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NMR LINESHAPES OF THE SOLID HYDROGEN QUADRUPOLAR GLASS*

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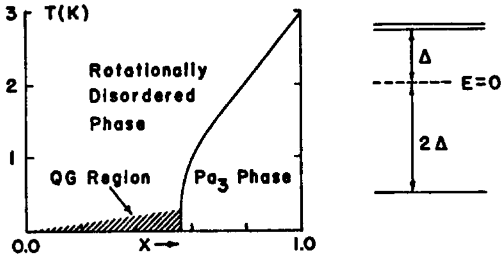
It is proposed that the low-lying excitations of solid hydrogen in the quadrupolar glass state may be described in terms of a distribution of "effective spin-one quadrupoles". This model provides a qualitative explanation for the temperature dependence of NMR lineshapes, and of the low temperature specific heat.

interaction between the rotational degrees of freedom of H_2 molecules in the solid state is dominated by the highly anisotropic electric quadrupole-quadrupole (EQQ) force.[1] The molecular angular momentum J is a good quantum number. For this reason the behavior of ortho-hydrogen (J=1) resembles a spin-1 antiferromagnet[2], while para-H_2 (J=0) molecules resemble nonmagnetic substitutional impurities. For ortho-concentrations X>0.6, hydrogen exhibits a transition to the four-sublattice Pa_3 structure which has an NMR absorption signal (in a polycrystalline sample) of Pake doublet shape. The doublet splitting is proportional to the orientational order parameter $S(T)=\langle 3J_z^2-2\rangle$ where z is a local symmetry direction. The transition temperature apparently goes to zero at a critical concentration $X_c \approx 0.56$ (Fig.1a).

NMR evidence for orientational ordering at very low temperatures for $X<X_c$ was first presented by Sullivan and Pound[3,4], and subsequently by other investigators[5-7]. The NMR line in this region of X and T (shown cross-hatched in Fig. 1a), is broadened, as it is in the Pa_3 phase, but it is not a simple Pake doublet.[6] Sullivan, et. al. have proposed a quadrupolar glass (QG) model,[7] in which the order parameter varies randomly from molecule to molecule, but has a nonzero time average for any particular molecule. Strictly speaking, the quadrupole moment is a tensor, and requires a second parameter to describe departures from axial symmetry. This results in a variety of lineshapes similar to the Pake doublet. In an axially symmetric field gradient, the energy levels of an ortho molecule are as shown in Fig. 1b, giving rise to a true Pake doublet. Sullivan, et. al. show that good agreement with experimental lineshapes can be obtained by making the simplifying assumption of axial symmetry and superposing Pake doublets with a distribution of widths. No rationale is proposed for the particular distributions of Pake doublet widths required to describe the ortho-concentration and temperature dependence of the experimental lineshape.



(a) (b)

Figure 1.a) Phase diagram for low temperature solid hydrogen. b) States of a spin-one quadrupole in an axially symmetric field gradient.

The specific heat $C_v(T)$ of solid hydrogen in the QG region of the (X,T) plane has recently been measured by Haase, et. al.[8], extending measurements at higher temperatures by Ramm, et. al.[9]. The specific heat was found to be proportional to temperature at low temperature, as is commonly observed for amorphous systems and spin glasses. For these other systems, the linear specific heat is usually explained by assuming a broad distribution of "tunneling state" excitations.[10] In a similar manner, we will assume the existence in solid hydrogen of "effective spin-one quadrupoles" (ESQs) with the energy levels of a real spin-one quadrupoles in axially symmetric field gradients (Fig. 1b), and with a broad distribution of energy splittings Δ. The ESQs represent collective excitations of the QG groundstate.

Let $P_{X,T}(S)$ be the probability distribution of the order parameter S necessary to describe the NMR line at the given X and T. $P_{X,T}(S)$ will be defined for the interval $0 > S > -2$. (We take $S < 0$ as it is for the Pa_3 structure.) Let the NMR lineshape, normalized to unit area, be given by $f_{X,T}(u)$ where $u = \nu - \nu_0$ and ν_0 is the Larmor frequency. The normalized Pake doublet with order parameter S is given by:

$$p(S,u) = (6S^2)^{-1/2}(g(-2u/S)+g(2u/S))$$
$$g(x)=(x+1/2)^{-1/2} \text{ for } -1/2 < x < 1$$
$$= 0 \text{ otherwise} \qquad (1)$$

In principle we can solve for the distribution of order parameters, $P_{X,T}(S)$, using

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$$f_{X,T}(u) = \int dS\, P_{X,T}(S)\, p(S,u) \qquad (2)$$

Define $Q_X(S_0, \Delta)$ as the probability density for an ortho molecule to have order parameter S_0 at T=0, and to be associated with an ESQ with energy splitting Δ.

With the level structure of Fig.1b the ESQ order parameter as a function of temperature is

$$S(S_0, \Delta, T) = S_0(e^{3\Delta/T}-1)/(e^{3\Delta/T}+2)$$

where S_0 is $S(T=0)$ (3)

If the distribution $Q_X(S_0, \Delta)$ were known, then $P_{X,T}(S)$ could be calculated:

$$P_{X,T}(S) = \int dS\, d\Delta\, Q_X(S_0, \Delta)(\, dS_0/\, dS) \qquad (4)$$

where $S_0(S)$ is defined implicitly by eqn. (3). Next we make two simplifying assumptions: (a) There is no correlation between S_0 and Δ in $Q_X(S_0, \Delta)$. (b) The probability distribution of ESQ energy splittings is uniform up to some cutoff Δ_0. Then

$$Q_X(S_0, \Delta) = P_{X,T=0}(S_0)/\Delta_0$$

for $0 < \Delta < \Delta_0$, and 0 otherwise. (5)

Using (5),(4) and (2) we can compute the NMR lineshape for all T > 0 on the basis of the T=0 lineshape and the single parameter Δ_0. We can also calculate the specific heat of such an ensemble of ESQs:

$$C_v(T) = (1/\Delta_0)\int_0^{\Delta_0} d\Delta\, A(T/\Delta) \qquad (6)$$

where $A(t) = (18Nk_B/t^2)/(e^{3/t} + 4e^{-3/t} + 4)$

N is the molar density of ESQs and cannot be determined from the NMR data. However, the functional form of $C_v(T)$ can be compared with experiment.

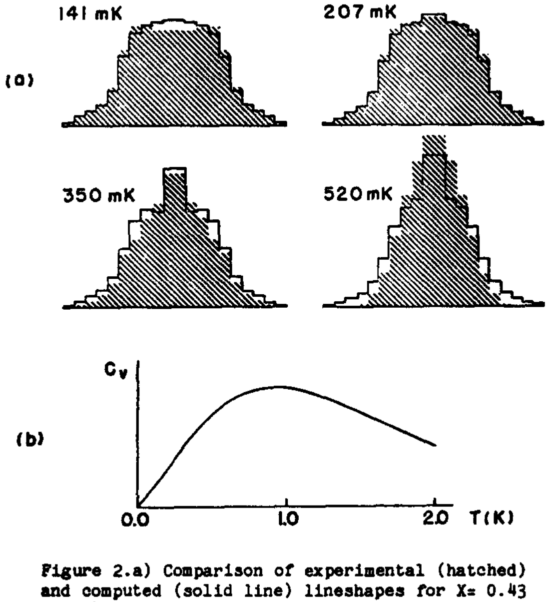

Figure 2.a) Comparison of experimental (hatched) and computed (solid line) lineshapes for X= 0.43 and Δ_0 = 1.25 K. The horizonal axis covers 320 kHz. b) Specific heat (arbitrary units) calculated with the same Δ_0.

We have measured NMR lineshapes of solid hydrogen in a field of 7 T for 100 mK < T < 4.2K and 0.15< X <0.75. The hydrogen samples were frozen directly from the gas into a cavity resonator filled with fine teflon insulated copper wires (each of which had one end soldered to the cavity), providing 240 cm^2 of thermal contact area per cm^3 of volume. Copper straps connected the cavity to the mixing chamber of a dilution refrigerator. Temperatures were determined from the area of the NMR absorption lines; the superconducting transitions of Cd (519 mK) and Zn (851 mK) were used as fixed points. Clear evidence was found for thermal gradients between the sample and the cavity, due to ortho-para conversion. Ortho concentrations were determined using the usual conversion rate law. Derivative NMR lines were digitized by a microcomputer, which provided integrated lineshapes and area determinations for thermometry.

At each ortho concentration, the lineshape at the lowest attainable temperature was used to compute the function $P_{X,T=0}$ in eqn. (5). The parameter Δ_0 was adjusted to give the best agreement between the sequence of lineshapes observed and those predicted by the theory above. For purposes of computation, the lines were split into 20 segments. Fig. 2a shows the result of this procedure for X= 0.43, which resulted in Δ_0 = 1.25 K. The specific heat calculated from eqn. (6) for this value of Δ_0 is shown in Fig. 2b. The range of temperatures over which the specific heat is linear compares favorably with that found in reference 8.

The overall agreement of this analysis with experiments is very good in spite of the simplifying assumptions used. We hope that it may provide a framework for more refined theoretical analysis.

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