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Orientational ordering: Computer studies of the quadrupolar "glass"

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The electric quadrupole-quadrupole model for orientational ordering on the rigid hcp lattice is studied with the use of standard computer-simulation techniques. Appropriate order parameters, which isolate various symmetries, are used to describe this system. It is found that several distinct admixtures of the long-range-ordered states are degenerate at and below the phase transition. The zero-temperature state appears to consist of randomly stacked ordered planes, and the ordering appears to be mediated by the presence of excitations of the "wrong" symmetry. Although the form of the zero-temperature order parameter appears to depend on the annealing schedule used, the observed susceptibilities do not.

I. INTRODUCTION

This paper presents a detailed account of Monte Carlo studies of a model system relevant to the orientational glasses. These include molecular solids in which either quadrupolar or dipolar intermolecular interactions may dominate. They are characterized experimentally by a quenching of the orientational degrees of freedom which occurs without an observable onset of long-range order.[1-11] The model is applicable to the quadrupolar systems (orthohydrogen-parahydrogen, orthodeuterium-paradeuterium, and N_2-Ar alloys) and has been developed to distinguish between two different aspects of the problem—namely, the respective roles of dilution-induced local symmetry breaking and intrinsic frustration effects associated with the lattice structure of the experimental systems in their "glassy" regimes.

A very brief review of the experimental data is given in Sec. II, together with a description of the model, previous theoretical and Monte Carlo (MC) work, and the relationship between experimental and theoretical results. It should be noted that most recent work on the subject has emphasized an analogy with the spin-glass problem, which also contains both frustration and dilution-induced disorder, but without examining the role of these various ingredients separately. In real materials there is an additional complication. The quadrupolar glass regime appears to coincide in all cases with a cubic-hexagonal structural phase transition, rather than with a well-defined quadrupole concentration. It now appears that the intermolecular interaction is strongly renormalized near the phase transition because of the translational fluctuations associated with this instability.[7,12,13] Although the renormalization is undoubtedly important, it is neglected in this study. All data are obtained for an EQQ (electric quadrupole-quadrupole) interaction on a rigid lattice. The simple observation that the orientational glass phase coincides with the existence of the hcp structure[14,15] does, however, lend credence to the claim that that role of intrinsic frustration deserves to be studied in its own right.

In this computation the quadrupolar molecules are treated as rigid classical rotators; i.e., quantum effects are also neglected. These effects may be expected to modify the results obtained in several ways, particularly as applied to hydrogen: (1) In the presence of large zero-point motion the translation-rotation coupling already mentioned may be large; its treatment is properly a quantum-mechanical problem. (2) In principle, the "multiplet" associated with the $J=1$ molecular functions must be split in the presence of crystal field. This splitting is in fact known to be small[15] and should produce little effect. Quantum phenomena in the case of N_2 are almost certainly negligible, the major modifications in this case being associated with the Lennard-Jones parameters and deviations from a simple EQQ interaction.[14]

There is one major difference between the present system and systems exhibiting spin-glass behavior. In both of the pure rigid crystalline forms the quadrupolar glasses possess a long-range-ordered configuration which lies at an energy minimum. One of the major results presented here is that in the hcp phase, the lowest-lying long-range-ordered state is at least degenerate with (and possibly at slightly higher energy than) a state which displays only two-dimensional long-range order (LRO), and which has a degeneracy of $2^{N^{1/3}}$. This fact appears to result from the form of the two lowest-lying configurations, from their relatively small energy separation and from the fact that a transition between them may be achieved locally through the fluctuations associated with yet another order parameter. A description of this phenomenon requires careful order-parameter definition. The analysis techniques are described in Sec. II, and in particular, a distinction is made between the order parameters useful in describing global symmetry and those associated with the remanence and accessibility phenomena appearing in glasslike systems.

The organization of the paper is as follows: In Sec. II, a review of the experimental and theoretical aspects of the problem is given. In Sec. III, the various possible order-parameter definitions are discussed, and a contrast is made between LRO problems, and problems where the predominant question concerns the accessibility of various portions of configuration space. (Both sorts of questions are important here.) In Sec. IV, the details of the MC procedure at finite temperature and of the ground-state search technique are given, and results are discussed.

II. REVIEW OF THE PROBLEM

The general designation "orientational glass" has been used in the literature to describe crystalline diatomic solids, usually with the introduction of inert impurities. In general, the diatomic species interacts via a Lennard-Jones potential and an electric multipole interaction. The precise form of the interaction depends upon atomic parameters, but for identical atoms, the dipolar contribution both from the Lennard-Jones part and from the electric multipole part must vanish by symmetry. In the so-called "quadrupolar glasses" this leaves terms which arise from the quadrupolar term in an expansion of the Lennard-Jones potential and from the electric quadrupole-quadrupole interaction. The paradigm systems for this case are the solid hydrogens and the N_2-Ar alloys, which are believed to form regular crystal lattices. Excellent reviews exist which give interaction details for both nitrogen[14] and hydrogen.[15] In this paper we are concerned with the quadrupole interaction alone. This appears to be the dominant potential in both systems. In all cases the quadrupolar species occupies the sites of a regular lattice, but shares this lattice with a spherically symmetric (i.e., nonquadrupolar) dilutant—argon in the case of interacting N_2, parahydrogen in the case of interaction orthohydrogen, and orthodeuterium in the case of interacting paradeuterium. The lattice structure depends upon the concentration of the quadrupolar species; schematic phase diagrams are shown in Fig. 1. The high-temperature solid phase is in all cases hexagonal close packed, and at high concentration the low-temperature phase is face-centered cubic. The transition at fixed concentration from hcp to fcc is accompanied by a long-range orientational order, with the molecular axes aligning in the fcc phase to form a Pa_3 structure. A sharp specific-heat anomaly appears at the expected temperature, and measurements probing structural order (x-ray experiments) are consistent with measurements primarily sensitive to local orientational field (various NMR experiments). These bulk thermodynamic properties are consistent with local structural and orientational information. This consistency obtains all along the phase boundary as long as the slope of the boundary curve dT/dx does not become too sharp. At lower values of x, well away from the x-T intercept, the structural data indicate clearly the persistence of the hcp structure to very low temperatures. It is in the low-temperature region of this concentration regime that the "glass" phase has been observed, both in N_2-Ar and in the solid hydrogens.

The most persuasive evidence for freezing of the local moments in hydrogen comes from NMR measurements, particularly from the analysis of the Pake doublet line shape given by Sullivan and co-workers. Some of the NMR experiments on a single-crystal sample,[7] however, indicate that symmetry properties when observed on a macroscopic scale remain characteristic of the full crystal group, even below the "freezing" temperature. Similarly, specific-heat measurements indicate a rounded peak at a temperature above the freezing temperature, and a nearly linear temperature dependence below this peak. This is reminiscent of specific-heat data obtained for glasses and spin-glasses under certain cooling conditions. More recent specific-heat,[11] NMR,[16] and neutron scattering[17] data on the N_2-Ar alloys in the hcp regime also are consistent with a slowing of the N_2 molecular rotation. This occurs over a broad temperature range below about 20 K.

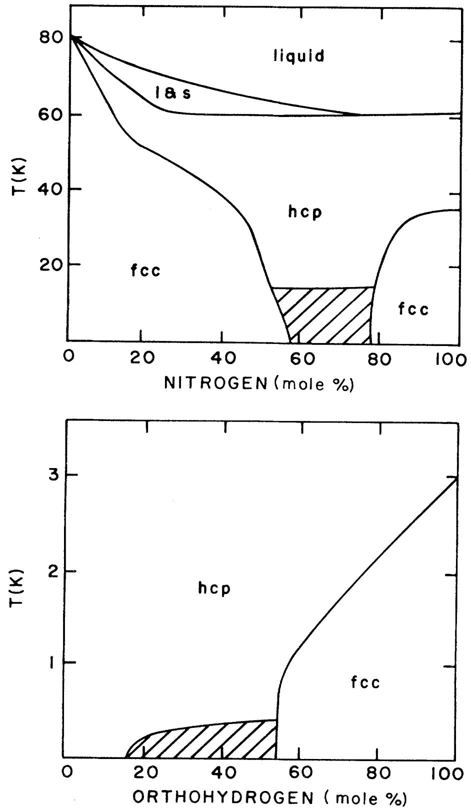

FIG. 1. Schematic phase diagrams for orthoparahydrogen and N_2-Ar mixtures. The figure is a summary of information contained in Refs. 14, 15, 1, and 11.

Because of the complicating factors mentioned above, it is difficult to distinguish unambiguously among several proposed descriptions of the experimental behavior. There is considerable controversy over whether the term "glass" is in fact appropriate. Without addressing the problem of semantics, it seems fair to say that the picture which emerges from the experimental data indicates a freezing which occurs on a local scale at a fairly sharp temperature, while bulk measurements indicate a broad temperature range for any anomalous behavior and an absence of global symmetry breaking. More recent experiments indicate some remanence effects as well.[13]

The most apparent similarity among the various experimental systems is the presence of a clearly LRO orientational configuration in the fcc phase, and the occurrence of this less clearly characterized behavior when the system retains its hcp structure at low temperatures. It has been recognized for some time that the energetics of the intermolecular interaction will be different in the two structural regimes, and both mean-field[18] and Monte Carlo calculations[19] were earlier carried out to study this problem. Although the analyses were based on the assumption that some sort of LRO occurs at low temperatures, both the multiple phase transitions predicted by mean-field theory and the indications of inaccessibility of the ordered state in the MC samples suggest that a number of nearly degenerate (and possibly metastable) configurations occur on the hcp lattice, even without dilution.

It has been suggested[20] that the dominant feature of the problem is local symmetry breaking by dilution, and a detailed analysis applicable to the NMR data has been carried out. This paper concentrates on lattice-induced frustration as the main feature, and on attempts to characterize the ordering and fluctuation phenomena. In particular the results of the group-theoretical classification of LRO configurations and mean-field analysis of the energetics are used in describing the system's behavior and in making quantitative statements about what appears to be a regime of coexisting phases.

In order to facilitate the discussion of Sec. II, the possible four- and eight-sublattice configurations[21,22] for rotors on the hcp lattice are shown in Fig. 2. The four-sublattice structures are obtained from the two possible formulas for stacking the two inequivalent triangular planes with rotors arranged in an H-type structure. The eight-sublattice structure consists of stacked "pinwheel" planes. The configuration labeled $H1$ represents the lowest in energy, with the molecular angles taking on values such that the three direction cosines are equal (the diagonal elements of the quadrupole tensor are thus zero). The mean-field results[18] indicate that a temperature-dependent shift occurs in the angles defining the position of the free-energy minimum within a given structure, that a crossover between structures occurs, and that the entropy contribution to the free energy appears to drive the predicted transitions. Furthermore, the free-energy minima for the three structures differ over a large temperature range by only several parts per thousand—probably the limits of accuracy of the calculation.

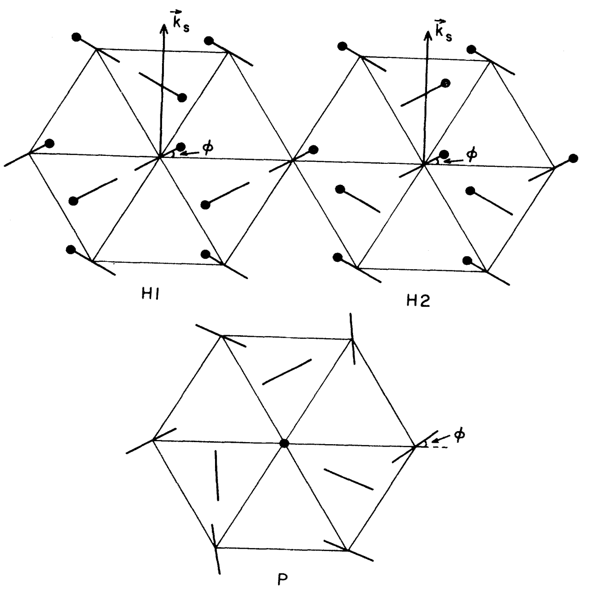

FIG. 2. Possible four- and eight-sublattice arrangements for classical quadrupoles on the hcp lattice (after Ref. 18). $H1$ and $H2$ are nearly degenerate and are associated with a lower internal energy than the P structure. These structures form the basis for the order-parameter definitions of Sec. III. Solid circles represent the ends of the molecules pointing upward from the paper.

It is interesting to note in this connection that the MC calculations of Ref. 19 apparently do not reach the $H1$ structure at all; the conjecture is made in that paper that the system ground state consists of randomly stacked pinwheel planes. Because the samples studied in that case were small, and because comparison of the temperature derivative of the internal energy with the fluctuation-determined specific heat indicates a nonequilibrium regime, a more systematic MC study seemed warranted using samples large enough to permit observations of defect formation and run times long enough to permit monitoring the relaxation process itself.

The role of dilution in changing the balance between symmetric structures, and perhaps in destroying long-range order altogether, has apparently not been studied. The present work has been extended to include this problem. Discussion will be carried out in a planned subsequent paper.

We turn now to the definition of the model. The interaction energy for a system of classical quadrupoles interacting via a Coulomb force may be written

$$H=\tfrac{1}{2}\Gamma \sum_{\substack{\alpha,\gamma,\\ \alpha',\gamma',\\ i,j}} Q_i^{\alpha\gamma}K_{ij}^{\alpha\gamma\alpha'\gamma'}Q_j^{\alpha'\gamma'} \tag{1a}$$

$$=\tfrac{1}{2}\gamma \sum_{\substack{i,j,\\ m,m'}} q_m(\hat{\omega}_i)t_{m+m'}(\hat{\Omega}_{ij})q_{m'}(\hat{\omega}_j) \times\langle 2,2,m,m' \,|\, 2,2,4,m+m'\rangle \;. \tag{1b}$$

Equation (1a) gives the Hamiltonian in Cartesian coordinates. The $Q_i^{\alpha\gamma}$ are the second-ranked tensors associated with the molecular orientation at site i; α,γ label Cartesian components. The fourth-ranked coupling tensor is given by

$$K_{ij}^{\alpha\gamma\alpha'\gamma'}=\frac{\partial^4}{\partial r_{i\alpha}\partial r_{i\alpha'}\partial r_{i\gamma}\partial r_{i\gamma'}}\left[\frac{1}{|\vec{r}_i-\vec{r}_j|}\right],$$

and only nearest-neighbor couplings are considered. This expansion forms the basis of the MC calculations, with all temperature and energies normalized to the parameter Γ in the curves displayed.

The second form [Eq. (1b)] is more convenient for analytic treatment of the problem, and in particular for the discussion of order parameters which appears in Sec. III. The qm are proportional to the spherical harmonics $Y_{2m}(\hat{\omega}_i)$ with $\hat{\omega}_i=(\theta,\phi)$ the solid angle describing molecular orientation at site i. Normalization has been chosen such that

$$\sum_{m=-2}^{2} |q_m(\hat{\omega}_i)|^2 = 1 \ .$$

$t_M(\hat{\Omega}_{ij})$ is similarly proportional to $Y^*_{4M}(\hat{\Omega}_{ij})$ with $\hat{\Omega}_{ij}$ the solid angle associated with the vector $\vec{r}_i - \vec{r}_j$. $\langle j_1,j_2,m_1,m_2 | j_1,j_2,j,m \rangle$ is a Clebsch-Gordan coefficient. There appear to be a number of "standard" notations in the literature. These for the most part take the form (1b) with a variety of normalizations of γ.

There are some similarities between the $Q_i^{\alpha\gamma}$ and classical Heisenberg spins. The analogy becomes more useful if it is recalled that the two-particle interaction of Eq. (1) has as its low-energy configuration a "*T*" in which the molecular axes are oriented at right angles to each other. Thus, the simple problem of packing low-energy pairs on a lattice is much like the similar problem for the antiferromagnet. In particular, the considerations leading to "frustration" effects for the Heisenberg antiferromagnet on the triangular plane (and on both fcc and hcp lattices) apply in the present case. The MC results displayed below indicate the existence of a near degeneracy associated with the (discrete) degree of freedom determining the stacking of hexagonal planes. In this respect the model is similar to the Ising antiferromagnet; the $N^{1/3}$ entropy which also occurs in the fcc Heisenberg antiferromagnet occurs with a continuous degree of freedom.

Any order parameter given as a function of the q_m (or $Q^{\alpha\gamma}$) only is not conserved. The anisotropy introduced by the interparticle coupling causes a gap in the excitation spectrum. This gap is removed when the rigid-lattice restriction is relaxed, since in this case the system is invariant under an operation which combines both translational and orientational molecular coordinates. The major shortcoming of the model probably lies in the fact that this coupling must be put in by hand as an interaction between phonon and libron excitations; in the regime of interest this is unlikely to be a simple perturbative effect.

III. ORDER-PARAMETER DEFINITIONS

The choice of order parameter is nonunique, since there are several low-energy configurations possessing long-range order and entailing loss of the full point-group symmetry of the crystal. In addition, both the experimental data and the present MC work suggest that the interesting problems concern a competition among these possible configurations and the role played by local symmetry breaking. There are three standard and complimentary methods for dealing with ordering phenomena, and it is useful here to compare the kinds of information available from each. They are, respectively, (1) standard Fourier analysis, (2) group-theoretic analysis, and (3) an inner-product analysis related to distances between configurations in phase space.

The techniques for dealing with global symmetry breaking are well developed and have been applied successfully to the long-range transition on the fcc lattice. On the other hand, a quantitative characterization of local order is much more difficult to achieve. Little can be done without explicit order-parameter definition; while it is simple to remark that some sort of freezing occurs and to find evidence for anomalies in a variety of characteristic time scales, it is less simple to isolate the mechanisms driving such a transition and to explain why both apparent temperature of onset and sharpness of onset vary widely from one experiment to another.

If the primary aim of analysis is determination of the orientational-excitation spectrum, the Fourier transform of the local quadrupole moment may be conveniently used to describe system behavior. The configurations of Fig. 2 are completely specified by the wave vectors $\vec{k} = \vec{0}$, and $\vec{k}$ representing each of the faces of the Brillouin zone. Since this represents a five-component order parameter at each of four wave vectors, these quantities taken together produce a twenty-parameter space. The advantage is that one may use standard many-body techniques—mean-field theory, random-phase approximation, and controlled approximations within perturbation theory—to calculate correlation functions in a straightforward, if somewhat cumbersome, manner. In addition, the results are simply related to other solid-state phenomena such as phonon or roton modes. One obtains immediately the energetics as well as the topology of the problem, and the framework provides a starting point for construction of the phenomenological Hamiltonians useful in developing a renormalization group.

If one depends only on the group structure of the system, the number of order parameters is reduced to the number of functions required to span the irreducible representations of the crystal point symmetry. For the hcp lattice, this number is eight. For the octahedral group appropriate to the fcc lattice, it is ten. The price one pays for this relative simplification is that the details necessary for a discussion of energetics is lost in particular, and in general, the specific functional forms are not derivable without additional information. For the case at hand, however, the following remarks should be made. If one can provide a set of explicit irreducible representations for the point group of the lattice, together with the basis functions $\Phi_s^{(j)}(\vec{r})$ belonging to the *s*th row of the *j*th irreducible representation, then any function $f(\vec{r})$ will be defined on the lattice, at least as far as its transformation properties are concerned, as follows:

$$f(\vec{r}) = \sum_{s,j} C_s^{(j)} \Phi_s^{(j)}(\vec{r}) \ . \tag{2}$$

This is true also for the order-parameter density functions describing a complicated phase transition. Standard Landau theory deals with the temperature dependence of the coefficients $C_s^{(j)}$ which are taken to be the order parameters. The classic argument states that a second-order transition (or one that is nearly second order in that it is driven by fluctuations) is unlikely to be associated with more than one such symmetry-breaking parameter, and simultaneous appearance of multiple symmetry-breaking functions is considered to be fortuitous.

Consider now the possible four-sublattice and eight-sublattice structures on the hcp lattice (Fig. 2). In Fig. 3 the classes of symmetry operations appropriate to the hcp lattice are described, and in Table I the character table is given.[23] In order to determine the number of basis func-

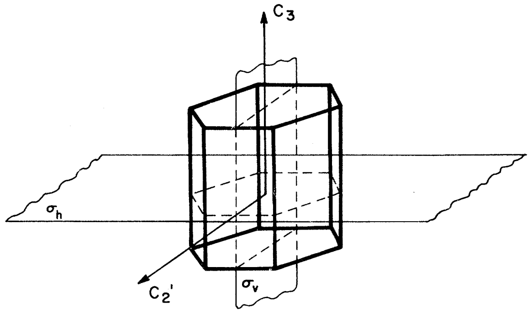

FIG. 3. Symmetry axes and planes defining the group operations of D_{3h}, the full group of the hcp lattice.

tions necessary to represent structures of the form shown, as well as the character row of the representation, consider the results of operation with the lattice-group elements. Each of the stacked H-type structure configurations ($H1$ and $H2$ of the figure) generates eleven similar structures under the full group.

None of these structures remains invariant under any of the operations. Thus a set of twelve distinct functions is needed to generate a representation for either order parameter. Since these must transform in a manner which describes the configuration transformations, one may construct the character row as shown in the table. From this it may be seen that order parameters describing both of these structures contain components of all six of the irreducible representations of the lattice symmetry. In contrast the "stacked pinwheel" configuration (P) generates only one other structure under the full crystal group. The two-dimensional representation contains only one basis function in addition to the identity.

Thus on the basis of symmetry considerations alone, one might expect the P configuration to form more easily than the H configuration. All of this neglects energies involved in formation of these configurations, and energy considerations depend not merely on system symmetry, but on the continuous parameters indicated in the figure—two specifying a solid angle in defining $H1$ and $H2$, and the single angle ϕ for P. Distinct values of these variables correspond to distinct order parameters. There are thus questions which cannot be answered by arguments such as the above: (1) What values do the continuous variables assume for minimum energy in each of the three configurations? (2) Is there an overlap in the sense that some of the configurations of a particular symmetry may be accessible from configurations of another symmetry; e.g., can $H1$ or $H2$ be obtained from P through a local distortion? The answer to (2) depends upon (1), for the energy minima must correspond to angular variables which are "close" by some measure. Clearly, the question is important. In the fcc lattice, for example, the Pa_3 quadrupolar order is described by an order parameter containing components of several of the irreducible representations of the octagonal group O. There are, however, no simpler order parameters having similar energies and similar angular variables throughout the unit cell. The orientational ordering in this case is known (from Monte Carlo studies in particular) to be long range in nature, and the transition is sharp, and is accompanied by a clear specific-heat anomaly.

TABLE I. Character table for D_{3h}, the point group appropriate to the hcp lattice (Ref. 23). Character rows for the structures of Fig. 2 are also shown. These may be decomposed to give $H1=H2=A_1'+A_2'+A_1''+A_2''+2(E'+E'')$, $P=A_1'+A_2'$.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	1	1	-1	-1
A_1''	1	-1	1	-1	1	-1
A_2''	1	-1	1	-1	-1	1
E'	2	2	-1	-1	0	0
E''	2	-2	-1	1	0	0
$H1,H2$	12	0	0	0	0	0
P	2	2	2	2	0	0

A different approach is more useful when the available evidence indicates that ordering entails broken ergodicity[24] rather than global breaking of spatial symmetry. This procedure works only when one has some notion of the structure of the phase space available to the system and can enumerate explicitly those configurations which act as traps in that space. It is interesting in this case to ask how close the system is to a given reference state, and an effective order parameter may be defined in terms of some suitable "overlap" between the actual state of the system and the chosen reference configurations. The concept of overlap arises naturally in any problem where freezing occurs without a clearly broken spatial symmetry. It enters into discussions of metastability and time scales, and has been introduced into the spin-glass problem through the Edwards-Anderson order parameter and its subsequent refinements. It becomes a useful concept not only in the absence of a unique thermodynamic long-range-ordered state, but also when such a state becomes inaccessible on experimental time scales. The emphasis in the quadrupolar glass problem has been on the evidence for abrupt freezing phenomena in the absence of a thermodynamically sharp phase transition. On the basis of the above discussion it is clear that a symmetry-breaking transition can occur on the hcp lattice, although both earlier and the present Monte Carlo work indicate that it occurs only on very long time scales. In order to discuss this accessibility problem, it becomes convenient to borrow the overlap concept from the spin-glass problem and to define an order parameter based on reference states which are closely related to the long-range states $H1$, $H2$, and P.

It is useful to consider a particularly simple analog before introducing the less transparent definitions needed for the quadrupolar problem. Consider the usual order parameter for the Heisenberg ferromagnet. This is the three-component magnetization,

$$\vec{M}=\frac{1}{N}\sum_i \vec{s}_i \;, \tag{3}$$

with $\vec{s}_i$, the classical or quantum-mechanical spin associated with site i, and N the system size.

One could, however, describe the state of the system through its projection on a particular reference state α—e.g., the state having all spins aligned upward along the z axis,

$$M_z \equiv \frac{1}{N}\sum_i \vec{s}_i \cdot \vec{s}_i^{\,(\alpha)} = \frac{1}{N}\sum_i s_{iz} \; . \tag{4}$$

Here the dot product is computed at each site between $\vec{s}_i$, the actual spin in the state of interest, and $\vec{s}_i^{\,(\alpha)}$ the spin which would be present on that site if the system were in the reference state α. To recover $\vec{M}$, the addition of two other uniform reference states will suffice. The norm of an arbitrary state γ is

$$||\gamma|| \equiv [(\gamma,\gamma)_s]^{1/2} \equiv \left[\frac{1}{N}\sum_i \vec{s}_i^{\,(\gamma)} \cdot \vec{s}_i^{\,(\gamma)}\right]^{1/2} = 1 \; , \tag{5}$$

and the "distance" between states is

$$\begin{aligned} ||\alpha-\gamma|| &= [\,||\alpha||^2 + ||\gamma||^2 - 2(\alpha,\gamma)_s]^{1/2} \\ &= \{2[1-(\alpha,\gamma)_s]\}^{1/2} \; . \end{aligned} \tag{6}$$

The notation $(\alpha,\gamma)_s$ has been introduced to emphasize that the given definitions do indeed specify a valid inner product, and $||\alpha-\gamma||$ is an acceptable metric. It provides a measure of the accessibility of the state α from the state γ.

Spacial structures may also be incorporated in a straightforward way, so that, for example, the antiferromagnetic order parameter is generated from a staggered array of spins:

$$N_z \equiv \frac{1}{Z}\sum_i \vec{s}_i \cdot \vec{s}_i^{\,(\alpha')} \equiv \frac{1}{N}\sum_i s_{iz} e^{i\vec{k}\cdot\vec{r}_i} \; . \tag{7}$$

The order-parameter definition for a quadrupolar array γ proceeds analogously,

$$\psi_\alpha \equiv (\alpha,\gamma)_q \equiv \frac{1}{N}\sum_{i,m} (q_{im}^{(\alpha)})^* q_{im}^{(\gamma)} \; , \tag{8}$$

with q_{im} the classical quadrupole moments described in Sec. II. (In the quantum case ψ_α becomes an operator and the order parameter is its expectation value.) The label α again specifies a reference configuration. With the normalization used here,

$$\begin{aligned} &|(\alpha,\gamma)_q| \le 1 \; , \\ &(\alpha,\alpha)_q = 1 \; . \end{aligned} \tag{9}$$

Given a set of reference configurations, this site-by-site overlap is particularly convenient for computer simulation, since microscopic arrays are available at each step. By direct transformation it may be related to the usual Fourier-component description,

$$\psi_\alpha = \sum_{\vec{k},m} [q_m^{(\alpha)}(\vec{k})]^* q_m(\vec{k}) \; , \tag{10}$$

with $\vec{k}$ extending over the Brillouin zone. In addition, by providing the explicit functional form for the $q_m^{(\alpha)}(\vec{k})$ or $q_{im}^{(\alpha)}$ for any symmetric and periodic structures which are of interest, one may make contact with the group-theoretic analysis. The inner-product definition is both more general and more cumbersome, however, since there are $2N$ molecular degrees of freedom. The usefulness of either the group-representation basis or of Fourier components at special $\vec{k}$ values to describe the order parameter depends on the fact that nearly all degrees of freedom of the system may be discarded as uninteresting for discussion of thermodynamic conditions. In cases, however, where metastable conditions obtain or where coexisting phases occur, the value of the inner-product order parameters permit a rational measure of the distance traveled by the system in its available phase space. It is the susceptibilities associated with these which display the well-known time-dependent cusp in simulations of spin-glasses.

In order for the notion of overlap to be useful, analysis of the energetics, or some other criterion should reduce the number of reference states to a manageable number. In addition, it is important to describe accessibility of one reference state from another. Since the Hamiltonian (1) on the hcp lattice is known to result in energy minima for the $H1$, $H2$, and P structures, it seems reasonable to use these as the basis states for analysis. There is a difficulty, however; the configurations corresponding to the energy minima are nonorthogonal, either by the usual definition obtained through the expansion of Eq. (2) or by the definition of Eq. (8).

Orthogonal reference states are useful for several reasons. Since ordering may occur in several distinct ways, an objective measure of the ordering magnitude is highly desirable. This is taken to be just the sum of the square of the various parameters defined below. In the case at hand, decomposition of MC configurations into the particular components chosen permits identification of the fluctuations driving the system toward order, even though the order parameter associated with these fluctuations may vanish in the fully ordered state.

Thus, one is led to use, instead of the configurations $H1$, $H2$, and P themselves, linear combinations of them which are orthogonal under the inner product definition of Eq. (8), and which, therefore, provide an unambiguous characterization of the state of the system.

That this initial basis is nonorthogonal simply reflects the fact that the configurations are accessible from one another, not for energetic reasons, but because of topological considerations alone. The fact that they are energetically similar leads to the requirement that a basis be used which permits identification of all of them. In view of the results which follow, it is particularly interesting to note that the overlap between the pinwheel structure and either of the H-type structures is associated with their mutual accessibility via a local distortion; this is clearly seen on examination of the constituent planar structures of Fig. 2. The two unit cells may be obtained from each other by significant reorientation of a single spin accompanied by minor readjustments of its neighbors. The MC data shown below indicate that such distortions represent the most important excitations of the system.

In principle, given an inner-product definition and a basis which spans the space of interest, some procedure such as the Gram-Schmidt process will automatically produce the required orthonormal basis. In the present case, however, it seems preferable to retain as much as possible of the crystal symmetry in the basis states. In particular, it seems sensible to isolate the P structure since it is characterized by only a single irreducible representation of the full crystal group. Since this configuration is invariant under a threefold rotation, an important crystal symmetry is retained. A second feature which is easily identified is the H-type structure axis (defined by $\vec{\mathrm{k}}_s$ in Fig. 2) in the $H1$ and $H2$ structures. Consider the symmetric and antisymmetric combinations of these two states (referring to Fig. 2):

$$|s^+)=|H1,\vec{\mathrm{k}}_s)+|H2,\vec{\mathrm{k}}_s)\ ,$$
$$|s^-)=|H1,\vec{\mathrm{k}}_s)-|H2,\vec{\mathrm{k}}_s),\quad s=1,2,3$$

i.e.,

$$q_{im}^{(s\pm)}=q_{im}^{(H1,\vec{\mathrm{k}}_s)}\pm q_{im}^{(H2,\vec{\mathrm{k}}_s)}\ . \tag{11}$$

obviously $(s^+,s^-)_q=0$ [by definition of Eq. (8)] and both $|s^+)$ and $|s^-)$ retain the H-type structure axis $\vec{\mathrm{k}}_s$. Now one may complete the order-parameter definitions for an arbitrary state $|\gamma)$ as follows:

$$\begin{aligned}\psi_0&=(P,\gamma)_q\ ,\\ \psi_s&=\frac{1}{N}\left[(s^+,\gamma)_q-(s^+,P)_q(P,\gamma)_q\right.\\ &\qquad\left.-\sum_{s'\neq s}(s^+,s'^+)_q(s'^+,\gamma)_q\right]\ ,\\ \bar{\psi}_s&=\frac{1}{\bar{N}}\left[(s^-,\gamma)_q-(s^-,P)_q(P,\gamma)_q\right.\\ &\qquad\left.-\sum_{s'\neq s}(s^-,s'^-)_q(s^-,\gamma)_q\right]\ ,\end{aligned} \tag{12}$$

where N and $\bar{N}$ are chosen so that $|\psi_s|=1$ and $|\bar{\psi}_s|=1$. Note that ψ_s and $\bar{\psi}_s$ represent correlations of equivalent planes.

One may thus identify the original configurations as follows:

(1) $\psi_0\neq 0$, $\psi_s=\bar{\psi}_s=0$ for all $s>0$. The system is in the P configuration.

(2) $\psi_s>0$, $\bar{\psi}_s>0$ or $\psi_s<0$, $\bar{\psi}_s<0$, and $\psi_0=0$. $H1$ structure obtains with axis $\vec{\mathrm{k}}_s$.

(3) $\psi_s>0$, $\bar{\psi}_s<0$ or $\psi_s<0$, $\psi_s>0$, and $\psi_0=0$. $H2$ structure obtains with axis $\vec{\mathrm{k}}_s$.

(4) $|\psi_s|>0$, $\psi_s=0$ or $|\bar{\psi}_s|>0$, $\psi_s=0$, and $\psi_0=0$. Long-range H-type structure order occurs in each plane with axes of successive planes aligned. The stacking rule determining $H1$ or $H2$ structures is broken, and stacking occurs randomly.

Other sets of order-parameter values correspond to coexistence of the various structures or to some unidentified long-range-ordered structure.

The functions of Eq. (12) are simply obtained from the arrays generated in the Monte Carlo process. The associated susceptibilities may be obtained from order-parameter fluctuations in the usual way,

$$\chi_\alpha\equiv\frac{1}{NT}\langle[\Delta(N\psi_\alpha)]^2\rangle\ , \tag{13}$$

where $\langle(\Delta x)^2\rangle=\langle x^2\rangle-\langle x\rangle^2$, angular brackets indicate averages over MC samples, and T is the temperature.

Internal energy[25] per quadrupolar "spin" and specific heat are independent of order-parameter definition [see Eq. (1)],

$$E=\frac{\Gamma}{2N}\sum_{\substack{\alpha,\gamma,\\ \alpha,\gamma,\\ i,j}}\langle Q_i^{\alpha\gamma}Q_i^{\alpha'\gamma'}\rangle K_{ij}^{\alpha\gamma\alpha'\gamma'}\ , \tag{14}$$

and the specific heat,

$$C=\frac{1}{NT^2}\langle[\Delta(NE)]^2\rangle\ . \tag{15}$$

IV. NUMERICAL PROCEDURES AND RESULTS

The simulations made use of the energy expression (1a) and the standard finite-temperature single-site rejection procedure. Because the glassy properties of the system are of interest and because earlier computer experiments indicate characteristics of slow relaxation, particular attention was paid to size effects (which are directly related to defect formation) and to run-time effects. In addition, a number of initial configurations were used at various temperatures, and comparisons were made for slow-warming, slow-cooling, and quenching runs. These comparisons included calculations both of various order parameters and their susceptibilities, and of internal energies and specific heat. Sample size varied between 128 and 2520 lattice sites; beyond about 500 sites final configurations appeared to be independent of sample size. Because of practical limitations most of the data shown were taken for 576 and 720 sites. Nonperiodic boundary conditions were used to avoid prejudicing the sublattice structure, and all bulk parameters were computed using only sites interior to the sample. In all cases both fluctuation-determined specific heats [Eq. (15)] and $\partial E/\partial T$ were calculated. Agreement of the two values, within statistical uncertainty, is generally accepted as a criterion for achievement of thermodynamic equilibrium. This agreement was *not* attained in each of the runs discussed. However, when all runs at a given temperature were averaged, statistical agreement was found to occur. This indicates that the initial conditions chosen were sufficiently diverse to permit sampling of the full configuration space of the system. (Relationships between thermodynamic and quasistable parameters are given in Ref. 24.) Run times ranged up to 2×10^4 Monte Carlo steps/spin (MCS/S) for temperatures in the transition region, and it was found that variation of this run time caused significant variation in the computed quantities. The results suggest that intermediate-length runs correspond more nearly to real experimental conditions.

In addition to "annealing" the samples in the usual way, the accessibility of the long-range-order configurations was investigated by means of a "ground-state" search from equilibrium states at temperatures in the transition region. This "quenching" process invariably produced a configuration different from that of the LRO ground state. The ground-state search was conducted in a manner analogous to the local-field technique used for classical Heisenberg spins.[26] In the present case one may compute a quadrupolar field tensor,

$$h_{\alpha\gamma}(\vec{r}_i)=\tfrac{1}{2}\Gamma\sum_{\substack{j\\ \alpha',\gamma'}}K_{ij}^{\alpha\gamma\alpha'\gamma'}Q_j^{\alpha'\gamma'}\,, \tag{16}$$

find the principle axes, and rotate the quadrupole moment at site i so that it is aligned along the direction for largest negative eigenvalue of $h_{\alpha\gamma}(\vec{r}_i)$, thus minimizing the energy. It should be noted that the present model yields a nondegenerate local field tensor.

The calculated values of energy and specific heat are summarized in Fig. 4. Data are displayed for three sorts of runs. The warming curve (closed circles) was prepared at $T=0$ in the lowest-lying LRO configuration. Each run consisted of between 4000 and 5000 MCS/S, and the final configuration of each run was used as the initial configuration at the next higher temperature. The temperature intervals varied over the transition region as shown, and increase in run times produced no discernible effect on the data. The open squares represent several cooling runs beginning from a random initial array at $T/\Gamma=5.0$, and reducing the temperature in steps of 0.5Γ to the transition region. The energy curves are virtually identical except very near $T/\Gamma=2.4$. At these relatively short run times, the transition appears to be first order, and the specific-heat peak, clearly observable in the warming runs, is truncated. Below this temperature the statistical noise in the specific heat persists to the lowest temperatures measured. (Although the MC run time is here called "short" or "intermediate," it is comparable to run times necessary for attainment of equilibrium in some of the well-studied nonpathological systems, such as Ising or Heisenberg magnet.) To study the time scale on which equilibrium is achieved—if in fact it can occur, the same initial configuration was "annealed" at $T/\Gamma=2.4$ for 2×10^4 MCS/S. A preliminary analysis of the autocorrelation function indicates that the system is in a nonexponential relaxation regime near this temperature; this is indicative of severe fluctuation effects, and suggests that the system may be characterized by several distinct time scales. The primary effect of annealing on the bulk properties is restoration of the second-order nature of the transition [see Fig. 4(a)] and in reintroducing a sharp specific-heat peak. Annealing experiments below about $T=2.0\Gamma$ appear to give results identical to those of the warming runs. Furthermore, below this temperature, times greater than about 3000—4000 MCS/S appear to be adequate to simulate cooling from the nonannealed array. That is, the system, *if annealed* in the vicinity of $T=2.4\Gamma$, undergoes an apparently ordinary phase transition over a narrow temperature range. On the other hand, increasing run times below this region appears to have little effect on the nonannealed arrays; while their energy is virtually indistinguishable from that of the annealed samples, large uncertainties persist in the specific heat (although not in the energy itself).

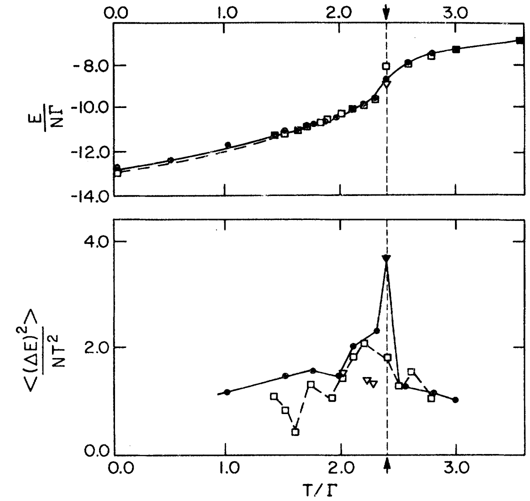

FIG. 4. Internal energy per quadrupole vs temperature (upper curve) and fluctuation-determined specific heats. Solid circles represent the warming curve, open squares, an intermediate time-scale cooling curve. Open triangles represent a cooling curve annealed at $T-2.4\Gamma$ (see text). Both temperatures and energies are normalized to Γ, the EQQ interaction constant. The arrows indicate the transition temperature, where annealing was carried out.

A more detailed description of the transition comes from examination of the order parameters as defined in Eq. (12). Data from the equilibrium runs of Fig. 4—i.e., from both the warming run and annealed cooling runs—are displayed in Fig. 5. The large positive values of ψ and $\bar{\psi}$ are consistent with a well-defined transition into the LRO ground state. The apparent transition temperature is consistent with the specific-heat peak and annealing point indicated in the previous figure. There is no evidence for the multiple LRO transition predicted by mean-field theory, but in the transition region a significant magnitude is observed for the order parameter ψ_0 which describes the P structure, and which has no overlap with either ψ or $\bar{\psi}$. As one would expect, given the form of the LRO ground state, ψ_0 vanishes as T goes to zero. The values plotted are averages over several thousand MCS/S. Thus although one should describe the behavior

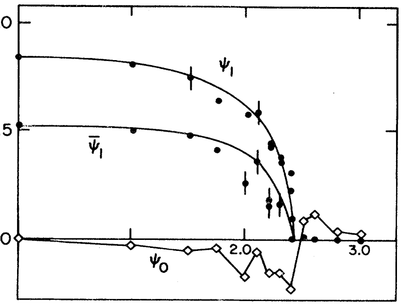

FIG. 5. Various nonzero order parameters specifying symmetry (computed per quadrupole) for "equilibrium" runs—i.e., for the runs showing a clear specific-heat peak in Fig. 1; ψ_1 and $\bar{\psi}_1$ are related to the H-type structures and describe correlations between equivalent planes. ψ_0 describes an ordering into the P structure.

of ψ_0 as dominated by fluctuation effects in this regime, these fluctuations occur over a relatively long time scale. The temperature range of the effect is of the order of the transition temperature itself.

The behavior of the nonequilibrium arrays may be contrasted with the above (see Fig. 6). Under intermediate time-scale cooling conditions, the system finally orders in planar arrays ($\psi_1 \neq 0$; the absolute sign is unimportant, since only relative signs of ψ_1 and $\bar{\psi}_1$ enter into a description of the symmetry), and the transition occurs at the same temperature as the LRO transition. However, there are two major differences in the order-parameter descriptions of the two cases. Here $\psi_0 \neq 0$ persists to $T=0$. The dotted lines on the figure indicate the result of a ground-state search from the point shown, and the data points indicate the results of several runs. It should be recalled that the parameters ψ_1 and $\bar{\psi}_1$ as displayed indicate the presence of the in-plane ordering into either $H1$ or $H2$ structures, but that the stacking arrangement is not well defined between inequivalent planes. Again the $\psi_0(T)$ curve indicates the occurrence of large but long-lived fluctuations. However, the persistence of a large value for this parameter after a ground-state search indicates that the P configuration is at least locally stable.

In order to clarify the phenomena it is useful to examine the generated arrays themselves and to compare them to the LRO structures. A temperature sequence for cooling on intermediate time scales is given for a small number of interior spins in Fig. 7. The topmost array represents a typical configuration at $T=2.0\Gamma$ and $t \simeq 6000$ MCS/S. Visual inspection of arrays produced at longer run times produce no obvious qualitative changes; however, the data of Figs. 4 and 5 indicate that the bulk parameters may be distinguished. The sample has clearly begun to order, and the relative orientation of inequivalent molecules suggests that the incipient order is predominantly that of the $H1$ structure. However, even within the small samples there are clusters of spins which are correlated as in the P structure, and these apparently represent the easily formed local excitations in the system. The same portion of the sample is shown as the temperature is lowered. The changes which take place appear to affect the small P clusters, and the defects are annealed out. A ground-state search conducted from this array produces the result in the upper $T=0$ configuration. This particular portion of the sample condenses into a pure $H1$ structure (the order-

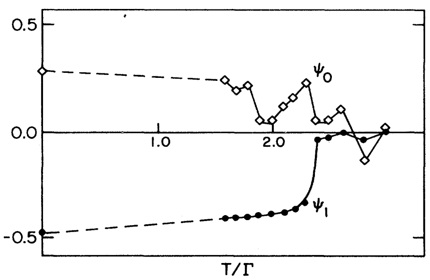

FIG. 6. Order parameters occurring in intermediate time-scale runs. The zero-temperature points were obtained by means of a local ground-state search from the points indicated by the dotted lines. $\bar{\psi}_1$ is essentially zero in this case.

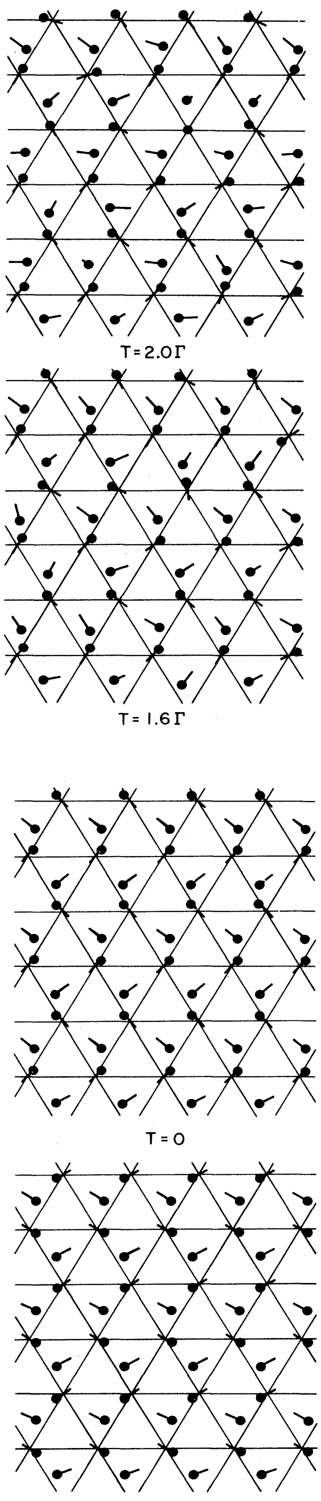

FIG. 7. Portions of the MC arrays at temperatures in the transition region and at $T=0$. Near T_c the sample contains clusters of quadrupoles arranged in the P configuration. At $T=0$ both H-type structure stacking arrangements appear in a single sample. (See text.)

ing is complete within the two planes shown). However, the two neighboring planes of the bottom figure have a pure $H2$ order. This variation in stacking appears to be random, with individual planes completely ordered. The shape of the sample was varied, but this appeared to have little effect on the results. The H-type structure axis of all planes appears to be aligned.

There is further evidence that the P-structure order parameter is associated with the driving fluctuations of the system; this is despite the fact that it appears never to represent the equilibrium configuration. In Fig. 8, its associated susceptibility [Eq. (13)] is shown. A sharp peak occurs in the transition region for both quenched and annealed runs; thus these excitations appear to dominate the ordering mechanism whether or not the long-range transition is permitted to occur. This is consistent with the visual appearance of arrays and with the local character of the excitations. It seems reasonable to conclude that the glasslike behavior of quadrupolar molecules on this lattice is at least partially a result of the local symmetry breaking which occurs. It is also worth noting that the correct order parameters have significantly smaller susceptibilities throughout the entire temperature range; there is no indication of an anomaly in either quenched or annealed runs. The apparent divergence of this order-parameter susceptibility near the phase transition is also consistent with the expectation that only one of the symmetry-breaking parameters of Eq. (2) should drive the transition.

One final piece of data concerns the entropy available to the system as it condenses below the transition temperature. The usual technique for evaluating this is to integrate C/T from $T=0$, with C evaluated either from Eq. (15) or from numerical values of $\partial E/\partial T$. In the present classical system, the expected $T=0$ limit of the specific heat is $\frac{1}{2}$ in the units used here, so that such an integration procedure is impossible. An additional consideration is that it is not clear, on the basis of the above discussion, whether the system samples a truly thermodynamic ensemble—the most likely candidate for equilibrium is the LRO state, but this appears not to be relevant to the glass regime.

An alternative procedure is to evaluate the entropy per spin,

$$S=S_\infty+\frac{1}{N}\int_0^{E(T_c)/N} dE\,\frac{\partial S}{\partial E}$$
$$=S_\infty+\int_0^{E(T_c)/N}\frac{1}{T(E)}\,dE\;, \qquad (17)$$

with $S_\infty=\ln(4\pi)$ for this classical model. This has the advantage that $E(T)\sim 1/T$ at high temperatures, and the uncertainty in estimating the integral of (17) is small. At the transition temperature order-parameter derivatives must be included in the entropy estimate, and since these may diverge, the estimate becomes impractical below this point.

With respect to the $T=0$ value of the specific heat, several comments should be made: (1) The derivative of the energy curve which represents warming from the LRO state is consistent with this value, and thus one has a check on the MC data. (2) At very low temperatures, the results given here cannot be compared directly to experiment, since in this regime quantum effects may be expected to modify the dynamics of the system. However, the qualitative variations which occur near the transition among the various processes considered should occur in the experimental systems as well. The conclusion to be drawn from Figs. 9 and 4(b) is that a significant amount of entropy is available to the system at the transition temperature and the form of the apparent entropy change at T_c may vary with cooling rate and sample preparation.

V. CONCLUSION

The conclusions to be drawn from the data displayed in Sec. IV may be summarized briefly. The undiluted quadrupolar system on an hcp lattice possesses a number of partially ordered states whose energies are nearly degenerate with the lowest-lying LRO state. These states appear to consist of configurations having long-range order in two dimensions, and an alignment of symmetry axes

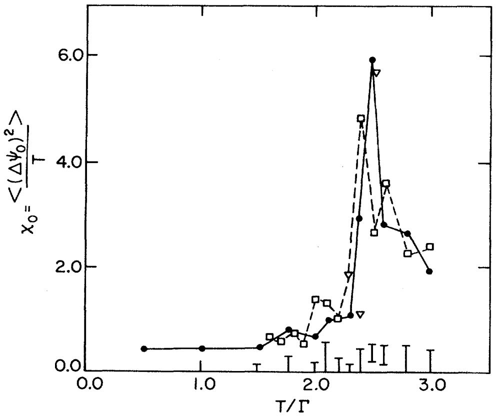

FIG. 8. Susceptibility associated with the order parameter ψ_0 vs temperature. Symbols are as in Fig. 1. The bars lying below $\chi=0.5$ indicate the range of magnitude of the susceptibilities associated with the "correct" symmetry of the system.

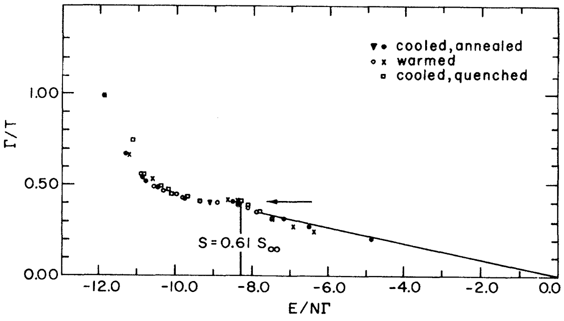

FIG. 9. Determination of entropy available to the system at the transition temperature. The data of Fig. 4(a) have been replotted to permit extrapolation of $\partial S/\partial E$ to $T=\infty$ $(E=0)$. The arrow indicates the apparent transition, as determined from Figs. 4, 5, and 8.

among planes. The degree of freedom determining the degeneracy of these configurations thus appears to be a stacking parameter which may take on one of two values (giving locally one of the two H-type structures of Fig. 2). This leads to an entropy which is proportional to $N^{1/3}$.

On the basis of run-time studies, it appears that the experimentally observed specific heats correspond, not to adiabatic cooling through the transition, which permits achievement of the LRO state, but to the nonequilibrium cooling which leads to stacking faults. The MC run times necessary to achieve the LRO state are comparable to run times necessary for glassy systems, and are longer than normally used in the annealing curves of well-behaved systems.

The order parameters specifying symmetry—i.e., those used in classical Landau theory—are significant in describing the behavior of the system, even when global ordering does not occur. In particular, the only susceptibility divergence observed corresponds to an order parameter containing only one basis function of the irreducible representations of the full crystal group. This is to be expected on the basis of the standard arguments. The susceptibility anomaly appears to be associated with localized fluctuations and these appear to mediate the transition to two-dimensional order. These results are consistent with a reinterpretation both of earlier MC work and mean-field results, and appear to resolve a conflict between the two. One does not expect multiple phase transitions, as the usual mean-field analysis would suggest, but one finds instead a locally-driven ordering which includes all of the coupled mean-field order parameters.

In a planned second paper, the role of dilution effects will be discussed in detail. A preliminary analysis suggests that a general broadening occurs with a decrease in concentration of the interacting species, but it is not yet clear whether the character of the transition is changed. The present data indicate strongly that the intrinsic topological properties of the hcp lattice determine the nature of the ordering to a significant extent, and must be considered together with dilution-induced phenomena.

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