thus be regarded similarly to the multiple ionization of gaseous atoms. An interesting theoretical aspect, which arises from the present observation, is the recombination probability for multiply charged ions in the vicinity of the metal surface. Obviously, the presence of the high electric field reduces the ion neutralization probability in a very drastic manner. The clarification of this point needs more theoretical effort in the basic understanding of electronic properties of highly charged surfaces as represented by a field ion emitter.

The n-fold–charged ion A^{n+} generated at energy level a displays an appearance-energy value given by

$$E_n^{\mathrm{app}}=n[e\delta_0(A^{n+})+\varphi_R]. \tag{2a}$$

Thus, E_n^{app} data as derived from measured energy-onset curves represent values for the ionic potential energy (with respect to the Fermi energy level) very near to the field-emitter surface atoms.[14] Experimental data for E_n^{app} as well as the observed relative abundances of differently charged field-desorbed ions are summarized in Table I.

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Study of the Quadrupolar-Glass Region in Solid D_2 via Proton Magnetic Resonance

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Cusplike behavior in the spin-lattice relaxation time of a probe molecule (o-H_2) is used to locate the transition temperature (T_c) to the quadrupolar glass phase of a host o-D_2–p-D_2 alloy for p-D_2 concentrations above 0.29. The values of T_c obtained here are higher than those obtained from line-shape measurements. The spin-echo height is also strongly affected by the collapse of the correlation frequency spectrum near T_c.

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Studies of solid hydrogen with use of various NMR techniques[1-3] have indicated that, for concentrations of $J=1$ (para) molecules below about $x=0.56$, a rotationally ordered phase can be observed below approximately 0.3 K. Following Sullivan, we will refer to this phase as a quadrupolar glass. Some samples were prepared by aging high–para-concentration samples in the ordered cubic phase (fcc) and then measuring the splitting of the NMR sidebands[1] as the temperature increased (T_{od}),[4] whereas others were mixed from the gas components and the measurements of the sideband structure, beats on the free induction decay,[2,3] and spin-lattice relaxation time (T_1)

made as the temperature decreased (T_{do}). More recently, however, x-ray measurements[5] have indicated that the glass phase is hcp and not fcc even if the samples are prepared by aging. If the same phase is obtained by the different sample-preparation techniques, then the various NMR results are not mutually consistent as pointed out by Gates *et al.*[5]

In solid D_2 with para ($J=1$) D_2 concentration below 0.52, we have observed via pulsed NMR measurements three effects that may illuminate the nature of the rotational ordering transition in the hcp structure:

(1) T_1 exhibits a cusplike singularity as a function of temperature that can be used to determine a transition temperature, T_c, and the critical exponents for this dynamical variable. These represent T_{od} in this experiment.

(2) A dramatic signal loss in the spin-echo height is observed in passing from $T > T_c$ through the transition to $T < T_c$ though no departure from Curie-law behavior is expected as the strongest magnetic interaction is the Zeeman interaction (~ 1.4 mK).

(3) The local rotational ordering (from the NMR line shape) begins at higher temperatures (> 4.2 K) and varies smoothly through T_c, in contrast to the behavior of T_1. No objective criterion for determining T_c from line shape changes was found.

Behavior similar to the cusplike singularity in T_1 was observed earlier,[2] of about the same magnitude and at the same temperature in H_2, but T_c was defined from the temperature at which the line shape stopped changing. Decreases in T_1 prior to the large increases characteristic of the ordered state were also seen by Husa and Daunt[3] but again T_c was determined rather arbitrarily from a line-shape change. Thus the data obtained in this experiment are consistent with previous experiments, but the determination of T_c from the singularity in T_1 gives rise to an entirely different interpretation.

For this study solid D_2 was chosen since both the real $J=1$ to $J=0$ conversion that would change the $J=1$ concentration, x, and the "resonant conversion" leading to quantum diffusion of the $J=1$ excitations are much slower in D_2 than in H_2.[6] However, the NMR spectrum has two contributions, one from orthodeuterium molecules with $I=2$ and $J=0$ and one from paradeuterium molecules with $I=1$ and $J=1$. For n-D_2 ($x=0.33$), the former signal is five times larger than the latter (the signal of interest). In fact, because of poor signal-to-noise ratio, the NMR sidebands in a continuous wave (cw) experiment used to probe the glass phase in H_2 have not been seen in D_2 for $x \leq 0.4$,[7] although the p-D_2 signal was easily observed in a pulse experiment with use of solid echo techniques.[8] To date inferences of the transition to the glass phase in D_2 have been made from increases in T_1 in the absence of the p-D_2 spectrum sidebands.

To study the glass-phase region of D_2 without a large background signal, we have added 1% ortho H_2 to D_2 samples having $0.03 < x < 0.52$ and observed the proton resonance spectrum using coherent pulsed techniques at 30 MHz. The samples were admitted to the sample cell as a liquid and slowly condensed around fine copper wires in contact with the mixing chamber of a dilution refrigerator. Preliminary studies,[9] adding small amounts of H_2 to D_2 (where the $J=1$ concentrations of D_2 were 2.2% and 83.5%), indicated that in the disordered phase T_1 for the proton resonance was comparable to that in solid H_2 for the same $J=1$ (para) concentration. Furthermore, sideband structure appeared on the proton NMR line [beats on the free induction decay (FID)] just at the ordering temperature (as measured via NMR on the deuterium spectrum) for the 83.5% p-D_2 sample. A large increase in T_1 was noted in the ordered state as well as a decrease in T_1 just before the line-shape transition. Based on these results, the proton resonance seemed to be a reasonable probe of the ordering of the rotational moments in solid D_2. HD impurities in the sample also gave a proton resonance signal. The concentration of HD impurities ranged from 0.5% for $x \leq 0.33$ to 0.12% in those samples prepared by ortho-para separation.[10] The proton resonance is observed first as a function of temperature before the o-H_2 is added and then restudied after addition of o-H_2. Since the second moment for the intermolecular dipolar broadening is the same for the o-H_2 molecule ($I=1$) as for the HD molecule ($I=\frac{1}{2}$), the FID of the o-H_2 molecules can be corrected to remove the intermolecular contribution by multiplying the signal due to the o-H_2's by $\exp(M_2 t^2/2)$ where M_2 is the second moment observed on the HD resonance. The resultant signal, $F(t)$, is then damped only by intramolecular interactions. Thus the address of a given probe o-H_2 molecule in frequency space is (neglecting fluctuations of the order parameters)[11]

$$\Delta\omega_i = \tfrac{3}{4} d[\sigma_i(3\cos^2\theta_i - 1) + 3\eta_i \sin^2\theta_i \cos 2\varphi_i], \qquad (1)$$

where $d = 57.7$ kHz, θ_i and φ_i specify the orientations of the local axis with respect to the applied field, and σ_i and η_i are local-order parameters given by $\eta_i = \langle J_{xi}{}^2 - J_{yi}{}^2\rangle$ and $\sigma_i = \langle 3J_{zi}{}^2 - 2\rangle$. Assuming the various local axes are randomly distributed in space, one must powder average the above expression to obtain the line shape. Unfortunately the powder average line shape of Eq. (1) with $\sigma_i = -2$ and $\eta_i = 0$ is so similar to that for $\sigma_i = 1$ and $\eta_i = 1$ that the low-temperature line shape cannot distinguish between these two possibilities.

The free-induction-decay signal, $F(t)$, the solid spin-echo response, and T_1 are measured for all temperatures for a given concentration. Since the spin-echo response, unlike $F(t)$, is not affected by amplifier blocking problems, the line shape, $I(\omega)$, is obtained by Fourier transforming the echo. To ensure equilibration near T_c, the temperature is changed in 10-mK steps at intervals of 1 to 2 h.

In Fig. 1(a), the scaled relaxation rate, $T_1{}^{-1}$, is plotted for three concentrations. Near T_c it was assumed that the contribution to this rate due to order-parameter fluctuations was equal to the observed rate minus the high-temperature rate (a background subtraction of about 4 $\sec^{-1}$) and diverged as $A_\pm\,|1 - T/T_c|^{-\mu}$. For both 50% and 42%, μ was equal to 0.43. A theoretical calculation of the NMR linewidth (and hence the relaxation rate, above T_c) leads to the result that $\mu \cong \nu(1-z)$ to a good approximation, where ν is the coherence-length critical exponent and z the dynamic exponent. For a nonconserved order parameter in three dimensions, the mean-field value is $\mu = \frac{1}{2}$ while dynamic scaling gives $\mu = \frac{1}{3}$ (in analog with antiferromagnets).[12] Comparing the values of A_+ for different concentrations, with $A_+ \propto \xi_0{}^{-3}$, where ξ_0 is the temperature-independent correlation length, gives the result that ξ_0 increases by a factor of 2 in going from $x = 0.50$ to $x = 0.33$. It is found that $\xi_0{}^{-1}$ scales roughly as $x - x_p$ where the percolation concentration x_p is taken to be 0.18.

At fixed pulse separation, the spin-echo height (corrected for Curie-law differences) decreases abruptly by about a factor of 20 as $T \to T_c$ and then increases slightly again for $T < T_c$ (for $x = 0.50$), as shown in Fig. 1(b). For lower concentrations, the loss is less dramatic as it is spread over a large temperature interval. These results are qualitatively similar to the spin-echo experiments in the CuMn spin-glass system[14,15] where a signal loss is also observed in the vicinity of the glass transition.

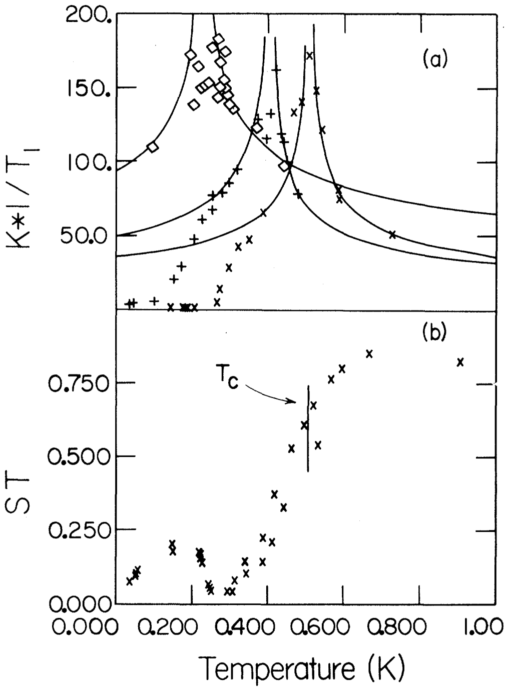

FIG. 1. (a) Temperature dependence of the relaxation rate $T_1{}^{-1}$ in $\sec^{-1}$ of o-H$_2$ molecules, scaled by a factor K, in a host D$_2$ lattice with $J = 1$ (para) concentrations of 0.50 (cross, $K=1$), 0.42 (plus sign, $K=\frac{1}{4}$), and 0.33 (open diamond, $K=\frac{1}{8}$). The solid lines are fits to $T_1{}^{-1} \propto |T/T_c{}^{-1}|$. (b) The spin-echo height (S), in arbitrary units, at fixed pulse separation, multiplied by the absolute temperature (T) is plotted against T for $x = 0.50$. The value of T_c obtained from the T_1 results is shown.

The echo envelope can be calculated using the Anderson-Kubo model.[16] When the molecular-reorientation correlation time, τ_c, is short ($d\tau_c \ll 1$) the echo envelope is weakly damped by the time constant $\tau^{-1} \approx d^2\tau_c$. By freezing the molecular reorientation, τ_c is increased and the envelope is then damped by the time constant τ_c (when $d\tau_c \gg 1$). The crossover between the two regimes depends on the magnitude of $\tau_c{}^{-1}$ as compared to the frequency $\Delta\omega_i$ [Eq. (1)] and is not sharp nor complete in a powdered sample such as ours. The loss in signal here is interpreted as resulting from large regions of the sample having $\tau_c{}^{-1} \approx \Delta\omega_i$ which makes the resonance line structureless and too broad to be seen on the FID. (T_2 could be as short as a few microseconds.) Relaxation during the pulses, when the pulse width is comparable to T_2, greatly reduces the spin-echo height. Thus both the relaxation rate and the spin-echo height show changes that are understandable in terms of

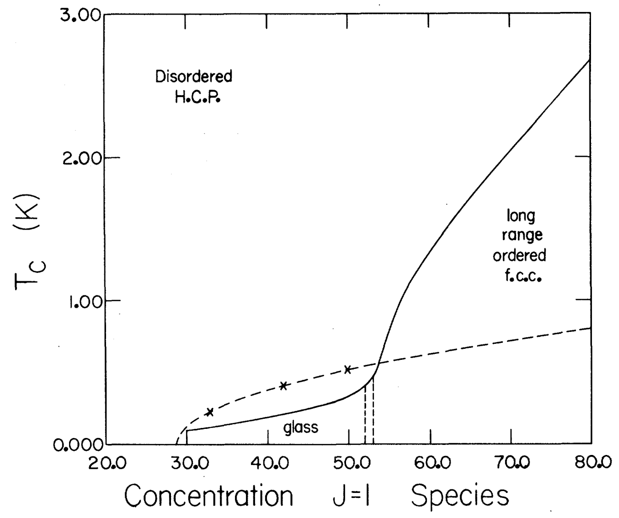

FIG. 2. The transition temperature, T_c, as a function of the $J=1$ (para) concentration. The solid line is from Ref. 7. The dotted line represents a fit to the values of T_c obtained in this work.

the effects of a critical collapse of the correlation frequency spectrum.

At high temperatures, the line shape is approximately Gaussian with a width of under 5 kHz. For $x \geqslant 0.18$, upon cooling the line departs from the Gaussian shape and becomes triangular or bell shaped as predicted for a white distribution of order parameters.[11] For those concentrations that show cusplike behavior for T_1 measurements, the low-temperature line shape is more like a Pake doublet in agreement with Vinegar *et al.*[17] For the other concentrations, at our lowest temperature, the frequency spacing of the derivative peaks is about 50 kHz as opposed to 140 kHz for $x \geqslant 0.33$.

Specific-heat data[10,18] above 0.3 K on n-D_2 provide some insight into this problem. It was found that there was a small broad maximum (near 2 K) in the "anomalous" heat capacity (measured value minus the lattice contribution) with no evidence of other peaks down to 0.3 K. Furthermore, smooth extrapolation of this measurement to $T = 0$ and integration to obtain the entropy gave the result that more than 80% of the expected rotational entropy ($\frac{1}{3}R\ln 3$) was accounted for. Thus at 0.3 K [above $T_c(x)$] for $x = 0.33$, the rotational system is essentially ordered. This result combined with the present NMR data suggests the following picture of the quadrupolar glass transition: The rotational moments begin ordering with respect to the local axes at temperatures as high as the triple point and this local order grows smoothly as more distant molecules [driven by the electric quadrupole-quadrupole (EQQ) interaction] order along a given axis enlarging the size of the "clusters". For concentrations above $x = 0.29$ (and possibly lower) the oriented clusters themselves freeze in a correlated fashion at T_c, but the number of degrees of freedom affected in this last process is only a fraction of the total number of rotational degrees of freedom of the system, leading to a small contribution to the entropy.

The transition temperatures to the quadrupolar glass phase determined here for $x \leqslant 0.50$ are quite different from those determined previously from line-shape changes.[19] The present results indicate that the cooperative nature of the rotational ordering due to the EQQ interaction disappears below about $x = 0.29$, as shown in the proposed phase diagram given in Fig. 2. From the T_1 results, using the maximum in the relaxation rate to locate $T_c(x)$, we obtain that $T_c = (1.12\text{ K})(x - 0.287)^{1/2}$.

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