

Evidence for quadrupolar glass phases in solid hydrogen at reduced ortho concentrations

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Low-temperature NMR studies of solid hydrogen at reduced ortho concentrations $X < 55\%$ are interpreted in terms of possible quadrupolar glass phases in which the ortho molecules are frozen into random configurations. The quadrupolar glass is an extension of the concept of the dipolar glass of spins introduced by Edwards and Anderson.

I. INTRODUCTION

Certain dilute magnetic alloys^{1,2} such as CuMn, AuFe, RhFe, ... can, over a certain concentration range of the magnetic component (typically less than a few percent), exhibit "magnetic" phases characterized by frozen-in local magnetic moments which point in random directions. There is no overall magnetic moment (ferromagnetism) nor is there any simple sublattice antiferromagnetism, but for these so-called "spin-glasses" there does exist a local order parameter $g = \langle \vec{S}_i(t_1) \cdot \vec{S}_i(t_2) \rangle$ which is nonvanishing for $t_2 \gg t_1$ and which can be determined self-consistently using the models described in Refs. 3-5. However, at elevated concentrations of the magnetic

component, these alloys can form ferromagnetic phases which become paramagnetic at high temperatures. The phase diagram can therefore be broadly divided into three regions: paramagnetic, ferromagnetic, and spin-glass.

There is a striking resemblance between the phase diagram for the magnetic alloys and those observed (see Fig. 1) for orientationally ordered ortho-hydrogen-para-hydrogen alloys⁶⁻⁸ where for large ortho concentrations ($X > 55\%$) the cooperative ordering is believed to result from the intermolecular electrostatic quadrupole-quadrupole interactions.⁹⁻¹¹

II. LOW-TEMPERATURE NMR LINE SHAPES

At high ortho concentrations the ordered state of solid hydrogen is characterized by a long-range order parameter $S(T) = \langle 3J_z^2 - 2 \rangle_T$, where J is the orbital angular momentum of an ortho molecule and \hat{Z} is a lattice axis. In the long-range orientationally ordered structure¹⁰ the \hat{Z} axes are the body diagonals of the fcc lattice. For a single crystal the partial lifting of the rotational degeneracy of the ortho molecules results in a fine structure for the NMR spectra^{7,12} consisting of a doublet separated in frequency by $\Delta\nu = \frac{3}{2}dP_2(\cos\theta_z) \times S(T)$, where θ_z is the angle between the external magnetic field and the crystalline axis \hat{Z} and $d = 57.7$ kHz. On averaging over all possible crystalline orientations for a powder specimen, one obtains the familiar Pake doublet for the NMR absorption spectrum shown in Fig. 2. For ortho-concentrations $X > 55\%$ one observes on warming an abrupt transition to an approximately Gaussian line shape at the critical temperatures $T_c(X)$ given by the solid line in Fig. 1. (The reader is referred to Ref. 12 for details of the line shapes at high concentrations.)

The transition temperatures decrease rapidly as the ortho concentrations approach 55% and this is in qualitative agreement with theoretical treatments of the orientational ordering which account

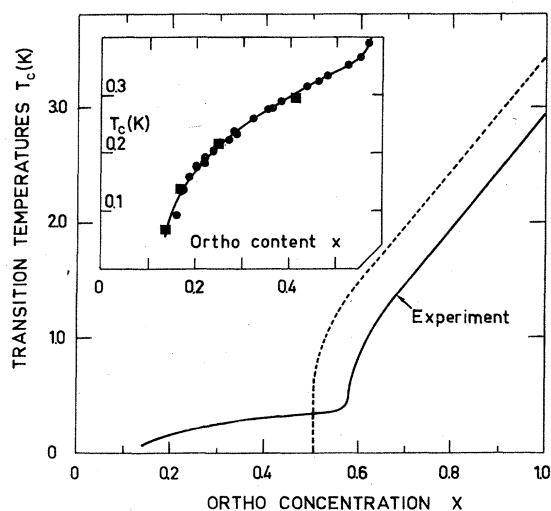


FIG. 1. Phase diagram of solid ortho-para-hydrogen mixtures. The solid lines indicate the transition hydrogen-temperatures $T_c(X)$ deduced from the NMR studies as described in the text. The broken line represents the critical temperatures calculated in Reference (12) for $X > 0.5$. The inset shows the glass phase transitions on an expanded scale. The solid circles are taken from this work and Ref. 8, and the solid squares are from Ref. 16.

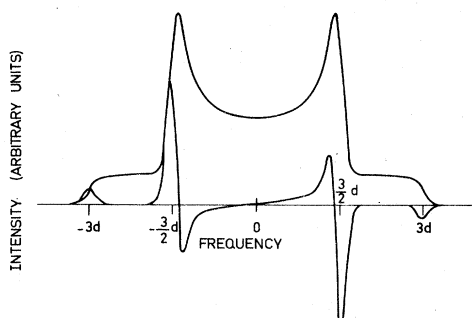


FIG. 2. Example of a theoretical Pake doublet NMR absorption spectrum and its derivative for the orientationally ordered phase. The intermolecular nuclear dipolar interactions have been accounted for by a Gaussian of width 7 kHz. $d = 57.7$ kHz.

for correlation effects.^{11,13} The calculated transition temperatures are indicated by the broken line in Fig. 1.

For ortho-hydrogen (and para-deuterium) concentrations less than approximately 55%, NMR studies¹² and thermodynamic measurements^{14,15} showed no evidence of orientational ordering for temperatures $T \geq 0.4$ K. However, NMR studies at very low temperatures^{6-8,16} ($T < 0.1$ K) show broad spectra whose features depart from the Pake doublet shape as the concentration is reduced. We describe here further low-temperature NMR investigations and interpret the results in terms of the "freezing" of the orientational degrees of freedom of the ortho molecules in what are assumed to be random solid mixtures of ortho- and para-hydrogen molecules.

We have studied samples condensed on a bundle of fine copper wires (0.1-mm diameter) anchored to the mixing chamber of a dilution refrigerator. The sample chamber, having a volume of 10^{-2} cm³, was constructed out of Kel-F and was located at the position of maximum homogeneity of a superconducting magnet. The hydrogen, initially 75% ortho, was allowed to condense slowly as the temperature was held close to 20 K and the temperature was then lowered over an approximately 30 min period to the freezing temperature after which the temperature was lowered as rapidly as possible. Studies at different ortho concentrations were carried out by aging the samples at 4.2 K between runs. The concentrations were then deduced from the ages assuming an ortho decay rate of 1.9% per hour and checked against the areas of the NMR absorption spectra at 4.2 K.

On one occasion an aged sample having a mean ortho concentration of 32% was melted and then refrozen. This was to ascertain whether the line shapes of samples of low X and their variation

with temperature depended on the method of their preparation which could affect the distribution of the ortho molecules in the sample. We observed no significant departure in the critical temperatures or the low-temperature line shapes other than that attributable to the difference in mean ortho concentration before and after melting and subsequent cooling.

The NMR spectra were observed at 100 MHz using a standard Q -meter circuit operating at low levels. The oscillator frequency was swept through the resonance line with the superconducting magnet held in the persistent mode. The magnetic field was modulated at 200 Hz with an amplitude of approximately 0.5 G. The derivative line shapes were then obtained by coherent phase detection. Absorption line shapes were also obtained directly by accumulating the output of the Q meter in a multichannel analyzer as the oscillator frequency was swept back and forth through the line while the field was held constant. The background signal due to the frequency dependence of the tuned circuit was removed by subtracting the output for an equal number of sweeps for a field well off resonance, the additional magnetic field being supplied by a small superconducting solenoid operated independently of the main field magnet.

The temperatures were monitored by a Speer resistor (220 Ω , type 1002) housed in the body of the mixing chamber. This was calibrated by comparing the areas of the NMR absorption spectra at low temperatures with the area observed at 4.2 K for the same sample. Corrections for the changes in the ortho concentrations during the time it took to lower the temperature of the samples were made by assuming an ortho decay rate of 1.9% per hour.

Typical low-temperature absorption spectra are shown in Fig. 3. These were recorded for temperatures $T \ll T_c(X)$ for which there was no significant residual temperature dependence. These lines are broad, varying from an almost rectangular shape at $X = 40\%$ to a bell shape at $X = 23\%$ and they are flanked by shoulders extending out to approximately twice the frequency separation of the extrema of the derivative line shapes in all cases studied ($X > 18\%$). We interpret these features in terms of a quadrupolar glass phase in which the orientational degrees of freedom of the ortho molecules are frozen at random. This is an extension of the concept of a dipolar glass of spins (as introduced by Edwards and Anderson³) to a higher tensorial order. The reason that we need to introduce tensorial orders higher than the vectorial order, which applies to a dipolar glass of spins, is discussed in Sec. III.

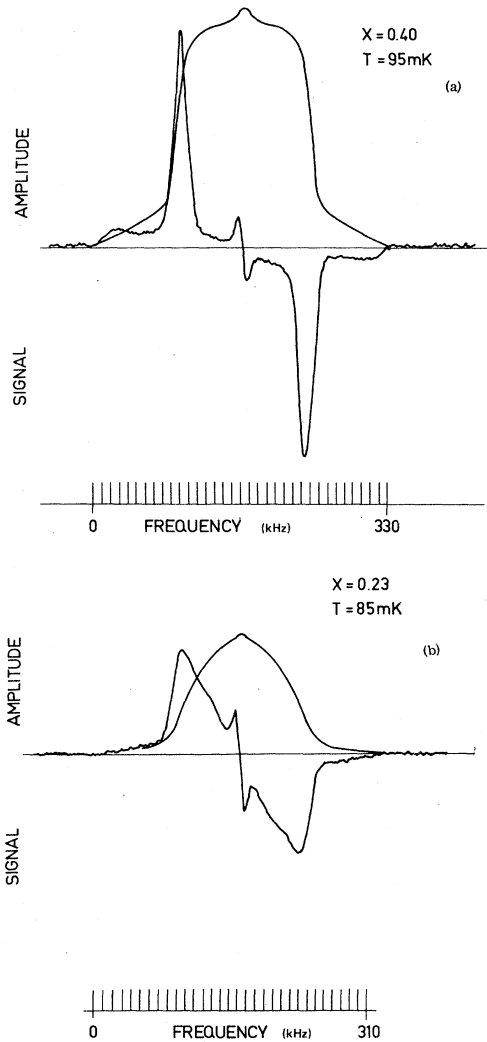


FIG. 3. Observed low-temperature [$T \ll T_c(X)$] derivative NMR absorption spectra and their integrated line profiles at 100 MHz for hydrogen condensed on fine copper wires. (a) $X=0.40$, $T=95$ mK and (b) $X=0.23$, $T=85$ mK. The spectrometer gain for (b) was higher by a factor of ~ 2 than that used for (a). The weak 8-kHz central component is believed to be due to isolated ortho molecules.

III. QUADROPOLAR GLASS PHASE

For a dipolar glass of spins $S = \frac{1}{2}$, we are only concerned with the ordering of the dipole moments whose directions are the only degrees of freedom. The dipole-dipole interactions lead to a vectorial breaking of the local spherical symmetry with the establishment of permanent *local* dipole moments. Although these moments can have a random distribution (when evaluated with respect to a fixed set of reference axes $\hat{X}, \hat{Y}, \hat{Z}$) so that $\sum_i \langle S_{iz} \rangle = 0$, the dipolar interactions can result in

a glasslike configuration in which the moments are locally frozen, i.e., the time-dependent correlation function $\langle \vec{S}_i(t_1) \cdot \vec{S}_i(t_2) \rangle$ is nonvanishing for $t_2 \gg t_1$.

In the general case of angular momentum $S > \frac{1}{2}$, one could also obtain dipolar glasses for which the dipole-dipole interactions lead to a random freezing of the dipole moments $\langle S_{iz} \rangle$. However, as a result of the increased number of degrees of freedom, one can also envisage glass phases for which interactions of a higher multipolar order (e.g., quadrupole-quadrupole, octupole-octupole, ...) lead to a freezing of the higher-order multipolar moments—e.g., the quadrupole moments $\langle 3S_z^2 - 2 \rangle$, $\langle S_x^2 - S_y^2 \rangle$... for a spin $S=1$. This is why we need to extend the concept of a dipolar glass of spins to higher tensorial orders for $S > \frac{1}{2}$.

For ortho-hydrogen molecules, we are concerned with the rotational degrees of freedom associated with an orbital angular momentum $J=1$. We only consider $J=1$ for two reasons. Firstly, the anisotropic intermolecular interactions are weak compared to the separation of the rotational energy levels and J can be regarded as a good quantum number. Secondly, for the experimental temperature range $k_B T \ll E(J=3) - E(J=1) = 845$ K and only the lowest rotational state $J=1$ of ortho-hydrogen is populated. The relevant moments which are the expectation values of the operator equivalents of the spherical harmonics in the manifold $J=1$ are given in Table I. (A general discussion of spin-1 systems has been given by Fano¹⁷).

For the interacting ortho molecules, we must consider the many-particle crystal wave function in order to account for the collective effects which tend to correlate the orientational degrees of freedom of the ortho molecules. The individual molecular states cannot be described in terms of pure states but in terms of a single-particle den-

TABLE I. Definition of the operator equivalents \mathcal{J}^n and \mathcal{O}^m of the spherical harmonics Y_1^n and Y_2^m , respectively.

Operator	Moment
Dipole	
$\mathcal{J}^0 = (1/\sqrt{2})J_z$	$M^0 = \langle \mathcal{J}^{0\dagger} \rangle$
$\mathcal{J}^{\pm 1} = \mp \frac{1}{2}(J_{\pm} \pm iJ_y)$	$M^{\pm 1} = \langle \mathcal{J}^{\pm 1\dagger} \rangle$
Quadrupole	
$\mathcal{O}^0 = 1/\sqrt{6}(3J_z^2 - 2)$	$Q^0 = \langle \mathcal{O}^{0\dagger} \rangle$
$\mathcal{O}^{\pm 1} = \mp \frac{1}{2}(J_z J_{\pm} + J_{\pm} J_z)$	$Q^{\pm 1} = \langle \mathcal{O}^{\pm 1\dagger} \rangle$
$\mathcal{O}^{\pm 2} = \frac{1}{2}(J_{\pm}^2)$	$Q^{\pm 2} = \langle \mathcal{O}^{\pm 2\dagger} \rangle$

sity matrix ρ_i determined by the moments Q_m and M_n :

$$\rho_i = \frac{1}{2} \mathbf{1}_3 + \sum_{n=0, \pm 1} M_n^i \mathcal{J}_i^n + \sum_{m=0, \pm 1, \pm 2} Q_m^i \mathcal{O}_i^m,$$

$\mathbf{1}_3$ is the unit operator.

A priori, we should consider eight degrees of freedom, but in the absence of dipolar interactions (diatomic molecules have no permanent electric dipole moment) the dipole moments are expected to vanish. Of the five remaining degrees of freedom, three can be used to define *local* axes ($\hat{x}_i, \hat{y}_i, \hat{z}_i$) and only two intrinsic quadrupolar degrees of freedom remain.

These degrees of freedom can be represented by two *local* order parameters

$$\sigma_i = \sqrt{6} Q_i^0 = \langle 3J_{zi}^2 - 2 \rangle$$

and

$$\eta_i = Q_i^2 + Q_i^{-2*} = \langle J_{xi}^2 - J_{yi}^2 \rangle$$

(This choice is made in order to be consistent with the parameters introduced elsewhere in the literature.¹⁰) As a result of the condition $\text{Tr} \rho^2 \ll 1$, these parameters must satisfy the inequality $\sigma_i^2 + 3\eta_i^2 \leq 4$.

At concentrations greater than 55%, the collective interactions lead to a configuration in which the molecules are oriented parallel to the body diagonals of the fcc lattice.¹⁰ The ordered structure consists of four interpenetrating simple cubic lattices such that in each sublattice the molecular orbitals are aligned parallel to one of the body diagonals. In these configurations of axial symmetry, $\eta_i(T=0)=0$ and (apart from small corrections) $\sigma_i(T=0)=-2$ at each site i . One can then introduce temperature dependent long-range order parameters

$$S_\alpha(T) = \langle 3J_{z\alpha}^2 - 2 \rangle_T,$$

for each sublattice associated with the body diagonals \hat{Z}_α . The temperature dependence of the NMR line shapes observed at high ortho concentrations has been analyzed¹² in terms of the expected temperature variation of the order parameters $S_\alpha(T)$.

At concentrations lower than 55%, this long-range orientational order is apparently no longer maintained. At low temperatures the local symmetry can now be broken so that the quadrupole moments σ_i and η_i are frozen at random from one lattice site to another. This is what we mean by a quadrupolar glass.

In view of the strong correlations of the orientations of the ortho molecules, one can make a simplifying assumption of axial symmetry for

which the η_i vanish. In this case, there are local axes of axial symmetry $\hat{\xi}_i$ whose directions vary from one site to another and for which the components $\sigma_i(T) = \langle 3J_{\xi i}^2 - 2 \rangle$ also vary at random. This is illustrated schematically in Fig. 4(c). Glasses of different tensorial orders are shown for comparison in Figs. 4(a) and 4(b).

As far as the NMR spectra are concerned, each occupied site i now contributes a doublet of frequency separation

$$\Delta\nu_i = \frac{3}{2} d \sigma_i(T) P_2(\cos \theta_i),$$

where θ_i is the angle between the applied magnetic field and the local axes $\hat{\xi}_i$. If the components σ_i had the same values at each site i [so that the randomness lay only in the orientation of the local axes $\hat{\xi}_i$ as illustrated in Fig. 4(d)], one would obtain a Pake-doublet line shape as observed for high ortho concentrations. The NMR line shapes observed at the temperatures $T \lesssim 0.1$ K show that this is not the case and we are led to consider the situation where the σ_i have widely different values within the limits $-2 < \sigma_i < 1$. The NMR spectra will now be determined by the distribution $P(\sigma)$ of the values of σ .

In the absence of a detailed microscopic theory of the quadrupolar glass which would lead to a prediction of the distribution $P(\sigma)$, we have assumed a "white" distribution: $P(\sigma) = \text{const}$ for $\sigma_{\min} < \sigma < \sigma_{\max}$, where $\sigma_{\min} = -2[1 + \alpha(X)]^{-1}$ and $\sigma_{\max} = 1[1 + \alpha(X)]^{-1}$ are adjustable parameters. For a powder specimen, one then obtains a broad spectrum in qualitative agreement with the observations at the lowest attainable temperatures.¹⁸ A calculated line shape assuming such a distribution is shown in Fig. 5 and this can be compared with the observed spectra at low ortho concentrations [Fig. 3(b)]. Almost rectangular line shapes including shoulders would be expected for a distribution $P(\sigma)$ intermediate between a "white" distribution and a δ function (for $X=100\%$).

It is interesting to note that if the axial symmetry is broken so that $\eta_i \neq 0$, the fine-structure splitting becomes

$$\Delta\nu_i = \frac{3}{2} d [\sigma_i(T) P_2(\cos \theta_i) + \frac{3}{2} \eta_i(T) \sin^2 \theta_i \cos 2\varphi_i],$$

where θ_i and φ_i are the polar angles specifying the orientation of the local axes $\hat{\xi}_i$ with respect to the external magnetic field. If the components σ_i and η_i varied independently within the limits $-2 < \sigma_i < 1$, $0 < |\eta_i| < 1$ and subject to the restraint $\sigma_i^2 + 3\eta_i^2 \leq 4$, the contributions from sites for which $\eta_i \approx 1$ would consist of spectra having an important narrow central component flanked by shoulders extending out to $\Delta\nu = \pm \frac{9}{4} d$. This is to be contrasted with the case of axial symmetry for which one obtains a broad bell-shaped line of width $3d$

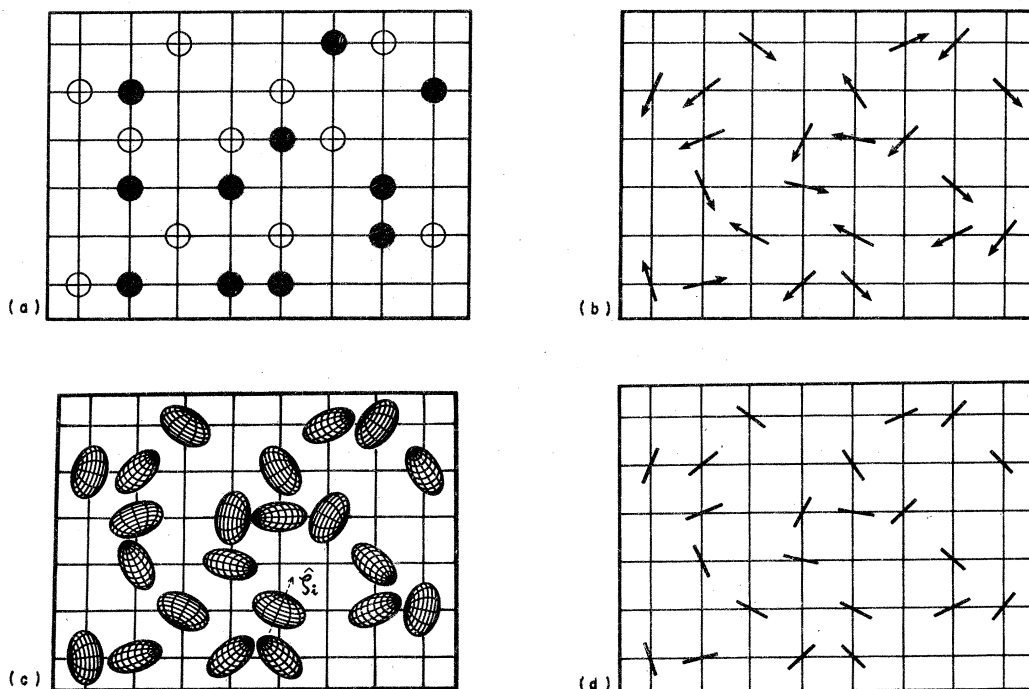


FIG. 4. Schematic sections of glasses of different tensorial orders. The square grids indicate the lattices. We have only indicated the dilute active elements. It is the random occupation of the lattice sites which results in the glass phases. (a) A scalar glass (rank 0)—an Ising spin-glass. (Solid circles, $S_z = +1$; open circles, $S_z = -1$.) (b) A dipolar glass of spins (rank 1)—Edwards and Anderson's model of dilute magnetic alloys—e.g., Ruderman-Kittel-Kasuya-Yosida (RKKY) or random Heisenberg interaction between spins. (c) A quadrupolar glass (rank 2)—a random distribution of ellipsoids which vary in orientations and shapes. Dilute solid ortho-hydrogen-para-hydrogen mixtures. The para-hydrogen molecules are inert and are not indicated. (d) A degenerate quadrupolar glass—a random distribution of rods.

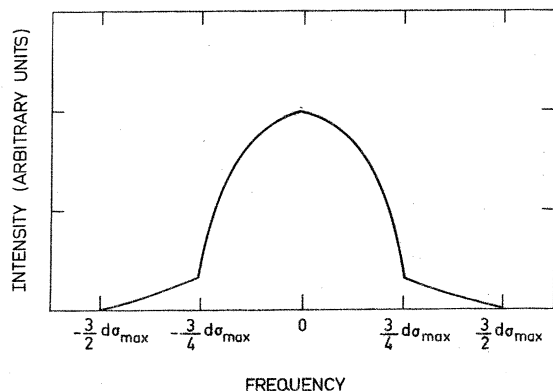


FIG. 5. Calculated low-temperature ($T \approx 0$) NMR absorption line shape for a quadrupolar glass assuming a "white" distribution for the local parameters $\sigma_i(0) = \langle 3J_i^2 - 2 \rangle_{T=0}$. This illustrates the characteristic shoulders extending out to twice the width of the central component, and is to be compared with the spectrum of Fig. 3(b). The separation of the extrema of the derivative shape is $\frac{3}{2}d|\sigma_{\max}|$. As discussed in the text $|\sigma_{\max}| \approx 2$ apart from renormalization factors (Ref. 7 and 12) which decrease with the ortho concentration.

accompanied by shoulders extending to $\Delta\nu = \pm 3d$ (assuming $|\sigma_{\min}| = 2$). Although one does observe very weak central components (Fig. 3), the predominant features of the spectra are consistent with the model of axial symmetry for which the η_i vanish. It would be difficult to account for the spectra if there were a significant number of sites for which the axial symmetry was broken. The residual central line is believed to result from sites for which an ortho molecule has no nearest-neighbor ortho molecules and estimations of the areas of the narrow (8 kHz) component of the spectra are consistent with the expected number of isolated ortho molecules for different mean ortho concentrations.

IV. TEMPERATURE DEPENDENCE OF THE NMR LINE SHAPES

Further evidence that the ortho molecules form a quadrupolar glass phase at low temperatures is given by the temperature dependence of the NMR spectra.⁸ On warming we find that the line shapes

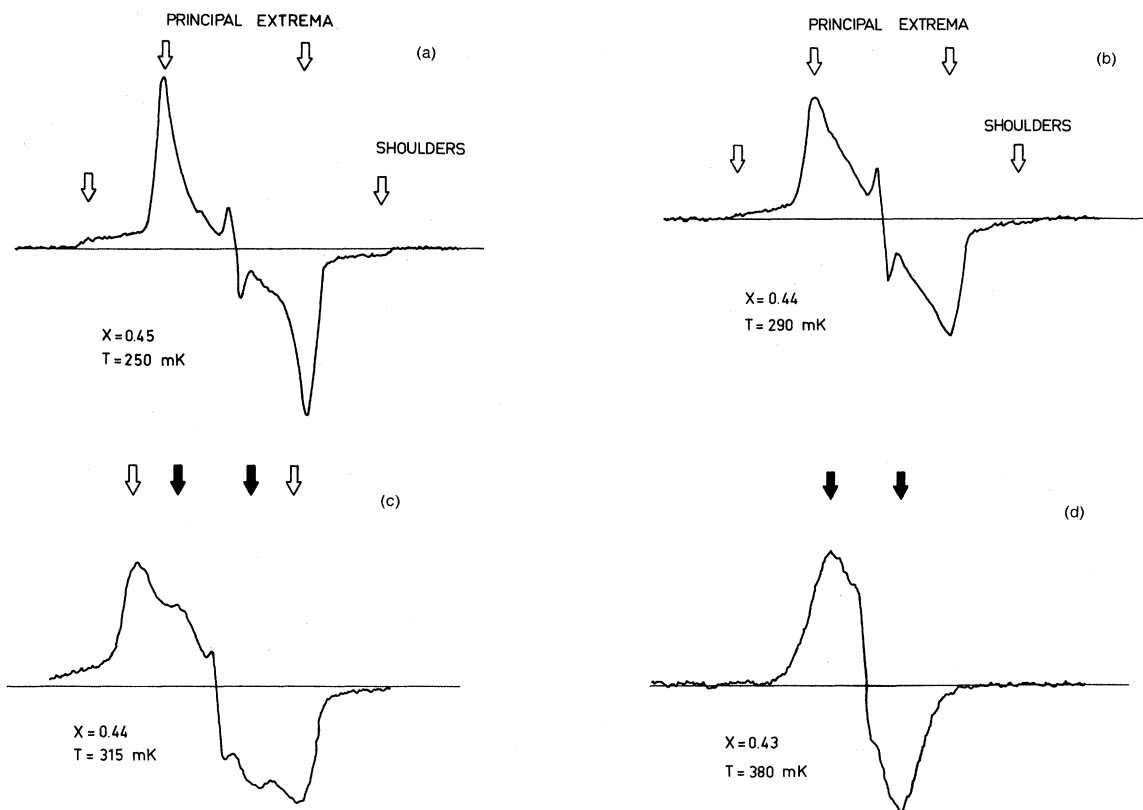


FIG. 6. Temperature dependence of the NMR absorption line shapes, observed as a given sample ($X \approx 0.44$) is warmed through the transition temperature $T = 315$ mK. The specific features of the low-temperature line shape indicated by the open arrows disappear rapidly near the transition. Over a narrow temperature interval (< 30 mK) at the transition temperature one observes the superposition of a *distinct* high-temperature line shape indicated by the solid arrows. At temperatures higher than the transition temperature, one observes only the narrower central component with no shoulders.

shown in Fig. 3 vary rapidly at a critical temperature where the shoulders disappear and the principal extrema of the derivative line profiles often become doubled over a narrow temperature range ($\Delta T < 15$ mK at $T_c = 150$ mK) indicating that a narrower line (≈ 50 kHz) grows at the center of the spectrum at the expense of the low-temperature component. This is shown in Fig. 6. These "critical" temperatures are shown by the solid line in Fig. 1.

The rapid variations of the line shapes with temperature (Fig. 7) can be interpreted as transitions from the glass phases to rotationally disordered phases. Husa and Daunt¹⁹ have recently observed rapid variations of the free-induction-decay pattern at the critical temperatures shown in Fig. 1 for $25\% < X < 35\%$. Ishimoto and co-workers⁸ also reported abrupt temperature variations of the relaxation times near $T_c(X)$ for reduced ortho concentrations condensed on fine wires. Vinegar *et al.*¹⁶ have recently studied bulk

specimens of solid hydrogen in the same concentration and temperature ranges, but observed only smooth variations of the line shapes with temperature. They condensed their samples directly onto

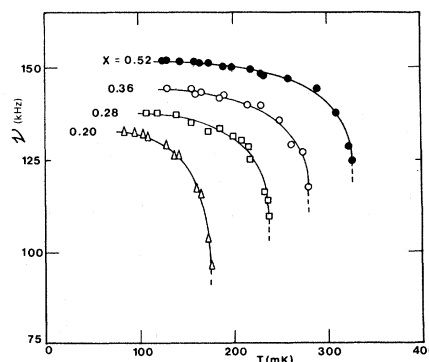


FIG. 7. Temperature dependence of the frequency separation of the derivative line shape extrema (open arrows of Fig. 6).

a cold surface ($T = 8$ K) and aged them at $T < 0.1$ K. The different temperature dependences might therefore be due to differences in the nature of the condensed state of the solid hydrogen for the two different condensation procedures. (The copper wires may stabilize the fcc phase with respect to the hcp phase while in the bulk crystalline phase transformations could accompany the orientational ordering.¹⁴) In the present studies no significant hysteresis was observed for concentrations less than 40%.

It is also possible that temperature gradients could occur in their samples if the transitions are accompanied by a significant heat-capacity peak near T_c and if the thermal conductivity²⁰ was too low to cool the sample uniformly for their refrigeration rate. Experimental determinations of the heat capacities for these concentrations and temperature ranges would be useful to clarify this point and also to confirm the transition temperatures.

Vinegar *et al.*¹⁶ compared the temperature dependence of their spectra with that expected for temperature-independent crystalline fields $\Delta(X)$ for a given concentration. This seems to be inconsistent with the spectra they observed at the lowest temperatures [$k_B T \ll \Delta(X)$] where one would expect a "clean" Pake doublet rather than a broad line.

V. DISCUSSION

The NMR experiments^{6-8,12} throughout the temperature range $80 \text{ mK} < T < 3 \text{ K}$ for ortho concentrations $0.18 < X < 0.99$ reveal a phase diagram which has three distinct regions. (i) An orientationally disordered phase. (ii) An ordered phase for $X > 0.55$ for which the transition temperatures are linear in X for $X > 0.65$. For $X \approx 0.99$, it has been shown²¹ that the molecules orient along the axes of the Pa_3 configuration. (iii) An ordered phase for $X < 0.55$ for which the transition temperatures have a dependence on concentration given empirically by

$$T_c(X) = 550 (X - 0.10)^{1/2} \pm 10 \text{ mK}.$$

We have interpreted this phase as a quadrupolar glass phase as discussed in Sec. III. The NMR spectra clearly show that the quadrupolar moments associated with the orientational degrees of freedom are frozen, at least within a time scale $\tau \leq 1/3d \sim 3 \mu\text{sec}$.

Two types of transitions to the quadrupolar phase can be envisaged. (a) A transition on warming and cooling for a fixed concentration as shown, for example, in Fig. 6. This is an abrupt transition which is indicative of a collective

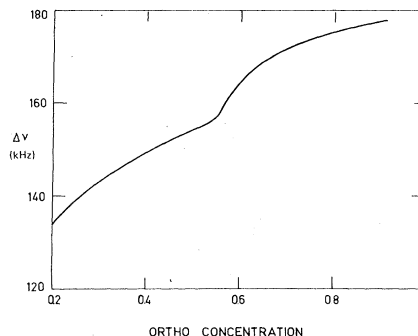


FIG. 8. Observed concentration dependence of the separation of the principal extrema of the low-temperature [$T < T_c(X)$] derivative NMR spectra reported in Ref. 7 and 12. The rapid variation $X \approx 55\%$ is consistent with a transition from the quadrupolar glass phase to the long-range orientationally ordered phase $X > 55\%$. [The present data give results in excellent agreement with the earlier work (Refs. 7 and 12)].

freezing of the rotational degrees of freedom of the ortho molecules. (b) A transition from high concentrations to low concentrations for a fixed low temperature, e.g., by aging. For temperatures very much less than the critical temperatures one does indeed observe an important change in the concentration dependence of the separation of the principal extrema of the low-temperature NMR line shapes. The experimental results are shown in Fig. 8. A question arises as to whether there is a continuous evolution of the glassy nature of the local order parameters as X goes through the value $X = 0.55$ or whether there is a brutal change in the symmetry of the ordered phase at $X \approx 0.55$.

In order to understand why the system would seek a quadrupolar glass phase at low ortho concentrations, we need to consider the "frustration"²² of the bonds between the ortho molecules. In pure ortho-hydrogen the molecules adopt a Pa_3 configuration consisting of four interpenetrating sublattices such that in each sublattice, the molecules are parallel to one of the body diagonals. In this case the bond energy between two nearest neighbors is $-\frac{10}{12}\Gamma$ which is almost a quarter of the minimum bond energy of -4Γ for an isolated pair. The Pa_3 structure results from the geometrical impossibility of having all the molecules orientated such that each bond has the lowest energy value of -4Γ . This "frustration" is distributed equally with respect to all bonds and results in a long-range orientational order for pure ortho-hydrogen.

At lower concentrations, the constraints imposing the Pa_3 structure become relaxed allowing the ξ_i axes to adopt orientations that differ from

the Pa_3 configuration and thereby reduce the frustration—i.e., approach the optimum energy -4Γ per bond. Since the ortho molecules are distributed at random throughout each microcrystal,^{12,16} it is reasonable to assume for the dilute alloys that the orientations of the $\hat{\xi}_i$ axes are also distributed at random. The additional randomness in σ_i comes from the fact that, as this frustration is reduced with dilution, the orientational correlations between neighboring molecules, $\langle \sigma_i^x \sigma_j^x \rangle$, can become important, and thereby increase the admixture of different J_{ξ} states into the ground state which is almost entirely $J_{\xi} = 0$ for pure ortho-hydrogen. J_{ξ_i} is no longer a good quantum number at low concentrations and σ_i can take all the different values between -2 and $+1$ because of the varying environments at different sites. Figure 4(c) is a simplified illustration of this point, although for simplicity, only two kinds of different admixtures are shown in the figure.

We have tried to explain qualitatively the dependence of the transition temperatures on the ortho concentration by taking advantage of the similarities between this system and the spin-glasses. One should note that the quadrupolar interaction between two ortho molecules cannot be treated as a random coupling in the same manner as the Rudderman-Kittel-Kasuya-Yosida (RKKY) interaction in the spin-glass problem. The reason for this is that the quadrupolar interaction is not intrinsically random from one site to another, but manifests itself as a "force" exerted on an ortho molecule by its neighbors and this "force" depends on the relative spatial arrangement of the bonds between this molecule and its neighbors. In dilute alloys, the geometrical distribution of these bonds is random. Neglecting correlation effects, this problem can be transformed into one in which the interactions are random and every site has the same environment. It is not clear if this assumption is justified for solid hydrogen. If we make a further step and treat the interactions as random with zero mean, we can use the techniques developed for spin glasses and predict a

transition from the disordered phase to the glass phase at critical temperatures $k_B T_g \sim (Z\gamma)^{1/2}$, where Z is the number of effective neighbors and γ the variance of the random interactions. Since the quadrupolar interaction is short ranged ($V_{ij} \propto |R_{ij}|^{-5}$), Z can be taken to be the mean number of nearest neighbors, $Z = 12X$. Although the prediction $T_g \propto X^{1/2}$ is in qualitative agreement with the observed concentration dependence of the transition temperature, simple estimations of γ lead to numerical values of T_g three times higher than the experimental values.

VI. CONCLUSION

Low-temperature NMR studies of solid hydrogen for ortho concentrations less than 55% reveal broad spectra having well-defined shoulders which can be explained by the random freezing of the quadrupolar moments $\langle 3J_z^2 - 2 \rangle$, $\langle J_x^2 - J_y^2 \rangle$ of the ortho molecules. These features disappear abruptly at well-defined temperatures for a given concentration. This can be interpreted as a phase transition from an orientational quadrupolar glass phase to be an orientationally disordered phase.

Some of the features reported here for the quadrupolar glass show similarities with the spin-glass models and we have exploited these similarities to discuss the general trends of the phase diagram. A complete theoretical treatment of the quadrupolar glass would however differ fundamentally from the spin-glass theories because the problem here consists of particles distributed at random on lattice sites but coupled with bond-independent interactions.

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