Short-Range Quadrupolar Order on a Dilute Simple-Cubic Lattice

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Computer experiments provide evidence that an intermolecular quadrupolar interaction on some crystal lattices can lead to short-range rotational "freezing" whose characteristics are similar to those of spin-glass ordering. Local order parameter and susceptibility are calculated as a function of temperature for a simple-cubic lattice, and the effects of dilution on the low-temperature limit of the order parameter are also discussed.

I present here data obtained from Monte Carlo calculations designed to study the rotational ordering of molecules placed on a lattice and coupled through an electric quadrupolar (EQQ) interaction. The possibility of a metastable local ordering in such systems under certain conditions seems to have been first suggested by the NMR study of solid hydrogen carried out by Sullivan *et al.*[1] An apparent phase transition was observed, and a phase diagram showing transition temperature versus quadrupole (orthohydrogen) concentration was derived and found to bear a striking resemblance to the analogous diagrams for spin-glasses,[2] with the "glass phase" occurring at ortho concentrations of less than 55%. My results do indeed lend support to the notion that a "quadrupolar glass" phase can occur, but I argue that its existence is *not* intrinsically a dilution effect, instead depending crucially on the lattice structure of the system, which may give rise to frustrated quadrupolar bonds even at full concentration. I have examined the suppression of the local zero-temperature order parameter Q, as the quadrupole concentration c is lowered through the percolation limit, and have found that the curve $Q(T=0)$ versus c follows closely the conductivity curve $\sigma(c)$ for site dilution in the simple-cubic lattice. It should be emphasized that the crystal structure chosen is much simpler than that found for solid hydrogen in the relevant concentration range; however, for reasons given below, I believe this to provide a suitable model for investigation of the effects peculiar to the three-dimensional quadrupolar glass. Because the EQQ interaction plays a significant role in the molecular ordering of many materials, it is likely that these effects will help to determine their structural and rotational configurations, particularly when the material is inhomogeneous and contains varying concentrations of "nonquadrupolar" impurities. The present data demonstrate in any case that an analogy may be drawn between the quadrupolar autocorrelation function, with its fluctuations, and the Edwards-Anderson order parameter,[3] with its associated susceptibility.

Because in the case of hydrogen, at least,[4,5] the salient features of the molecular interaction are adequately described by theories which treat the molecules as rigid classical rotators, I have set up a Monte Carlo procedure nearly identical to that used in the study of continuous-parameter spin systems.

The energy expression from which I start is

$$U=\Gamma_Q \sum_{\substack{ij\\ \alpha\gamma\\ \alpha'\gamma'}} D_i^{\alpha\gamma} K_{ij}^{\alpha\gamma\alpha'\gamma'} D_j^{\alpha'\gamma'} \pi_i \pi_j. \tag{1}$$

For simplicity I keep nearest-neighbor interactions only and write the coupling constant as

$$\Gamma_Q = e^2D^2/R_0^{\,5}, \tag{2}$$

where eD is the quadrupole moment of the molecule, and R_0 is the nearest-neighbor spacing. The π_i take on the values 0 or 1 and account for the presence of nonquadrupolar impurities. The $D_i^{\alpha\gamma}$ are, of course, defined classically in terms of the molecular charge distribution. They comprise five independent matrix elements, but once the symmetry axis of a given molecule is known, these matrix elements are specified through a simple rotation; thus the number of independent variables per site is reduced to two. The effects of the crystal structure are contained in the (normalized) quadrupolar exchange

$$K_{ij}^{\alpha\gamma\alpha'\gamma'} = \frac{R_0^{\,5}}{6} \frac{\partial^4}{\partial r_i^{\alpha}\,\partial r_i^{\gamma}\,\partial r_j^{\alpha'}\,\partial r_j^{\gamma'}} \left(\frac{1}{r_{ij}}\right). \tag{3}$$

r_{ij} is the distance between sites i and j. Greek superscripts specify Cartesian coordinates for our purposes.

The standard means of treating such systems has been to decompose the crystal lattice into various sublattice structures, parametrize these through the molecular orientation on the sublattices, and compare the rotational free energy of the various cases considered. This procedure assumes that the crystallographic space group for which the lowest free energy is found is in fact stable with respect to configurations having no long-range order. That this need not be the case can be seen in the case of the hcp lattice, which is the stable form of solid hydrogen at $c < 55\%$. On seeking the lowest-energy state for classical quadrupoles, one reproduces the quantum mechanical result of Ref. 5 if one assumes the existence of some long-range order; that is, one finds that the system prefers the $Pca2_1$ structure to other simple structures (and the relative sublattice orientations turn out to be similar to those of the quantum mechanical calculation). However, if one picks out a single lattice site and examines the near-neighbor orientations, one finds that some neighbors are parallel to the central molecule and thus in a high-energy (frustrated) configuration. In fact, given the field set up by its near neighbors, the central molecule is not at an orientation corresponding to a potential minimum. Thus, although local ordering may well occur, the existance of *long-range order* in this phase seems unlikely. Repeating such arguments in the case of the fcc ($Pa3$) structure, which is stable at high ortho concentration, one finds that a given molecule does indeed sit at a potential minimum with respect to its neighbors and local excitations are thus unlikely to destabilize the long-range order.

The simple-cubic lattice, on which I base my present calculations, is similar to the hcp structure in the sense that local stability is not guaranteed when the system assumes the ordered structure corresponding to a minimum of the average interaction energy. This minimum corresponds to a two-sublattice configuration with the molecular symmetry direction of one sublattice pointing along a cube axis and the other sublattice orientation pointing in *any* direction perpendicular to that axis.

Details of the Monte Carlo procedure itself will be given elsewhere, and will include checks made on relaxation times and possible size effects. The method is the single-site rejection algorithm used for the three-dimensional Heisenberg model.[6] An array is specified by two orientational angles per site, and the energy at each site is computed using Eq. (1). The system is allowed to evolve by choosing sites at random, choosing new angles at that site at random, and accepting or rejecting the new angles in such a way that the distribution $e^{-\beta U}$ is obtained (with β the inverse temperature). The effects of dilution are modeled by choosing $(1-c)$ sites of the array at random and setting the π_i of Eq. (1) to zero at those sites for the duration of the run.

Running averages are kept of the (long-range) order-parameter components parallel to the crystal axes, of the local order parameter, of the energy, as calculated from Eq. (1), and of fluctuations in these quantities. As one expects in simulations dealing with metastable states, some of the quantities computed depend on the initial array configuration chosen. For this reason, I have used both random initial arrays and ordered arrays with the molecular symmetry axes arranged along the crystal axes in a low-energy configuration. The runs made were not particularly long (300 to 500 Monte Carlo steps per "spin") and the samples for which data are shown here consisted of 810 sites. Some longer runs and runs on larger samples were made, and monitoring of the convergence of the Monte Carlo procedure convinces me that the conclusions drawn below are in no way artifacts of size or finite-time effects.

The analog of the Edwards-Anderson order parameter most easily evaluated in simulations of the present sort is the autocorrelation function for components of the quadrupole tensor defined with respect to *local* axes. The quantity which I display as a function of temperature T in Fig. 1(a) is written explicitly as

$$\langle Q(T)\rangle = \lim_{t\to\infty}\left\langle \frac{1}{N}\sum_i \tfrac{1}{2}\left[3\cos^2\theta_i(t)-1\right]\right\rangle \tag{4}$$

(brackets mean average over Monte Carlo configurations). The time parameter t is measured in Monto Carlo steps per "spin," and in parctice the $t\to\infty$ limit means estimating the asymptotic behavior of the system. This is accomplished by setting the local axes (with respect to which the θ_i are measured) to correspond to the molecular axis at the beginning of the run, then to allow the system to age while the time dependences of Q and U are monitored; the local axes are reset to the new molecular axes when the system has reached apparent equilibrium, and the values used are the long-time limit of θ_i with respect to the equilibrium axes. More detailed discussion of this procedure will be given elsewhere.

The associated quadrupolar susceptibility is given in terms of fluctuations in Q:

$$(\Delta Q)^2/T = (\langle Q^2\rangle - \langle Q\rangle^2)/T. \tag{5}$$

Experimentally this represents a response to an electric field *gradient*, and it is not clear whether it is directly measurable. Theoretically it is of

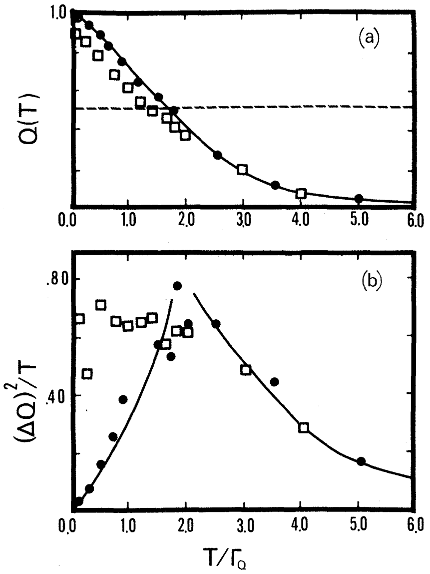

FIG. 1. (a) Order parameter $Q(T)$ as defined in Eq. (4) plotted as a function of temperature normalized to the quadrupolar coupling constant. The dotted line marks the value $Q = \frac{1}{2}$. Squares represent runs whose initial state was an ordered low-energy configuration and solid circles represent initially random arrays. (b) Order-parameter susceptibility, as defined in Eq. (5).

considerable interest, however, because one of the most consistent characteristics of the usual spin-glass transition is the broad anomaly in the magnetic susceptibility with a cusp at the transition temperature. This effect is observed in virtually every experimental spin-glass and arises from both Ising and continuous-spin models of the transition.

My temperature-dependent results for the *undiluted* simple-cubic lattice are shown in Fig. 1. The open squares represent data from samples whose initial configuration was ordered; the closed circles represent data from initially random samples. I believe that the random initial configuration produces statistically more reliable results, but display both sets of data for completeness's sake. In both cases the local order parameter tends toward its maximum value of 1 at zero temperature, and the fluctuations in Q tend toward 0 at least as rapidly as T. In the case of the initially ordered arrays of low T, examination of the Monte Carlo procedure indicates that the sample may still be disordering slowly at the times over which Q was computed; Q still contains significant average components parallel to the crystal axes. In the initally disordered system, these average components are zero within the statistical error. It is noteworthy that discrepancy between the two sets of data occurs only for temperatures below about $2\Gamma_Q$ and disappears at higher temperatures. This would seem to indicate that the onset of metastable ordering occurs at some reasonably well-defined temperature. If one accepts the assumption that the data showing the smaller statistical variation in Q provide the better representation of the physical system, then the quadrupolar susceptibility obtained [solid lines of Fig. 1(b)] bears a striking resemblance to the classic spin-glass susceptibility. In *both* sets of data, fluctuations in Q reach a maximum value at $T \simeq 1.75\Gamma Q$ (where Q takes on the value $\frac{1}{2}$); its tendency toward zero at $T = 0$ is indicative of some sort of rotational locking.

The average energy per spin and its variance has also been computed as a function of temperature. An anomaly is observed, for the case of *random* initial configurations only, at a temperature very close to the ordering temperature deduced from the data of Fig. 1. Both random and ordered initial configurations lead to a divergence of the specific heat at low temperatures, but these results contain considerable statistical noise. The energy curves at low temperatures are rather clean and indicate strong local order in the pure lattice.

We turn now to the effect of dilution on the low-temperature behavior of the system. We are dealing, after all, with site dilution of a lattice structure in which characterization of the purely geometrical aspects of the problem have been treated in considerable detail.[7] The canonical functions for dealing with any percolation problem seem to be the percolation probability $P(c)$ and the generalized conductivity of the lattice $\sigma(c)$, both of which are shown in Fig. 2 for the infinite simple-cubic lattice. The data points represent the $T = 0$ limit of the order parameter Q as a function of quadrupole concentration c. It is clear that as nonquadrupolar impurities are added to the system, the zero-temperature order parameter is suppressed, and rather remarkably, this suppression seems to be identical to the suppression of the conductivity of the corresponding dilute network. The deviation from the $\sigma(c)$ curve at low c is almost certainly a size effect; the finite-lattice conductivity curve would show similar behavior. In order to understand the correspondence between network conductivity and $Q(T = 0)$, one needs to carry out an examination of the dy-

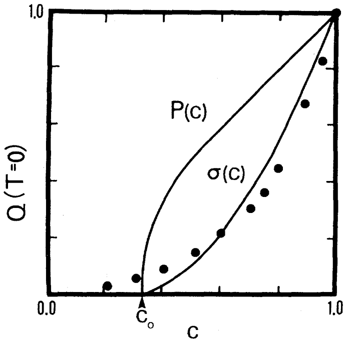

FIG. 2. Zero-temperature order parameter as a function of quadrupole concentration. The solid curves show percolation probability $P(c)$ and conductivity $\sigma(c)$ for the infinite simple-cubic lattice, as given in Ref. 7. c_0 is the percolation threshold.

namic response of the quadrupolar system and to understand the form of the excitation spectrum present in this sort of glasslike ordering. This is obviously a nontrivial undertaking, and to my knowledge, remains to be done.

My results lead me to believe that a quadrupolar interaction can cause local metastable ordering in certain crystal structures. This ordering is characterized by a rotational freezing, with some proportion of the molecules locked into a locally defined orientation. It seems to be accompanied as well by the sort of susceptibility cusp typical of the usual spin-glass susceptibility. My results with respect to energy and specific heat are somewhat more ambiguous and suggest no strong specific-heat anomaly at the transition. As the quadrupole concentration is lowered, the ordering is destroyed in a manner reminiscent of the reduction of the analogous network conductivity, at least for the particular lattice studied. Work currently in progress includes study of the behavior of the temperature-dependent properties of such systems as they are diluted, and of their dynamic response functions.

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[1] N. S. Sullivan, M. Devoret, B. P. Cowan, and C. Urbina, Phys. Rev. B 17, 5016 (1978).

[2] J. A. Mydosh, in *Amorphous Magnetism II*, edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977).

[3] S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975).

[4] O. Nagai and T. Nakamura, Prog. Theor. Phys. (Kyoto) 24, 432 (1960), and 30, 412 (1963). See H. M. James and J. C. Raich [Phys. Rev. Lett. 16, 173 (1966), and Phys. Rev. 162, 649 (1967)] for the corresponding quantum mechanical treatment.

[5] H. M. James, Phys. Rev. 167, 862 (1968).

[6] M. A. Klenin, Phys. Rev. B (to be published).

[7] S. Kirkpatrick, Rev. Mod. Phys. 45, 574 (1973).

Phase Transitions in Potassium-Intercalated Graphite: KC_{24}

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Two structural phase transition in KC_{24} have been observed by x-ray diffraction: an order-disorder transition at $T_U = 126.0 \pm 0.5$ K and a structural transition T_L at about 93 K. Details of these transitions are presented, as well as the stacking sequences of the intermediate and low-temperature phases.

The existence of graphite intercalation compounds in which metal-atom layers are inserted between graphite layers has been known for almost fifty years. These systems have been of interest recently because of the high basal-plane conductivity and the highly two-dimensional na-