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Observation of thermal remanence in a quadrupolar solid

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We have measured the specific heat of solid hydrogen as a function of temperature and orthohydrogen concentration in the region of the fcc-hcp phase boundary, and have found a dependence of this quantity on thermal history. Samples isothermally converted from the fcc to the hcp phase showed a slow continuous change to molecular disorder, which is somewhat analogous to remanence in spin-glass field-cooling experiments. New Monte Carlo simulations indicate remanence can be caused by the hcp geometry and quadrupolar-site dilution, independently of the fcc-hcp structural change.

The problem of orientational order in solid hydrogen has received considerable attention in the past few years because of an experimentally observed glasslike behavior.[1] The nature of the rotational "freezing" seems to depend critically upon the concentration of interacting quadrupolar molecules (orthohydrogen species). In the present research we consider the effect of an ordering field or mechanism upon such a rotational glass, analogous to measuring the effect of an external magnetic field on a spin glass. As shown below, however, the details of the H_2 solid allow an investigation of concentration dependences unavailable in the spin-glass systems. The glassy transition occurs in the low quadrupolar concentration regime, where the crystalline structure is hcp. At higher quadrupole concentrations and low temperature the system is in an fcc ($Pa3$) phase.[2] Structural and orientational transitions into the $Pa3$ phase occur at a single well-defined temperature as the sample is cooled at fixed concentration, and the combined transition has the earmarks of the onset of long-range order with symmetry breaking. The description of the low orthohydrogen concentration, low-temperature regime is considerably less straightforward because the hcp crystal structure itself leads to frustration effects, and in addition, site dilution of quadrupoles by spherical parahydrogen molecules leads to local symmetry breaking. Remanence in the solid hydrogens has been seen in two NMR experiments,[3,4] but not in other NMR experiments[5] or in measurements of bulk properties.[6,7] Although the body of experimental data indicates a gradual loss of the orientational degress of freedom, results have been obtained on single-crystal samples which indicate no deviation from full crystal symmetry on a macroscopic scale.[5]

We present the results of experiments which measure the specific heat of solid H_2 samples near the hcp-fcc phase boundary. Because the orthohydrogen species converts slowly to parahydrogen[2] it is possible to follow both isothermal and quasi-fixed-concentration paths on the system phase diagram. By cooling the H_2 sample into the fcc molecularly ordered phase and then isothermally converting the sample into the disordered hcp phase, we have been able to investigate effects similar to the field-cooling remanence in spin glasses.[8] We discuss these experimental results in light of our recent computer experiments,[9,10] which suggest that the ordering is primarily two-dimensional in nature and that the molecular arrangements which occur on real experimental time scales deviate significantly from full long-range order.[11] We also present new concentration-dependent numerical results.

We have measured the specific heat of solid H_2 samples by a thermal relaxation technique described elsewhere.[7] The samples were grown from $X=0.75$ gas at the triple point and cooled to $T=0.4$ K within 4 h. The orthohydrogen-parahydrogen conversion rate was checked by measurement of the hcp-fcc transition upon cooling and also thermal analysis of the sample gas after the experiment.

Two different laboratory experiments were done. The first was an isothermal measurement of C_v as a function of time, i.e., orthohydrogen concentration, after the sam-

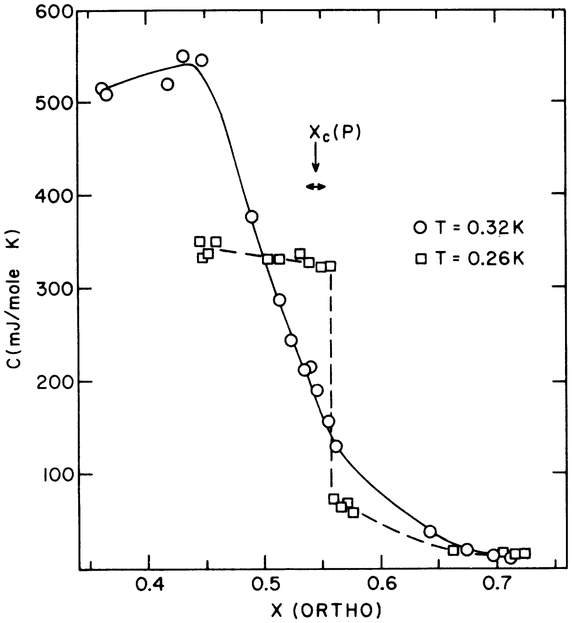

FIG. 1. Specific heat vs orthohydrogen concentration X for two samples. The 0.32-K sample was held at that temperature during the entire run. The 0.26-K sample was heated to 1 K and quickly recooled twice: at $X=0.557$ and $X=0.446$. $X_c(P)$ denotes the location and width of the pressure transition observed in Ref. 12.

ple was initially cooled into the molecularly ordered *Pa*3 phase. The results of this experiment are shown in Fig. 1. At $T = 0.3$ K the primary contribution to the specific heat is the orthohydrogen molecular rotation. The C_v data show a gradual change in the rotational specific heat with decreasing orthohydrogen concentration. This may be interpreted as a gradual disordering of the molecular moments from the initial ordered configuration in the fcc phase. This contrasts with the sharp transition seen in the $P(X)$ data of Haase *et al.*,[12] but is not contradictory. Ramm *et al.*[13] have shown (and we have corroborated that[12]) for $X < 0.6$ the pressure change on cooling from the hcp to the fcc phase is positive. However, the C_v anomaly seen at higher X is very small or nonexistent at $X \leq 0.6$. In agreement with Harris *et al.*,[5] we take this to mean that the $P(X)$ data indicate the change in crystalline phase but are not so sensitive to the status of rotational order as is C_v. The x-ray diffraction experiments of Gates *et al.*[14] indicate that the conversion to the hcp phase is not complete, leaving a small fraction of the fcc structure. This remaining fcc fraction is removed by heating the sample but is concentration independent if the sample is kept at constant temperature.

In the second experiment the samples were cooled to the measurement temperature and kept at constant temperature until $X = 0.55$. The sample was then warmed to $T = 1.0$ K and recooled to the measuring temperature within 20 min. The measurement of $C_v(X)$ proceeded as shown in Fig. 1. The effect of the warming and recooling of the sample was to increase C_v by a factor of roughly 3 at $X = 0.53$. The amount of disorder shows a behavior similar to that of the previous sample for $X < 0.49$.

We interpret these data to mean that the orthohydrogen rotational moments retain the long-range order over some period of time even after conversion into the hcp crystal phase, provided that the sample is kept at a low temperature. Heating the sample induces thermal disorder and the loss of the memory of the rotational order. This relaxation may be seen as analogous to relaxation occurring in field-cooling experiments in spin-glasses.[8] The fcc structure clamps the rotational moments in a long-range ordered *Pa*3 phase. Removal of the fcc structure, like removal of the ordering magnetic field on a spin-glass, allows the moments to slowly reorient to a disordered configuration. Since the fcc to hcp phase transition involves a sliding of crystal planes perpendicular to the *c* axis, it is reasonable to conjecture that in-plane order is maintained in the crystalline transition. A further illustration of this behavior is shown in Fig. 2. A sample of $X = 0.55$, which had been prepared in the ordered fcc phase, was heated to 0.7 K and then recooled over a period of 4 h, while C_v was measured as a function of temperature. The C_v data do not indicate a sharp phase transition upon heating, yet there is a large hysteresis upon recooling. The cooling curve is in reasonable agreement with C_v calculated from the $(\partial P/\partial T)_V$ data[6] for a sample which was never cooled into the ordered phase.

The occurrence of the observed remanence may be attributed to either intrinsic remanence in the molecular spin system or/and the presence of remanent fcc crystallites in the hcp phase. Our computer simulation of ordering through an electric quadrupole-quadrupole (EQQ) interaction was aimed at understanding both dilution and frustration phenomena occurring on the rigid hcc lattice. The complications induced by the structural phase change have not been considered. Detailed results for the case $X = 1$, as well as a description of the algorithm, are given elsewhere.[10]

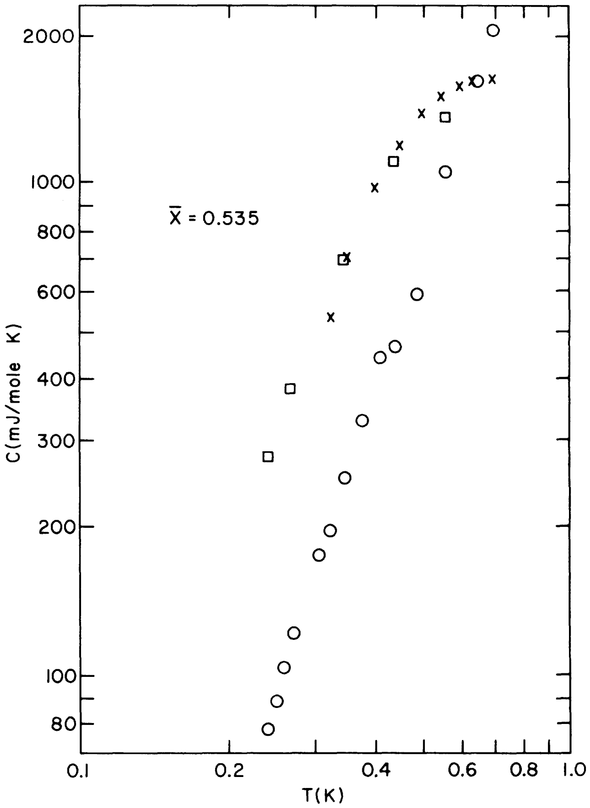

FIG. 2. Specific heat vs temperature of a H_2 sample of $X = 0.535$ upon warming and cooling. The sample was prepared by cooling to $T = 0.24$ K at $X = 0.70$ and held at that temperature until $X = 0.55$. ○, warming. □, cooling. The × indicate C_v points calculated from $(\partial P/\partial T)_V$ data on a sample ($X = 0.55$) which had not been cooled into the rotationally ordered phase.

In carrying out Monte Carlo work, order parameters defined by means of a site-by-site comparison between a generated array and some reference state are particularly convenient. Such order parameters are used here, with the reference states being closely related to the states suggested by mean-field theory.[11] In the present case it is particularly useful to isolate the configuration which corresponds to a classical Landau transition—i.e., the configuration associated with only a single order parameter. It turns out that this is *not* the most stable state of the system energetically, but that it is accessible locally from the low-energy states, and thus it is associated with the order-parameter fluctuations which drive the transition. The quadrupolar arrays corresponding to this order parameter are shown in Fig. 3.

The long-range-ordered states which are energetically preferred consist of stacked planes which contain molecules arranged in a "herringbone" pattern. The herringbone axes of the planes are aligned, and the configurations differ only in the relative position of identical molecular

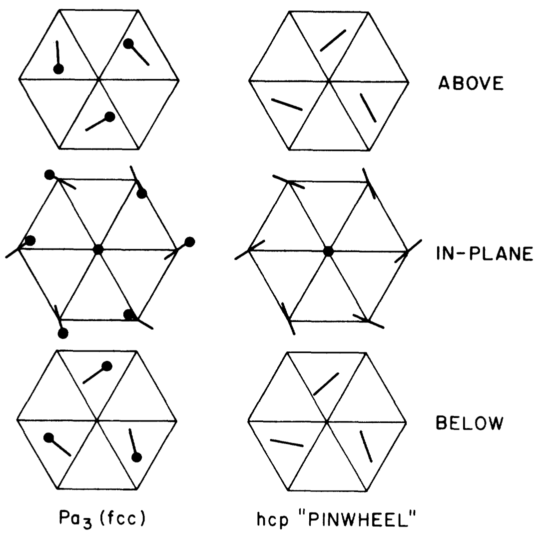

FIG. 3. Stacking of triangular planes in the fcc and hcp lattices. The molecular orientations on the *Pa*3 structure and the pinwheel structure on the hcp lattice. Circles indicate the ends of the molecules which point upward from the page. The two structures may be obtained from each other locally by a simultaneous rotation of molecular positions and orientation in a single plane, and minor readjustment of the orientation of the remaining molecules.

orientation as one pasess between the inequivalent planes of the hcp lattice. The two possible stacking arrangements are very nearly degenerate. This leads to a strong dependence of order parameter (but not energy) on annealing schedule [see Fig. 4(a)]. In addition, because of the special role of the "pinwheel" configurations of Fig. 3 in mediating the transition, the behavior of the system in the transition region becomes extremely complex, and shows many of the characteristics of other glasslike systems. We have found that a planar quadrupolar arrangement which retains components of all of the possible symmetric structures is nearly degenerate with the lowest-lying fully ordered state at all temperatures and is very slightly favored at $T=0$. We also found that our observed specific-heat curves depend on time scale, and we are led to the conclusion that the intermediate time-scale results, not the very long-time limit, are consistent with the specific-heat measurements.[6,7,12]

A separate computer experiment was carried out to examine possible metastability of the system under quenched conditions. A ground-state search[10,15] based on single-site quadrupole alignments in the local field leads us to the conclusion that all of the permissible four- and eight-sublattice structures are locally stable. This implies that if a sample is prepared in any of these states at low temperature, it will move to another configuration, only very slowly. Of particular interest here is that the eight-sublattice pinwheel configuration mentioned above possesses a common rotational symmetry axis with the *Pa*3 structure. It may be obtained locally through the same distortion which produces the crystalline phase change from fcc to hcp if that distortion is followed by a local orientational shift. Although the pure pinwheel configuration is not the most favorable state of the system, a detailed analysis of Monte Carlo (MC) data taken at full concentration indicates that it occurs locally with a high statistical probability, particularly under quenched conditions. Once formed in a large domain, the configuration is metastable. Thus, even without the inclusion of dilution effects, we expect to find evidence of remanence on experimental time scales after a shift from fcc to hcp.

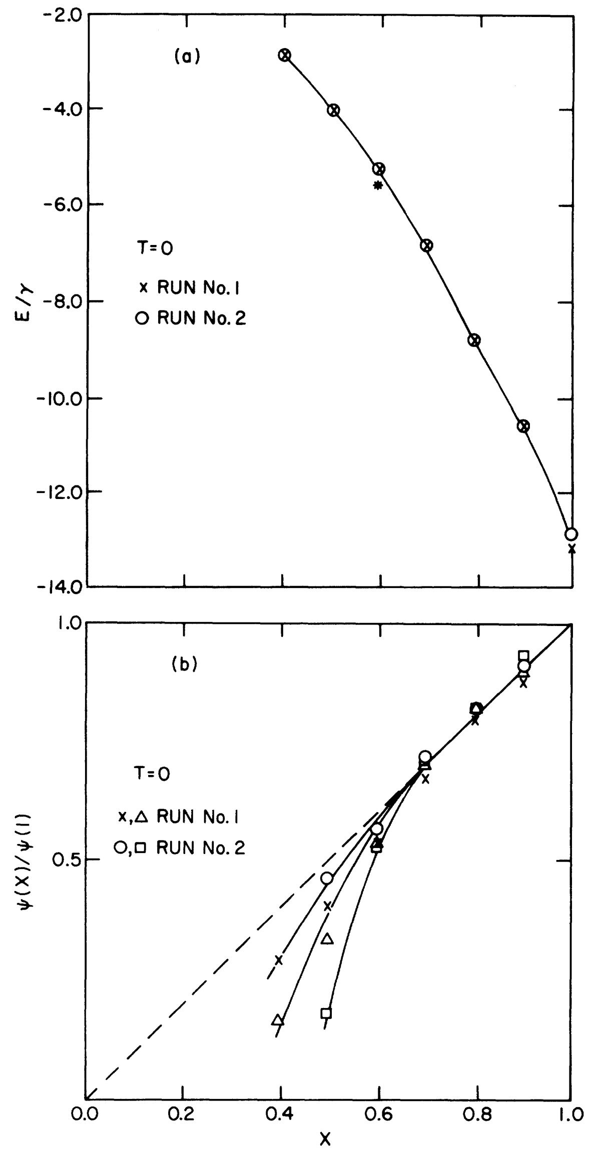

FIG. 4. Monte Carlo data showing energy and normalized order parameters per quadrupole as a function of quadrupole concentration. (a) Energy obtained from down conversion at $T=0$. ○, down conversion from the long-range ordered "ground state"; ×, from a configuration of randomly stacked planes. The single asterisk shows the energy obtained on cooling a sample slowly at $X=0.6$. (b) Symmetry-specifying order parameters for the same runs. × and ○ represent the extent of two-dimensional ordering. △ and □ are necessary to complete the description of the $X=1.0$ configurations and are related to interplanar correlations. In each case, the concentration-dependent order parameter has been normalized to its value in the initial array of the down-conversion run.

To illustrate the role of dilution in this problem, we display in Fig. 4(b) the behavior of order parameters specifying system symmetry as the quadrupolar concentration of a hcp MC solid is decreased at $T=0$. The order parameters ψ displayed are designed to give an indication of the correlation among equivalent planes ($\times$ and $\circ$). The residual order parameters describe either correlation of nonequivalent planes ($\triangle$) or the presence of pinwheels ($\square$). In the two separate runs displayed, quadrupolar down conversion was simulated from two microscopically distinguishable $X=1$ starting states. Run no. 1 started from the long-range-ordered ground states of James.[11] Run no. 2 started from quenched conditions and consisted of randomly stacked planes, each of which contained a fully ordered molecular configuration. The energies of the two structures were virtually indistinguishable at low temperatures.[16] The runs remained microscopically distinguishable as X decreased, although they were degenerate in energy over the entire concentration range.[17] The plots of reduced-order parameter appear to follow a universal curve for $X \gtrsim 0.6$, which coincides with the standard high-concentration percolation probability curve.[18] The fact that the order parameters no longer scale for smaller X indicates a loss of system symmetry. It is perhaps fortuitous that this occurs in the vicinity of the two-dimensional percolation limit, but we have reported similar curves at finite temperature[9]—i.e., generated by a different algorithm and using a somewhat different order-parameter definition—and this fact suggests that the ordering is planar in nature.[19]

Neither of the zero-temperature down-conversion curves agrees—in energy or in order-parameter values—with simulation data obtained by slow cooling at $X=0.6$ [see Fig. 4(a)]. As one might expect, careful annealing at the transition and below lead to a lower energy. The local and global symmetry properties of the configuration so generated are being investigated.

Our experimental results indicate clearly that the microscopic state of a given sample depends upon its past history. We cannot state conclusively whether the primary remanence effects occur in the crystalline structure or in the orientational ordering. On the basis of our numerical work, however, we conclude that, even given a completely sharp and uniform transition from fcc to hcp lattice, the "preparation" of the orientational configuration in the cubic phase may lead to the metastability of a nearly long-range ordered state with energy slightly higher than that of the ground state. It is fair to assume that structural order and orientational order are strongly coupled, and means of probing the transitions separately are being studied.

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[16] All energies shown are normalized to the EQQ constant used in Refs. 9 and 10.

[17] The symmetries of the $X=1.0$ configurations are different for the two runs shown. The definition of the planar order parameter is the same in each case, but the order parameters describing the stacking of planes differ between the two cases. We have plotted only those parameters which differ from zero to a statistically significant degree.

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[19] At high concentration the normalized order parameter lies on the line $f(X)=X$—i.e., the order parameter per quadrupole is proportional to the number of sites remaining in the systems infinite cluster. At lower concentrations, the various order parameters show different behavior, indicating that parameterization in terms of a single percolation threshold is inappropriate.