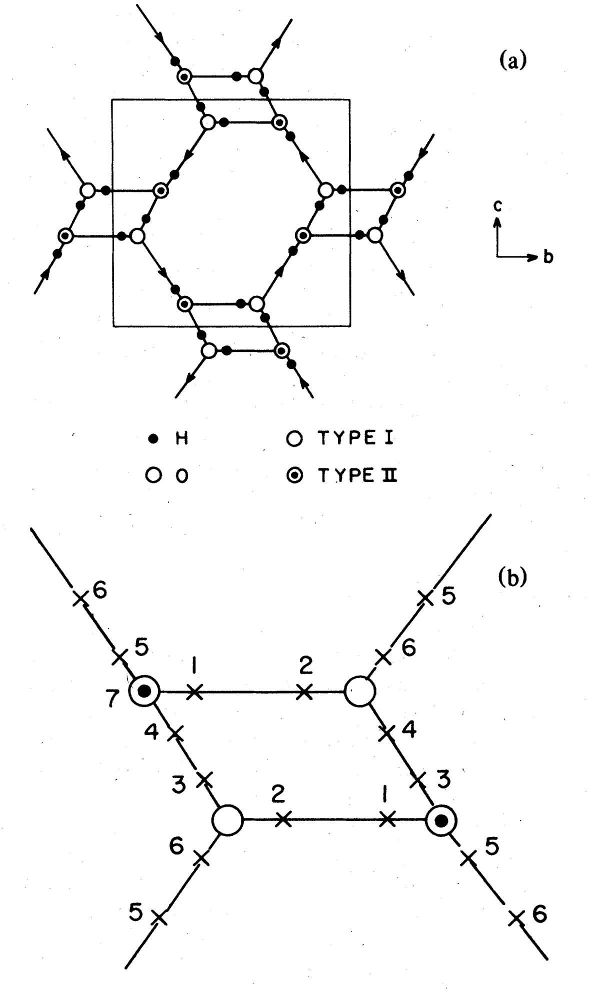

FIG. 1. (a) Shown schematically is the structure of a water layer in the ordered phase. Arrows are drawn on the bonds external to the cities, in order to show the staggered polarization. (b) Crosses indicate the position of those hydrogen atoms that participate in the disorder. The sites are numbered as in the work of Kiriyama *et al.* (Ref. 8). There is always a hydrogen atom at position 7.

Assuming the ice rules—that each bond must be occupied by one hydrogen, and precisely two hydrogens must be near each oxygen—we see that any allowed configuration corresponds to a pairing of Type-I and Type-II oxygens. On only one of the three bonds surrounding each Type-I (Type-II) oxygen can the hydrogen be at the far (near) end of the bond. This situation can be discussed in terms of a dimer model. One associates a "dimer" with each bond on which the hydrogen is closer to the Type-II oxygens. Then, allowed network configurations are those for which each oxygen is touched by precisely one dimer. Salinas and Nagle proposed and solved[6] such a model for SCD. They found that for some assignments of dimer energies, the system has a second-order phase transition. Certain qualitative features of this model, which we will call "the SCD model," show up in the experimental data.

Presumably, the ice rules are only approximately valid for real SCD. In this case, the dimer model no longer strictly applies. However, provided that the overall hydrogen population of each city remains constant, the basic six-vertex character of the system (to be discussed shortly) survives. At present, the defect concentration in SCD is not accurately known. Diffraction studies do not unambiguously test the ice rules; Bragg intensities depend only on average site occupancies, not directly on correlation functions, and it is sometimes difficult even to extract the occupancies from the data. In their preliminary report, Kiriyama *et al.*[8] concluded that there is a substantial number of defects, but this conclusion was revised later[1]; the latest results are consistent with the ice rules. In this work, we will keep the simplifying assumption of the ice rules.

B. Staggered polarization

Before we discuss our neutron-diffraction results, we pause to establish the connection between the SCD model and the family of six-vertex models. It is useful to characterize the state of the hydrogen-bond network by its "staggered polarization." The quantity we extract from our data cannot rigorously be identified with the staggered polarization we consider here, but the relation is very close, and the discussion in terms of this parameter is very simple.

One sees in Fig. 1 that each "city" has a total of six internal hydrogens: four hydrogens on each of the internal bonds, and one more on each of the Type-II oxygens. The ice rules mandate that the four oxygens in the "city" should have a total of eight hydrogens; therefore, on the four external bonds, two hydrogens must be adjacent to the city, and two farther away. This is the six-vertex condition: there are six possible configurations of the external bonds of a city. If we represent the position of each hydrogen on the external bonds by an arrow, each configuration corresponds in an obvious way to one of the traditional six vertices.

Suppose we formally associate a polarization vector with each arrow. This could represent some change in local dipole moment, but need not; at this point, we are discussing lattice statistics, not charge displacement. Note that if we sum all the moments associated with a unit cell in the ordered phase of SCD (see Fig. 1), we find that the net moment is zero; each individual moment is canceled by another. The exact cancellation is a consequence of symmetry; the space group $P2_1/c$, valid for both phases of SCD, rules out the possibility of any net polarization being associated with the unit cell.

The kind of ordering shown in Fig. 1 is sometimes called "staggered polarization." We define a parameter P_s , which we call staggered polarization, by

$$P_s \equiv \rho_6 - \rho_5 \quad , \tag{3}$$

where ρ_i is average occupancy of the ith hydrogen site. (P_s is the order parameter of the Rhys F model.) To specify occupancies of the sites internal to a city, one needs to specify energy differences between these sites, in addition to specifying P_s. It is reasonable (following Salinas and Nagle[6]) to approximate the situation in SCD by assuming that the internal bonds of each city are energetically equivalent. This is not required by symmetry, but it seems to be essentially true, in that the occupancies of sites 1 and 3 [Fig. 1(b)] are nearly equal[1] at $T=297$ K. Then the temperature dependence of $\{\rho_i\}$ is essentially the temperature dependence of the single parameter P_s. Using these assumptions, we will show that the Bragg diffraction intensities depend in a very simple way on P_s. We will see that this set of assumptions does a reasonably good job of describing the data.

We refrain from calling P_s an order parameter in SCD, because it does not vanish in the high-temperature phase.

III. NEUTRON-DIFFRACTION RESULTS

Single crystals of $SnCl_2 \cdot 2D_2O$ ($SnCl_2 \cdot 2H_2O$) were grown by evaporation of solutions of $SnCl_2$ and DCl in D_2O (or HCl in H_2O). Diffraction measurements were performed at the DR3 reactor at Risø on several different samples. The data analyzed here taken using a neutron beam of wavelength $\lambda = 0.9282$ Å incident on a sample of $SnCl_2 \cdot 2D_2O$ measuring $3 \times 4 \times 14$ mm.[3] The temperature of the sample was controlled by a nitrogen flow cryostat, and monitored by computer.

Certain Bragg reflection intensities are especially sensitive to changes in the staggered polarization P_s. Let us assume that the only temperature dependence in Bragg reflection structure factors comes from the temperature dependence of P_s. Thus, we are neglecting the possibility of heavy atom shifts, the possibility of hydrogen-site shifts, etc. Then the scattering amplitude may be written as a simple function of P_s. The Bragg structure factor of a unit cell is

$$\begin{aligned} F(hkl) &= \sum_i b_i \rho_i e^{i2\pi(hx_i + ky_i + lz_i)} e^{-W_i} \\ &\equiv \sum_{\substack{\text{atoms in}\\ \text{asymmetric unit}}} b_i \rho_i f_i \quad , \end{aligned} \tag{4}$$

where

$$f_i = e^{-W_i} \sum_{\substack{\text{atoms equivalent}\\ \text{to } i\text{th atom}}} e^{i2\pi(hx_j + ky_j + lz_j)} \quad ,$$

b_i is the scattering length of the ith atom, ρ_i is the occupancy of the ith site, (x_i, y_i, z_i) are the coordinates of the ith atom, (hkl) are the Bragg indices, and W_i is the Debye factor of the ith atom. Assuming

$$\rho_1 = \rho_3 \quad , \quad \rho_2 = \rho_4 \quad , \tag{5}$$

and assuming the ice rules,

$$\begin{aligned} &\rho_1 + \rho_2 = 1 \quad , \\ &\rho_3 + \rho_4 = 1 \quad , \\ &\rho_5 + \rho_6 = 1 \quad , \\ &\rho_1 + \rho_3 + \rho_5 = 1 \quad , \\ &\rho_2 + \rho_4 + \rho_6 = 2 \quad , \end{aligned} \tag{6}$$

we have

$$F = F_0 + P_S F_1 \quad , \tag{7}$$

where

$$F_0 = \sum_{\substack{\text{heavy}\\ \text{atoms in}\\ \text{asymmetric unit}}} b_i f_i + b_H \{ f_2 + f_4 + f_6 + \tfrac{1}{4} [f_1 - f_2 + f_3 - f_4 - 2(f_5 - f_6)] \} \quad ,$$

$$F_1 = \tfrac{1}{4} b_H [f_1 - f_2 + f_3 - f_4 - 2(f_5 - f_6)] \quad ,$$

b_H is the scattering amplitude of the appropriate isotope of hydrogen. Bragg peaks for which $|F_0| \sim |F_1|$ are therefore a sensitive measure of P_s.

Note that the amplitudes F_0 and F_1 change drastically when hydrogen is substitued for deuterium. This comes about because the scattering lengths b_H are quite different: $b_{\text{hydrogen}} = -0.374$, $b_{\text{deuterium}} = 0.667$.[9] The temperature dependence of the (014) reflection is shown in Figs. 2(a) and 2(b) for $SnCl_2 \cdot 2H_2O$ and for $SnCl_2 \cdot 2D_2O$. We see that the two are completely different. These figures show both the effect of the change of sign in b_H and the effect of deuteration on the phase-transition temperature. As explained in the caption, these figures taken together are evidence that most of the temperature dependence of the Bragg intensities comes from the change in the hydrogen-site occupancies, and that the form we will shortly assume for P_s [Eq. (8a)] is reasonable.

Figures 2(b) and 2(c) show data for two Bragg reflections in $SnCl_2 \cdot 2D_2O$ scanned as a function of temperature. One sees that, at T_0, the slope becomes nearly vertical. There is a small gap at $T_0 = 234$ K, implying that the transition is first order. The same conclusion was drawn from the specific-heat study. There is a significant resemblance between these figures and plots of the temperature dependence of the Raman intensities,[10] which have also been interpreted as measuring populations of particular hydrogen atom positions.

Least-squares fits were performed on the data in an attempt to extract information about the temperature dependence of P_s. The form used was

$$P_s = c\,\text{sign}(T - T_c)\left|\frac{T - T_c}{T}\right|^{1-\alpha} , \tag{8a}$$

$$F^2 = (F_0 + P_s F_1)^2 , \tag{8b}$$

with F_0, cF_1, T_c, and α as fitting parameters.[11] (The reason for choosing this form for P_s will be clear from the discussion given in Sec. IV, where we compare the Rhys F model to the SCD model.) The results of the fits are shown in Table I. The curves are shown in Figs. 2(b) and 2(c). This form is clearly a reasonable empirical description of the data, but, not surprisingly, there are indications that the temperature dependence of Eq. (8a) is too simple to describe the data. In particular, when data for $T > T_1$ and $T < T_0$ are fit separately, $T_c^+ \neq T_c^-$, which should not be the case. Also, there is correlation between the exponent α and cF_1. Fitting both curves over the whole temperature range [effectively, forcing $T_c^+ = T_c^-$, $(cF_1)^+ = (cF_1)^-$, etc.] gives somewhat different parameters, but although the fit is worse, the difference is hard to detect visually.

Given the recent structural data, we may estimate F_1 and f_0, at least in the high-temperature regime, and then calculate the scale factor c. The necessary data are not available for all atoms in the low-temperature regime; the values of c given in Table I, which have been averaged over the two reflections, have been obtained on the assumption that the high-temperature positions and Debye factors are valid for all temperatures. This may explain why cF_1 for

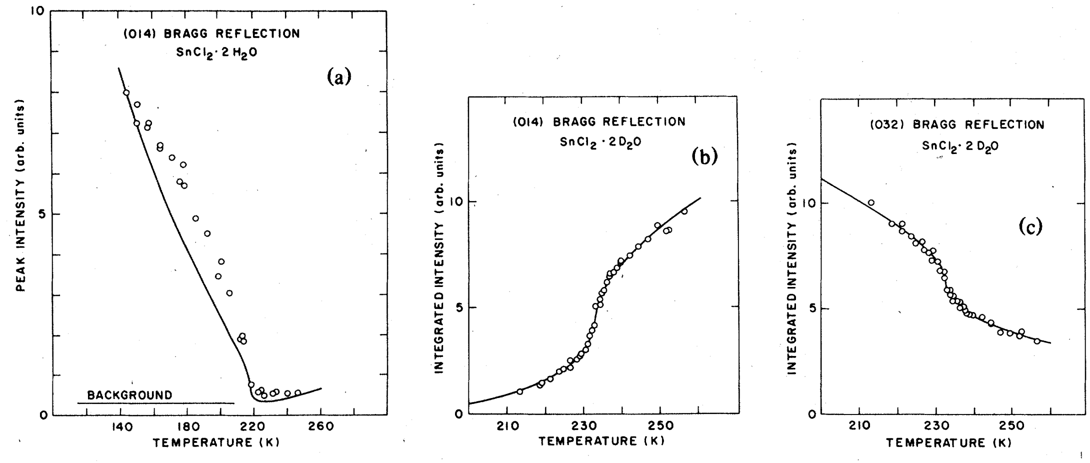

FIG. 2. Shows the temperature dependence of the intensities of different Bragg peaks near the order-disorder transition. (a) shows the peak intensity of the (014) reflection in $SnCl_2 \cdot 2H_2O$. The curve drawn is derived by taking the parameters from fits to the $SnCl_2 \cdot 2D_2O$ data and then allowing for the change in T_0. No allowance is made for possible changes in the positional coordinates, the Debye-Waller factors, or in the temperature dependence of the staggered polarization, P_s. (b) and (c) show the temperature dependence of the integrated intensity of (014) and (032) in $SnCl_2 \cdot 2D_2O$. The full lines are the results of fits to Eq. (8) in the text. Taken together, these three figures are qualitative, pictorial evidence that nearly all of the intensity changes represent the evolution of P_s, and that P_s is approximately symmetric around T_0.

TABLE I. Parameters derived from fitting Eq. (8) to the data in Figs. 2(b) and 2(c). The units of F and cF_1 are such that using these values in Eq. (8) gives intensities in units 10^3 times smaller than those of Figs. 2(b) and 2(c). Values of A and α derived from our diffraction data [refer to Eqs. (12)–(15)] are to be compared with values of $A_\pm$ and $\alpha_\pm$, obtained from the specific-heat results of Matsuo *et al.* (Ref. 2) [refer to Eq. (16)].

		(014)		(032)			Diffraction		Specific heat	
Regime	T_c	F_0	cF_1	F_0	cF_1	c	A	α	$A_\pm$	$\alpha_\pm$
$T < T_0$	232.5 ±0.2	64 ±2.0	140 ±11	79.6 ±0.8	−82 ±7	1.74	1.47	0.41 ±0.03	1.155	0.49
$T > T_0$	234.6 ±0.5	73 ±3.0	100 ±16	75 ±2	−67 ±12	1.29	1.09	0.41 ±0.1	1.148	0.49
Both	232.8 ±0.1	65.7 ±0.3	115 ±4	79.3 ±0.2	−69 ±3	1.44	1.12	0.47 ±0.01	---	---

$T < T_0$ is so different from the other two values. In any case, it is clear from the error bars on the other parameters that the values of c are significant only to around 15%.

IV. DISCUSSION

In this section, we will discuss the results presented in Sec. III, together with the published specific-heat results. In the SCD model, there is a simple relation between P_s and the specific heat; we will show that this relation holds approximately in the data, although the SCD model's quantitative prediction of the temperature dependence is incorrect. Moreover, both P_s and the specific heat are predicted to be symmetric around the transition temperature; again, the data are approximately in accord with this prediction. This follows from a comparison between the SCD model and the Rhys F model. This comparison also leads to a simple qualitative prediction about the temperature dependence of the dielectric constant.

A. Symmetry of the free energy around T_c

It was mentioned earlier that the SCD model is a kind of six-vertex model. The SCD model has been included in a general study[12] of the staggered six-vertex problem, but for our purposes, a simpler and more revealing comparison between SCD and this model family may be drawn from the work of Baxter.[7] He showed that in the special case when the model parameter Δ vanishes, the F model in an applied staggered field is equivalent to the dimer problem involved in the SCD model. The SCD model allows for a slightly more general assignment of dimer energies, but we have specialized (Sec. II B) to the case in which internal bonds are equivalent; our problem is now formally identical to the one studied by Baxter.

Applying a staggered field[13] S in the F model at $\Delta = 0$ is like changing the temperature in the SCD problem. The correspondence is

$$\frac{1}{2}S = \frac{1}{2}\ln 2 - \frac{\epsilon}{kT} \ . \tag{9}$$

$S = 0$ corresponds to $T = T_c$ in the SCD model, while $S \gtrless 0$ corresponds to $T \gtrless T_c$. The temperature-dependent competition between energy and entropy in the SCD model amount to an effective temperature-dependent staggered field coupling to P_s. Because of the free energy of the F model is an even function of S, the free energy of the SCD model is an even function of t' [refer to Eq. (2)]. Thus, P_s is an odd function of t'; moreover, since $E = \frac{1}{2}\epsilon(1 + P_s)$, the specific heat should be an even function of t', apart from a factor of T^2.

Clearly, T_c is a point of special symmetry in the SCD model. T_c is the temperature at which all cities become translationally equivalent, in a lattice statistical sense; at T_c, the system corresponds to an F model without a staggered field, while at any other temperature, two sublattices are distinguished by the effective staggered field. From this point of view, it is natural for the two phases to have the same symmetry. (This is not the first time an isostructural phase transition has been modeled as a system in an effective field; see for example Barma *et al.*[14]) It is also natural that T_c is never achieved, the phase transition being slightly first order; at T_c, the bond network would achieve an effective symmetry higher than that of its enviroment.

The basic S shape of the intensity curves is in qualitative agreement with the dimer model prediction, but the singularity in the slope is much stronger than one would have expected from that model. The exponents derived from the fits are essentially equal in the two phases, but the amplitudes F_1 are about 30% greater in the low-temperature phase. (Recall that part of this may be due to changing Debye factors, etc.) There is some change in the effective F_0's between the two temperature regimes; this is indicative of some changes in the average atomic positions and Debye factors at the phase-transition temperature. This somewhat complicates the interpretation of cF_1 and α; at this point, the experimentally determined P_s is a parameter whose significance is, strictly speaking, only phenomenological. But we have shown that P_s is approximately antisymmetric in t', and we have shown that most of the temperature dependence is that of hydrogen-site occupancies.

B. Relation between P_s and the specific heat

An important feature of the SCD model is that the energy is assumed to be dependent on a linear combination of site occupancies, rather than on a sum of products of site occupancies. That is, states which are allowed by the ice rules have energies which can be expressed as the sum of individual hydrogen bond energies; we have in the SCD model

$$E=\tfrac{1}{2}\epsilon(1+P_s) \ , \qquad (10)$$

rather than (for example)

$$E=\sum_{ij} J_{ij}\rho_i\rho_j \ . \qquad (11)$$

In the SCD model, then, determination of P_s is tantamount to a determination of E. Indeed, the specific heat,

$$\frac{\partial E}{\partial T}=\frac{1}{2}\epsilon\frac{\partial P_s}{\partial T} \qquad (12)$$

is related to the slope of the Bragg intensities versus temperature, since

$$\frac{\partial F^2}{\partial T}=2(F_0+P_sF_1)F_1\frac{\partial P_s}{\partial T} \ .$$

As we have seen, there are indeed obvious singularities in the Bragg intensities. Having extracted P_s from the data [Eq. (8)], we may use Eq. (12) and the relation

$$\epsilon=\tfrac{1}{2}kT_c\ln 2 \qquad (13)$$

(from the SCD model) to predict a specific heat of the form

$$C\sim A\left|\frac{T-T_c}{T}\right|^{-\alpha} \ , \qquad (15)$$

where $A=\frac{1}{4}NKc(1-\alpha)\ln 2$, N is the Avogadro constant, and k is the Boltzmann constant. Values of A and α derived from the diffraction data are given in Table I. Matsuo *et al.*[2] report (for $SnCl_2\cdot 2H_2O$)

$$C\sim A_{\pm}\left|\frac{T-T_c}{T_c}\right|^{-\alpha_{\pm}} \ , \qquad (16)$$

with values of $A_{\pm}$ and $\alpha_{\pm}$ given in Table I. In an earlier work,[3] in which fitting was performed over a wider temperature range, they reported $\alpha_+=0.574$ and $\alpha_-=0.544$ for $SnCl_2\cdot 2D_2O$ and $\alpha_+=0.534$ and $\alpha_-=0.478$ for $SnCl_2\cdot 2H_2O$. In this earlier work, they did not extract $A_{\pm}$, but their Fig. 8 shows that these are quite comparable between the two compounds.

It it clear that there are large error bars on our values of A and α. It is also clear that the value of α extracted from both experiments depends on how the fitting is performed (e.g., what range of temperature is used). Taking all this into account, one concludes that the agreement is surprisingly good. We conclude that, as in the SCD model, the energy is given approximately by

$$E=\tfrac{1}{4}kT_c\ln 2(1+P_s) \ . \qquad (17)$$

Because the SCD model predicted $\alpha=0$, a result completely irreconcilable with the specific-heat measurements, Salinas and Nagle[6] were led to suspect that other degrees of freedom were contributing to the specific-heat anomaly. The present result suggests that it is unnecessary to invoke this; the temperature dependence of P_s can more or less account for the specific heat. The important question is why P_s itself behaves in this way.

C. Dielectric constant

The dielectric properties of SCD have also received considerable attention. There is an anomaly in the dielectric constant near the phase-transition temperature; $\epsilon'\sim 1800$ near T_0, and falls off very sharply for T different from T_0.[5] Although there is some rounding of the peak, a critical exponent $\gamma\simeq 1.75$ has been used to describe the dielectric data in a carefully selected temperature interval.[5] Since SCD is believed to be centrosymmetric in both phases, and because of the apparent lack of a traditional order parameter, the significance of the dielectric measurements has remained unclear (see the discussion in Salinas and Nagle[15]). In this section, we point out a possible connection between these dielectric results and an interesting property of the SCD model.

Baxter's work[7] on the F model includes a treatment of applied direct fields, as well as the applied staggered field. In language appropriate to the SCD model, one would say that Baxter calculated the response of SCD to an applied field that couples linearly to the vector polarization defined in the introduction for the external bonds. When the staggered field is different from zero—that is, for T different from T_c— the response is zero for small fields. If this vector polarization can be argued to be proportional to the electric polarization induced by a small applied electric field, Baxter's calculation says that the dielectric constant is zero when $T\neq T_c$. The experimental data mentioned above show that the dielectric constant is, indeed, small except when

$|T-T_0|<2.5\,°$. (See Fig. 1 of Ref. 5.)

It is possible that this property of the SCD model has nothing to do with the dielectric measurements, since it has not been demonstrated that the electric polarization in SCD is simply related to hydrogen-site occupancies. Indeed, KH_2PO_4 is a famous example of a substance undergoing a ferroelectric phase transition involving hydrogen atom displacements which do *not* account for the spontaneous electric polariztion. Even in that case, however, the hydrogen displacements are part of the "ferroelectric mode," and thereby proportional to the polarization. In the case of ice, on the other hand, it is widely believed that much of the low-frequency dielectric response is precisely the sort of reallocation of hydrogen-site occupancy that we are discussing here. It is interesting to note in this connection that the dielectric response of SCD is large at very low audio frequencies (tens of Hz rather than tens of thousands of Hz); it is natural to associate this with a cooperative long-ranged reorientation of permanent moments, rather than (for example) molecular polarizability.

A different approach to this subject has been advanced by Salinas and Nagle.[15] Motivated by the original report of Mognaschi *et al.*[16,17] that ϵ' peaks at a $T>T_0$, they constructed a model which invoked strong intraplanar ferroelectric interactions and weak three-dimensional antiferroelectric interactions. In this model, as T_0 is approached from above, intraplanar polarization fluctuations increase until $T-T_0$ becomes small; then, the antiferroelectric interactions tend to force adjacent layers to fluctuate in opposite directions, leading to a decrease in ϵ'. This model is not vitiated by the newer dielectric results (which do not say that the peak occurs at $T>T_0$), but it raises more questions than it answers. From the point of view of the SCD model, all the experimental results mentioned here are natural properties of this particular hydrogen-bond network; from the point of view of the previous model of SCD's dielectric behavior the isostructural character of the phase transition seems mysterious.

Of course, the dielectric constant is not really a δ function of temperature; it is significantly broader than the resolution of the experiment. A more complete theory is needed; such a theory should take into account Bjerrum defects, as well as the sort of hypothetical interactions invoked by Salinas and Nagle. But Baxter's treatment shows that the competition between staggered polarization and direct polarization is a property of the network; to the extent that the field-induced polarization is also a property of the network, it is important to take this competition into account in treating the dielectric constant.

V. SUMMARY

Except for the character of the singularity at the phase transition, all of the aspects of SCD's behavior that we have discussed here are natural consequences of the assumption that go into the SCD model. The phase transition is isostructural; the specific-heat peak is highly symmetric around T_0; the staggered polarization is approximately linear in P_s; and the anomaly in the dielectric constant occurs in a very narrow temperature range. Given the serious discrepancy concerning the character of the singularity at T_0, one might have considered the model hopelessly wrong; but in view of the above, the basic approach seems to deserve further attention.

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