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Study of Nuclear-Magnetic-Resonance Line Shapes in Solid H_2*

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A detailed study of the NMR line shapes in solid H_2 has been carried out. The ortho-H_2 concentration c was between 0.09 and 0.95, and the temperature ranged from $T=0.5$ to 10°K. In the hcp phase, a systematic compilation of the second and fourth moments as a function of c and T was made. In the cubic phase the splitting of the doublet structure was measured as a function of temperature. From an extrapolation of the measurements in the hcp phase to the limiting case of pure ortho-H_2, it is concluded that in the temperature region where thermal diffusion is unimportant, the second and fourth moments are independent of temperature, their values being, respectively, 80 ± 2 kHz^2 and $(14.8\pm0.8)\times10^3$ kHz^4. The contribution to the second moment from intermolecular nuclear dipole interactions (this is the second moment extrapolated to $T=\infty$) is obtained as a function of orthoconcentration and is compared with theoretical predictions. Good agreement is found if one takes into account the correlation between nearest H_2 neighbors, an effect that decreases the average value $\langle R^{-3}\rangle$, where R is the distance between nearest neighbors. Experiments with $0.64<c<0.74$ indicate that, as the temperature is increased, the rotational ordering in the cubic phase disappears at almost the same temperature as does the last evidence of this phase. Extrapolation of this result to pure ortho-H_2 indicates that the rotational ordering disappears at about 3.0°K. No evidence of a transition to a rotationally ordered phase is observed at concentrations below $c=0.60$. This would indicate that the critical ordering concentration is approximately $c_{\mathrm{crit}}=0.6$, which is much higher than anticipated for theoretical models of cubic H_2. For the concentration of $c=0.71$, the cubic-to-hcp transition is followed by plotting the ratio of the intensity of the nearly Gaussian line (representing the signal from the hcp phase) to the total intensity. This ratio is compared with the results from x-ray measurements. The present data are discussed in connection with entropy results and the theory of rotational ordering in this phase. The doublet splitting in the cubic phase, extrapolated to $T=0$, has been obtained as a function of orthoconcentration c and has been found to decrease slightly with c, which is in qualitative agreement with theoretical expectations.

I. INTRODUCTION

THE NMR line shapes in solid H_2 with orthoconcentrations c between 0.09 and 0.95 and over a temperature range between 0.5 and 10°K have been studied. The purpose of this paper is to present information on the rotational excitations in solid H_2 based on the NMR data. An earlier paper[1] covered the lower orthoconcentration range, where line shapes due to isolated pairs were observed and analyzed.

Although there have been previous cw studies[2-7] of line shapes in solid H_2, the present one covers a far greater range in both orthoconcentration and temperature. Moreover, the results constitute the first systematic study to be expressed in terms of the moments of the absorption line[8] which are of direct theoretical interest. Although at this time quantitative comparisons between theory and experiment can be made for only a few of the results, two main conclusions emerge that characterize the extrapolated behavior of pure ortho-H_2. Firstly, the theoretical second moment[8] in the hcp phase due to intermolecular nuclear dipole interaction agrees with the experiment, if correlations between nearest neighbors are taken into account.[9] Secondly, we conclude from experiments with increasing temperature that the rotational ordering in the cubic phase, as measured by the NMR doublet structure,[3] disappears about 0.1°K above the center region of the crystallographic cubic-to-hcp transition temperature, ~2.9°K.

Another conclusion concerns the hcp phase at concentrations below $c=0.6$, where this phase is stable over the whole temperature range. There the NMR data show no evidence of a doublet which would reflect rotational ordering, although at the lowest temperatures reached, the rotational entropy (at least for concentrations $0.45\lesssim c\lesssim0.6$) is less than 10% of its value for free rotation, $R\ln3$ per mole of orthohydrogen. From the strong increase of the second moment with decreasing temperature, it is concluded that appreciably lower temperatures than 0.5°K must be reached for the line shape to be representative of the rotational ground state.

After a brief survey in Sec. II, the experimental methods are described in Sec. III. In Sec. IV, a systematic study of the second and fourth moments is presented and the results are discussed in terms of the theory of Van Vleck.[8] In Sec. V, we describe NMR measurements in the cubic phase, where the doublets

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are observed. The temperature dependence of the spacing between the satellites is then analyzed in terms of the rotational order parameter.

II. THEORETICAL AND EXPERIMENTAL SURVEY

Solid H_2 and solid D_2 are to some extent analogous to a dilute magnetic system. The ortho-H_2 and the para-D_2 molecules have a rotational angular momentum $J=1$, while the para-H_2 and the ortho-D_2 molecules have zero angular momentum. The $J=1$ molecules therefore resemble magnetic ions with spin 1, while the $J=0$ molecules are analogous to diamagnetic surroundings. Both H_2 modifications are mutually soluble in all proportions, and one can speak of randomly dilute ($J=1$) solution. This situation is very interesting, since one can study the directional interaction between $J=1$ molecules as a function of dilution.

It seems now generally accepted that the alignment of the $J=1$ molecules at low pressures is caused by electric quadrupole-quadrupole (EQQ) interaction, as first shown by Nakamura.[10] At high enough concentration c of the $J=1$ molecules, this mechanism is responsible for a crystallographic transition[11–13] from a hexagonal to a cubic structure as the temperature is decreased below T_{h-c}. The transition back into the hcp phase occurs at a temperature $T_{c-h}>T_{h-c}$. The reasons for this hysteresis are not yet clarified but are probably due to the complication of having two components (ortho and para) involved in the transformation. The molecular rotation in the hcp phase above T_{h-c} is almost free, but it is quenched in the cubic phase, as can be deduced from NMR measurements.[3] Evidence of orientational ordering comes from neutron scattering experiments in the cubic phase of enriched para-D_2.[13] A careful series of x-ray measurements,[12] both in solid H_2 and D_2, has shown that both crystalline phases coexist over a certain temperature range.

In the last few years, there have been several attempts to calculate the orientational arrangements of the orthomolecules in different lattice types. Felsteiner[14] and also Miyagi and Nakamura[15] found that the rotational ground-state energy of pure ortho-H_2 was lower in the cubic phase than in the hcp phase. The thermodynamic properties, with emphasis on the order-disorder transition temperatures T_c in both crystalline phases, have been calculated.[16–24] For convenience we recapitulate the results in Table I together with the approximations made in the calculations. T_c is expressed in units of the EQQ coupling constant $\Gamma=6e^2Q^2/25R^5$, where eQ is the quadrupole moment of the orthomolecule and R is the nearest-neighbor distance. Using the value[25] $Q=0.137\times10^{-16}$ cm^2 and $R=3.755\times10^{-8}$ cm,[11] one calculates $\Gamma/k_B=1.00$°K. The experimental value is $\Gamma/k_B=0.82$°K.[1,26]

Harris[9] points out that the Ising model usually overestimates the transition temperature by about 20–25%. Taking this overestimation into account one expects the orientational ordering in the cubic phase to substantially increase at

$$T\approx5.81\times\tfrac{3}{4}\Gamma/k_B\approx3.5°\text{K}. \tag{1}$$

Predictions of the variation of T_c in the cubic phase with orthoconcentration have been made using a Weiss molecular field and a Bethe-Peierls approximation.[27] It was found, as expected from such models, that T_c is approximately proportional to c, at least at high enough orthoconcentrations. This result is not very different from that obtained for a dilute Ising ferromagnet[28,29] with fcc lattice[30] where the critical spin concentration is about 0.12.

A similar behavior could be expected for the hcp lattice, with the order-disorder transition occuring at a slightly lower temperature[17,23] than for the cubic phase. On the basis of the molecular field approximation, one might expect to see some evidence of pronounced ordering in solid H_2 in the hcp phase above $T=0.4$°K for orthoconcentrations larger than about $c=0.3$. This expectation will be compared with the experimental results in Sec. V.

The rotational ordering strongly affects the NMR line shape. At high enough temperatures, when the molecules rotate freely in the lattice, the *intra*molecular nuclear dipole-dipole interaction is cancelled out and the linewidth is caused by *inter*molecular nuclear dipole interaction. As the temperature decreases and the rotational motion becomes ordered, the line gradually broadens due to the intramolecular dipolar interactions. Harris[31] has calculated the first terms of an expansion

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of the second moment in powers of T^{-1}, assuming EQQ interaction only. He obtains

$$M_2=M_{2,0}+(36/5)d^2y^4zc(1-c)\times[1-(72/30)y-(498/64)yc], \quad (2)$$

where

$$y=\tfrac{5}{6}(\Gamma/k_BT).$$

Here $M_{2,0}$ is the well-known[8] moment of a system of spins $I=1$ located on the lattice sites of the crystal, $d=57.7$ kHz is the nuclear intramolecular dipolar coupling parameter,[32] and $z=12$ is the number of nearest neighbors. Assuming random distribution of orthomolecules in the lattice, one has[8]

$$M_{2,0}=c\times\left(\frac{3}{5h^2}\right)g^4\beta^4I(I+1)\sum_j R_{ij}^{-6}, \quad (3)$$

where I is the nuclear spin, β is the nuclear magneton, g is the corresponding Landé factor, and R_{ij} is the distance between the molecules i and j. Taking the ratio of the lattice constants to be $a/c=0.616$ [11] and using a recent computation of the hcp lattice sum[33] in Eq. (3), one obtains for solid H$_2$ with $R=3.755\times10^{-8}$ cm,

$$M_{2,0}=c\times89.2\ \text{kHz}^2. \quad (4)$$

In the cubic phase, where the rotational ordering is nearly complete until close to T_{c-h}, the NMR line shape shows a doublet. This shape can be understood from the nuclear-spin energies in a strong magnetic field.[3] Neglecting at first intermolecular dipolar interactions, one has transitions between different nuclear energy states giving[3]

$$\nu=\nu_0\pm\tfrac{3}{4}d(3\cos^2\Theta_{Z,\mathbf{H}_0}-1)\langle n|2-3J_Z{}^2|n\rangle. \quad (5)$$

Here ν_0 is the Larmor frequency $g\beta H_0/h$, $\Theta_{Z,\mathbf{H}_0}$ is the angle between the symmetry axis Z of an orthomolecule and the magnetic field $\mathbf{H}_0$, J_Z is the projection of the rotational momentum J on this axis, and $|n\rangle$ is a rotational state. Assuming that the transition rate between different states of the molecule is much faster than $3d$, we can substitute into Eq. (5) the thermal average

$$\langle 2-3J_Z{}^2\rangle_T=\sum_n \langle n|2-3J_Z{}^2|n\rangle \exp-\left(\frac{E_n}{k_BT}\right)\Bigg/\sum_n \exp-\left(\frac{E_n}{k_BT}\right). \quad (6)$$

Assuming the solid sample to be a randomly oriented powder, and averaging over all the angles $\Theta_{Z,\mathbf{H}_0}$, one obtains the line shape calculated by Reif and Purcell.[3] (Fig. 2 of Ref. 3.) The two principal satellite peaks will be separated by

$$\delta\nu=\tfrac{3}{2}d\langle 2-3J_Z{}^2\rangle_T. \quad (7)$$

Raich and Etters[18,19] show that at $T=0°$ K, $J_Z{}^2=0$ if one neglects a small correction due to zero-point motion.[34] Accordingly, $\delta\nu$ is expected to be 173 kHz.

Because of the additional intermolecular dipolar interaction, the peaks are slightly pushed together. A computer calculation, based on Eqs. (20)–(25) in Ref. 3, shows that the observed splitting $\delta\nu_{\text{obs}}$ of the broadened line is related to $\delta\nu$ by

$$\delta\nu=\delta\nu_{\text{obs}}+13.1c^{1/2}\ \text{kHz}. \quad (8)$$

Hence the experimental value of $\delta\nu$ as a function of T will give the order parameter $\langle 2-3J_Z{}^2\rangle_T$ which can be compared with that calculated by Raich and Etters.[18,19] At the same time, this measurement will approximately locate (by extrapolation) the rotational ordering region for the cubic phase.

Similarly, in the hcp phase at intermediate orthoconcentrations one expects Pake doublets to be seen when orthomolecules are sufficiently close to the ground state. From Eq. (7), one sees that the splitting as $T=0°$K cannot be larger than $\delta\nu=3d$, since $0\leqslant J_Z{}^2\leqslant1$. For the molecular field approximation, one expects $\langle J_Z{}^2\rangle_{T=0}$ to be either ≈1 or ≈0. The observation of an intermediate value would indicate that this approximation is not applicable. For an isolated ortho pair, the rotational energy levels have been solved; there $\langle J_Z{}^2\rangle_{T=0}=\frac{1}{2}$.[1]

III. EXPERIMENTAL METHODS

The apparatus and the methods of preparing and analyzing the H$_2$ samples were the same as described elsewhere.[1] Hydrogen gas with orthoconcentration of $c=0.97$ was kindly supplied by Mills of the Los Alamos Scientific Laboratories.

The time was recorded at which a given NMR line structure in solid H$_2$ was measured. From the orthoconcentration analysis before and after the experiments, the rate of ortho-para conversion was determined using the equation

$$dc/dt=-Kc^2, \quad (9)$$

and it was then possible to assign a certain orthoconcentration to each recorded line. The ortho-para rate constant so obtained, $K=18.5\times10^{-3}\ h^{-1}$, is in excellent agreement with previous work.[35] The NMR measurements were taken at a predetermined set of temperatures that were the same for each experiment. This systematic procedure allowed the interpolation of the measured moments to values at "standard" orthoconcentrations at these temperatures.

The radio frequency of the cw detection system was 12 MHz and was measured by an electronic counter. The field modulation was carefully monitored and usually chosen to be less than 15% of the linewidth.

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TABLE I. Orientational transition temperatures in solid ortho-H_2.

Phase	Space group	Approx.	$T_c\times(\Gamma/k_B)^{-1}$
hcp	$Pca2_1$	a and b	6.5[d]
hcp	$Pca2_1$	a and b	6.6[e]
hcp	$Pca2_1$	a and b	5.55[f]
cubic	$Pa3$	a and b	6.86[g]
cubic	$Pa3$	a and c	6.7[h]
cubic	$Pa3$	a	No transition but rapid variation of order parameter in the region $5.81\Gamma/k_B<T<6.86\Gamma/k_B$[i]

[a] Ising model.
[b] Molecular field approximation.
[c] Bethe approximation.
[d] Reference 17.
[e] Reference 23.
[f] Reference 22.
[g] Reference 16.
[h] Reference 27.
[i] Reference 24.

A systematic study by Smith[36] has shown that under these circumstances the line shape experiences only negligible distortion. During an experiment, the derivative of the line shape was recorded graphically and punched on IBM cards. The integrated line shapes and the second and fourth moments were then obtained by computer. Corrections for field modulation, as described by Andrews,[37] were applied to the moments and were less than 1% for M_2 and 2% for M_4.

Measurements of moments can be delicate if the lines have extended "wings"; therefore, great care was taken to assure that the line derivative was observed over a long enough frequency range and was not affected by any drift in the electronic equipment. Computation of the first moment M_1, which should ideally be zero, showed any deviation from symmetry of the line shape about its frequency center. This quantity was found more sensitive to irregularities in the line recording than were visual inspections of the line. Absorption lines for which $M_1^2/M_2>0.001$ were discarded from any further analysis.

As will be noted from the results tabulated below, the lines become considerably broadened as the temperature is decreased. This feature, already observed by Sugawara *et al.*,[4] increases the scatter in the moment computation. Moreover, M_2 and M_4 show a maximum near $c=0.4$ at temperatures below 2°K. This maximum was reproducible from experiment to experiment (although not quantitatively so) and is responsible for additional uncertainty near $c=0.4$. The difficulty may be due to an inability to obtain perfect powder samples. An order-of-magnitude estimation of the anisotropy of the moments was made in which samples with ortho-concentrations around $c=0.3$ were recrystallized several times during an experiment, and their line shapes remeasured. It was found that the moments were not appreciably affected at temperatures above 2°K, but the systematic deviations in M_2 from the average could reach about ±10% at 0.5°K.

In a recent paper,[38] evidence for clustering of orthomolecules has been described. Isolated orthomolecules surrounded by paramolecules were shown to be able to move through the lattice and form clusters of orthomolecules that are thermodynamically more stable. This phenomenon is very marked at very low orthoconcentrations and temperatures below about 2°K, but is not observed in the concentration range studied in the present paper. Pending more detailed investigations, ortho-para conversion is believed to mask any effect of clustering on the line shapes.

The best determination of the moments was at high temperatures and high orthoconcentration where the moments changed only moderately with T. The uncertainty at temperatures above about 3°K ranges from less than ±5% for M_2 and ±10% for M_4 for $c>0.7$ to, respectively, ±10 and 20% for $c<0.2$. At the lowest temperatures and concentrations the uncertainty could be as large as ±15% for M_2 and ±30% for M_4. For this reason M_4 has not been tabulated below temperatures of $T=1.27$°K.

For a given line, the error in M_2 and M_4 is in the same direction. The uncertainty in M_4/M_2^2 is of the order ±10%.

IV. LINE SHAPES AND MOMENTS IN hcp PHASE

Approximately 430 NMR lines were analyzed, and the moments so obtained at a given temperature were plotted as a function of orthoconcentration. Interpolated values at standard orthoconcentrations are presented in Tables II and III. The moments $M_{2,0}$ and $M_{4,0}$ were obtained by extrapolating to $T=\infty$. For these extrapolations, the moments at 10°K were not used, since at this temperature the linewidth has narrowed somewhat because of thermally excited diffusion.[39,40]

Typical derivatives of line shapes at two orthoconcentrations are shown in Fig. 1 for several tempera-

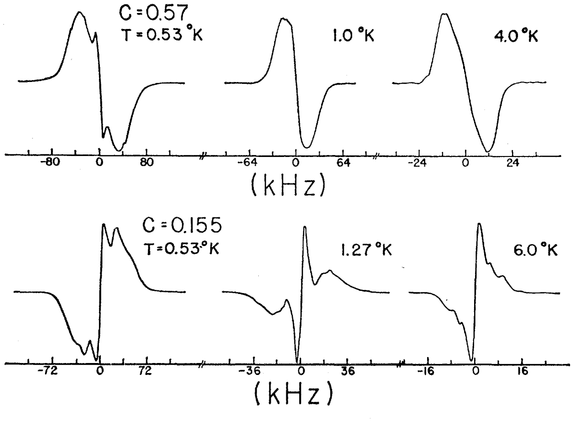

FIG. 1. Representative derivatives of line shapes at two orthoconcentrations in the hcp phase at various temperatures.

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Table II. The second moment M_2 in kHz for hcp H_2 as a function of orthoconcentration and temperature.

T(°K) c	∞[a]	10.0	8.0	6.0	5.0	4.0	3.0	2.35	2.0	1.7	1.5	1.27	1.00	0.816	0.707	0.635	0.578	0.535
0.95	77.5	73.4	76.7	78.3	78.3	78.6	79.9											
0.90	74.5	69.6	73.9	75.9	76.2	76.6	79.8	81.5										
0.85	70.0	65.7	70.5	72.9	73.5	75.4	79.5	82.9	86.0									
0.80	66.0	61.8	66.8	69.0	70.2	74.2	78.8	84.0	88.8	96								
0.75	61.5	58.2	62.0	64.0	66.7	72.5	77.7	83.8	93.5	103	111							
0.70	55.5	53.8	56.2	58.4	62.7	70.2	74.4	84.5	96.2	110	121							
0.65	49.0	49.1	50.1	53.0	57.2	66.0	73.0	84.5	98.7	114	132	153	223					
0.60	43.5	44.7	45.7	49.3	53.6	60.5	70.6	85.0	99.1	138	162	232	307					
0.55	41.0	42.5	43.2	47.1	50.0	55.9	67.1	85.6	100.2	120	142	172	241	331	435	512	627	764
0.50	40.0	41.5	52.5	45.8	48.1	55.9	65.6	86.6	104.2	126	152	190	266	365	466	549	642	811
0.45	38.5	38.0	40.9	45.0	48.3	55.9	70.2	97.5	118.0	142	177	235	323	406	514	593	664	800
0.40	34.0	33.5	37.6	43.2	49.5	55.1	75.9	113.8	134.0	163	202	244	339	439	539	614	676	766
0.35	30.5	28.4	33.8	39.2	45.2	55.0	71.9	109.5	136.5	166	205	243	342	444	531	604	663	720
0.30	26.0	24.0	29.4	34.1	40.0	50.1	65.7	105.5	127.1	160	200	238	333	428	502	572	629	672
0.25	22.5	20.3	25.0	29.1	34.6	44.7	60.0	101.3	117.5	152	194	234	319	410	463	538	592	624
0.20	18.5	17.0	20.5	24.1	29.2	39.2	54.1	88.1	108.3	143	185	230	306	392	429	505	555	575
0.15	14.0	13.5	16.1	19.0	23.9	33.6	48.3	86.8	100.6	135	177	227	293	371	403	467	519	525
0.10	10.0	10.0	11.6	14.0	18.5	27.8	42.0	73.5	93.0	125	168	223	280	349	379	430	479	479

[a] By extrapolation, after neglecting the points at 10°K.

tures. Where comparison of our data could be made with those presented by Sugawara *et al.*,[4] qualitative agreement was found. In Fig. 2, a plot of the ratio M_4/M_2^2 for several concentrations is shown as a function of temperature.

Only two previous experimental studies of M_2 and M_4 have been reported. The first[6] was on a sample of H_2 with $c=0.74$ between 4.2 and 1.7°K, where the NMR detection system was similar to the one in the present work. The second study was by Metzger and Gaines[41] on a sample with $c=0.74$ at 4.2°K, where pulse techniques were used.

Our new data are in excellent agreement with those reported in Ref. 6, but in disagreement with those of Metzger and Gaines,[41] who obtained smaller values for the moments. However, the M_4/M_2^2, found in the different experiments, is in close agreement.

A. Line Shape for Pure Ortho-H_2

Inspection of Table II shows that as $c=1$ is approached, the temperature dependence becomes small, as expected from Eq. (2). Unfortunately, the series in powers of T^{-1} in this equation is found to converge very slowly and more terms have to be computed before any quantitative comparison between experiment and theory can be carried out. The extrapolation of the M_2 and M_4 data to the limit $c=1$ (Table IV) shows that these quantities do not change with temperature down to the phase transition point $T_{c-h}=2.9$°K, below which the hcp phase becomes unstable.[12] This extrapolation can be continued below T_{c-h} to give M_2 and M_4 for the hcp phase, were it stable and were no order-disorder transition to occur. This is shown in Table IV by the values in the parentheses. The moments are then found

Table III. The fourth moment M_4 in 10^3 kHz^4 for hcp H_2 as a function of orthoconcentration and temperature.

T(°K) c	∞[a]	10	8.0	6.0	5.0	4.0	3.0	2.35	2.0	1.7	1.50	1.27
0.95	13.4	12.9	13.5	13.6	13.9	14.2	14.6					
0.90	12.2	11.4	12.3	12.5	12.8	13.2	14.3	15.3				
0.85	10.9	10.1	11.1	11.5	11.9	12.6	14.0	15.8	17			
0.80	10.0	8.9	10.1	10.6	11.0	12.4	13.7	16.5	18.5	24		
0.75	8.8	7.7	8.9	9.5	10.1	12.5	13.3	17.5	22	27.5	35	
0.70	7.0	6.7	7.4	8.2	9.0	12.0	13.0	18.0	24.2	31.5	40.5	
0.65	5.7	5.9	6.2	6.8	7.6	10.3	12.55	19.0	26.0	35	48	68
0.60	5.0	5.2	5.3	6.0	7.0	8.4	12.1	19.0	27.0	38	55	82
0.55	4.4	4.6	4.7	5.4	6.2	7.4	11.7	19.0	27.0	42	63	100
0.50	4.2	4.1	4.6	5.2	6.0	7.5	11.7	20.5	31	46	72	120
0.45	4.0	3.6	4.1	5.0	5.9	8.0	12.0	27	40	57	84	150
0.40	3.2	3.0	3.7	4.8	5.8	8.4	14.5	33.9	51	72	95	155
0.35	2.6	2.5	3.0	5.3	5.5	7.5	14.8	34	53	73	101	152
0.30	1.9	2.0	2.2	3.2	4.3	6.4	14.0	32	50	70	105	150
0.25	1.5	1.5	1.7	2.3	3.3	5.3	10.0	28	40	65	104	148
0.20	1.0	1.1	1.3	1.8	2.5	4.2	8.6	24	35	62	99	148
0.15	0.6	0.7	0.9	1.3	1.9	3.3	7.6	20	30	55	80	139
0.10	0.3	0.3	0.5	0.8	1.3	2.4	6.0	15.5	26	40	76	127

[a] Extrapolated.

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[41] D. S. Metzger and J. R. Gaines, Phys. Rev. **147**, 644 (1966).

TABLE IV. Extrapolated second and fourth moments for ortho-hcp H_2 as a function of temperature. The estimated uncertainty above 3°K is about ± 2 kHz^2 for M_2 and about $\pm 1\times 10^3$ kHz^4 for M_4. For an explanation of the numbers between parentheses, see text.

$T°$(K)	∞	10.0	8.0	6.0	5.0	4.0	3.0	2.35	2.0
M_2 (kHz^2)	81	77.2	78.2	80.2	79.5	79.5	80.0	(79.0±5)	(76±8)
M_4 (10^3 kHz^4)	14.8	14.7	15.0	14.8	15.0	14.5	14.8	(14.5±2)	(15±3)

to stay constant with temperature, at least down to about 2°K, within the uncertainty of the extrapolation.

B. Line Shape at $T=\infty$

The M_2 and M_4 values extrapolated to $T=\infty$ are presented in Tables II and III. In Fig. 3 the $M_{2,0}$ values are compared with the theoretical expectation for a rigid lattice, Eq. (4). At high orthoconcentration, where the relative accuracy is best, the discrepancy between experiment and theory is well outside the experimental error. However, Harris[9] has shown that because of the quantum-crystal nature of solid H_2, the average distance $\langle R^{-3}\rangle^{-1/3}$ between nearest neighbors is slightly higher than the equilibrium value of R for the rigid lattice. For further neighbors, this effect is negligible. The second moment should be written as

$$M_{2,0}=c\times\left(\frac{6}{5h^2}\right)g^4\beta^4\Big(12\langle R^{-3}\rangle^2+\sum_k R_{ik}^{-6}\Big), \qquad (10)$$

where k refers to other than nearest neighbors.

Since the contribution of nearest neighbors to the second moment is the most important one, M_2 will be appreciably reduced. Using an estimated ratio $R^3\langle 1/R^3\rangle=0.95$ from Harris's calculation, one obtains

$$M_{2,0}=82c\ \text{kHz}^2\quad\text{(quantum solid)}. \qquad (11)$$

This result is now in good agreement with experimental results at high orthoconcentrations. The systematic deviation below about $c=0.7$ has not been explained so far.

It should be noted also that $M_{4,0}/M_{2,0}^2$ tends to increase systematically from the value 2.3 at $c=1$ to about 3 at low concentrations. It would hence appear that, as the number of orthoneighbors for a given orthomolecule diminishes, the line approaches the ratio 3.0 expected for a Gaussian line.[42]

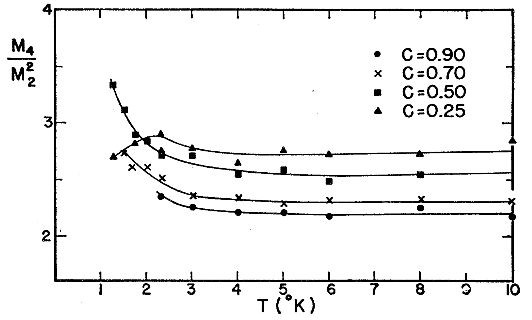

FIG. 2. Plot of M_4/M_2^2 for several orthoconcentrations as a function of temperature.

C. Line Shape at Temperatures below 1°K

As Fig. 1 indicates, there is no evidence of an NMR doublet structure at the lowest temperatures reached, even close to the highest orthoconcentration at which the hcp phase is stable. In Fig. 4 the second moment, expressed as $\Delta M_2=M_2-M_{2,0}$, is plotted as a function of the reduced entropy $\sigma=S/(Rc\ln 3)$. Here S is the molar entropy of solid H_2 and $R\ln 3$ is the maximum molar entropy for a system of $J=1$ molecules. The quantity σ gives a measure of the state of the rotational motion, $\sigma=1$ meaning "free rotation." The entropy is calculated from thermodynamic data.[26,43,44] It is seen that orientational ordering in the hcp phase proceeds smoothly as a function of decreasing entropy. This conclusion is consistent with thermodynamic measurements,[26,43,44] where no lambda-shaped maximum in C_p and $(\partial P/\partial T)_V$ was found at orthoconcentrations below $c=0.6$.

The strong temperature variation of M_2 at low entropy σ indicates that doublets might be observed only when the rotational ordering is practically complete, this is at temperatures below 0.3°K. The expected second moment of such doublets is of the order of $(\frac{3}{2}d)^2=7.2\times 10^3$ kHz^2, assuming $\langle J_{z}{}^2\rangle_{T=0}=0$. In contrast, Pake doublets appear in the cubic phase for $\sigma\lesssim 0.2$ at $c=0.62$, $\sigma\lesssim 0.4$ at $c=0.75$, and $\sigma\lesssim 0.6$ at $c=1.0$, as can be seen from Fig. 4. The moment M_2 increases rapidly below T_{c-h}, and from line-shape measurements in the cubic phase combined with results from specific-heat data,[44] it appears that M_2 has approximately reached its limiting value, $\sim 7\times 10^3$ kHz^2, at $\sigma\lesssim 0.1$. Hence, the behavior of the cubic and hcp phases close to $c=0.6$ with respect to orientational ordering is rather different.

V. LINE SHAPE IN CUBIC PHASE

The effect of ortho-para conversion is to shift T_{c-h} and T_{h-c} to lower temperatures as a function of time. Because of the long time involved in stabilizing the cryogenic system at a desired temperature and recording one NMR absorption line, roughly 20 min, it was found more convenient to study the transition coming from

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[42] See, for instance, A. Abragam, *The Principle of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. 4.

[43] R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954).

[44] B. W. A. Ricketson, thesis, The Clarendon Laboratory, Oxford University, 1956 (unpublished).

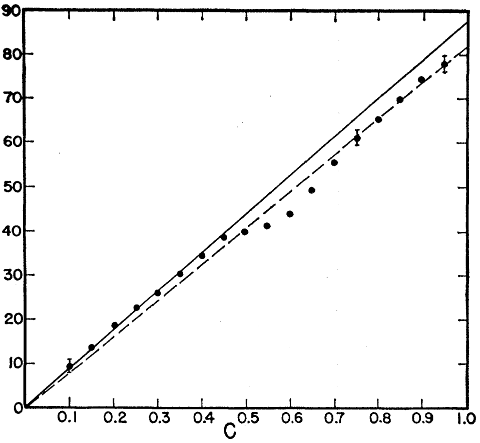

FIG. 3. The second moment for intermolecular nuclear dipole interaction ($T=\infty$) as a function of orthoconcentration. Closed circles: experimental results, second column of Table II. Solid line: calculated $M_{2,0}$ from Eq. (4). Dashed line: Calculated $M_{2,0}$ from Eq. (10), where the "static" correction (Ref. 9) to $\langle R^{-3}\rangle$ between nearest neighbors has been taken into account.

the cubic phase, this is the low-temperature side. This section reports on experiments carried out during the first thermal cycling.

Two variations of the experimental techniques were used for the study of the doublet splitting as a function of temperature. The first one consisted of cooling rapidly a freshly formed sample to 0.5°K where $\delta\nu$ has reached its limiting value. The NMR pattern was then recorded at successively increasing temperatures until the Pake doublet disappeared. In the second method, the first line was again recorded at 0.5°K and the temperature was quickly increased to about 0.2°K below T_{c-h}. Absorption derivatives were then recorded at this temperature as a function of time, while the orthoconcentration decreased.

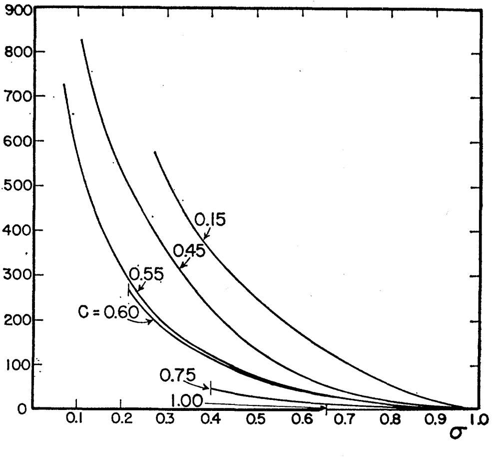

FIG. 4. The second moment in the hcp phase expressed as $\Delta M_2=M_2-M_{2,0}$ versus the reduced entropy $\sigma=S/Rc\ln 3$ for various ortho-H$_2$ concentrations. The small vertical bars indicate the hcp-to-cubic transition. At the left side of the vertical bars, ΔM_2 increases to its limiting value, of the order of 7×10^3 kHz^2, which is reached at $\sigma\approx0.1$.

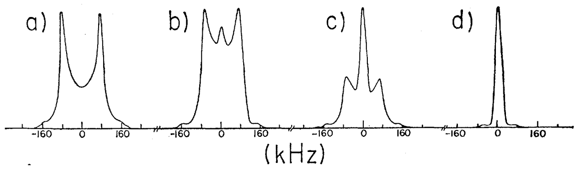

FIG. 5. Computer-integrated line shapes in the cubic phase as a function of increasing temperature. The average orthoconcentration is $c=0.71$, and $T^*\simeq1.64$°K. (a) $T/T^*=0.38$; (b) $T/T^*=0.92$; (c) $T/T^*=0.93$; (d) $T/T^*=0.97$.

In the first method the number of points was limited by the conversion, which changes the concentration by about $\Delta c=0.01$/h for a $c=0.75$ ortho sample, so the experiments lasted only a few hours. In this time, about 10 lines were taken. High-gain and slow-frequency sweep were necessary for best resolution of the doublet close to T_{c-h}. Since ortho-para conversion is still faster at higher orthoconcentrations, no such experiments were taken above $c=0.75$. Typical line shapes are shown in Fig. 5. At 0.5°K, only the doublet and the shoulders are observed, in agreement with the line shape obtained by averaging Eq. (5) over Θ_{Z,H_0}. As the temperature increases, a peak in the center of the structure appears and becomes gradually stronger. This peak probably reflects the presence of domains where the hcp phase is stable. Eventually, the doublet intensity becomes very weak and the peaks are poorly defined. As the splitting diminishes, the satellite structure becomes finally absorbed by the center line. This indicates that the critical order-disorder region in the cubic phase (located around a temperature T^*) is very close to, perhaps slightly above, the temperature where the last evidence of the cubic phase disappears. For a given orthoconcentration, a lower limit of T^* was estimated by extrapolation of $\delta\nu(T)$ to zero. Uncertainty in the extrapolation arises from the difficulty in resolving small splittings. However, from the limiting observed slope $d(\delta\nu)/dT$ and from the expected behavior

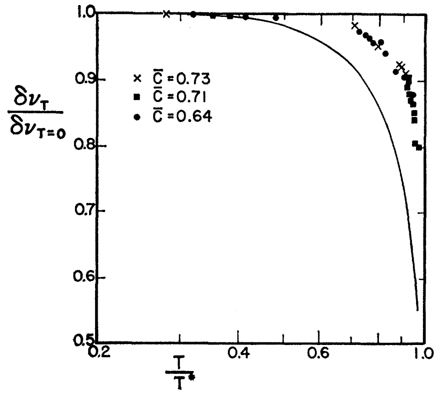

FIG. 6. Reduced plot of $\delta\nu(T)/\delta\nu(T=0)$ versus T/T^* for three orthoconcentrations. For $c=0.64$, 0.71, and 0.73, T^* is, respectively, 1.28, 1.64, and 1.75°K. The solid line is the theoretical curve of Raich and Etters (Ref. 19), where crystalline field splitting effects are not included. For this curve we put $T^*=T$.

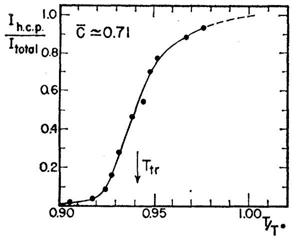

FIG. 7. Ratio of the center line intensity to the total line intensity as a function of reduced temperature T/T^* for $c=0.71$, $T^*=1.64$°K. Some of the points in this figure were obtained from the curves shown in Fig. 5. T_{tr} denotes the center of the transition region.

close to an order-disorder transition, we conclude that T^* is probably not more than about 0.05°K above the values quoted for Fig. 7. A small correction to the data was made to take into account the slight change of orthoconcentration during the experiment and the final result then gave the curves for constant orthoconcentrations, shown in Fig. 6.

It might be noted here that the cubic-to-hcp transition temperature is often defined as the temperature at the center of the interval over which a certain parameter varies during the transition. Such a parameter is the intensity of an x-ray reflection[12] or the pressure at constant volume.[26] For all our experiments, the lower limit of T^* was found to be higher than T_{c-h} by about 0.07°K. If these observations are extrapolated to pure ortho-H_2, then T^* is about 3.0°K, in fair agreement with the estimate by Harris.[9] An extrapolation to lower orthoconcentrations, based on the T_{c-h}-versus-c data,[12,26] shows that the cubic phase will not be stable for $c \lesssim 0.6$. From the results of Sec. IV, the absence of a cubic phase implies the absence of a rotational transition and hence this concentration $c=0.6$ must be considered close to the critical one, c_{crit}. This value is much higher than one would expect from the theoretical models mentioned before.[19,28,29]

The reduced plot from the second method of recording data was made keeping T constant and putting $T^*=Ac+B$, which is an acceptable approximation over the orthoconcentration range covered. The constants A and B were determined from the extrapolation of $\delta\nu$ to zero for several orthoconcentrations. The qualitative agreement between theory[19] and experiment is as good as can be expected, considering the approximation in theory and the uncertainty in the data analysis. A choice of a larger T^* will shift the experimental curve to the left. The presence of a large and variable proportion of the hcp phase in the sample near T^* could possibly influence $\delta\nu(T)$ and introduce further uncertainty in the interpretation of the results. Because of this, no attempt was made to include crystalline field effects[18] in fitting the theory to the experiment.

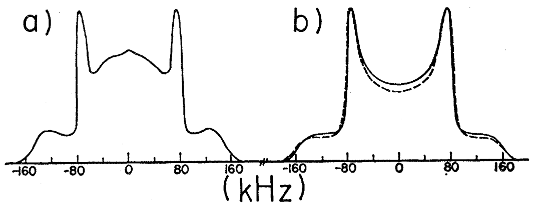

FIG. 8. Effect of the rate of crystallization on the line shape in the cubic phase. Orthoconcentration $c=0.65$, $T=0.5$°K (a) after slow crystallization, and (b) the same sample after fast crystallization. Dashed curve: theoretical curve for a powdered sample, taking into account intermolecular dipolar broadening.

Schuch, Mills, and Depatie[12] have followed by means of x-ray diffraction the structure changes from hexagonal to cubic to hexagonal. After repeated thermal cycling, the hcp phase reappeared only incompletely upon warming, and the authors suggested the formation of an intermediate close-packed structure. Since in our experiments only one thermal cycling was carried out, we have assumed the proportion of this intermediate phase to be small. We have therefore attributed the nearly Gaussian center line to the hcp phase and the NMR doublet structure to the cubic phase. In Fig. 7, we have plotted the ratio $R=I_{\text{hcp}}/I_{\text{tot}}$ versus T/T^*. Here I_{hcp} is the integrated intensity of the nearly Gaussian center line, and I_{tot} is the total integrated absorption intensity. The temperature range ΔT over which the two crystalline phases coexist is wider than indicated from x-ray measurements,[12] where it is approximately 50 mK. This discrepancy is not understood, unless the nature of the container of the H_2 sample and thermal history influence ΔT.

A survey of the cw data analysis showed that the splitting $\delta\nu$ at 0.5°K varied somewhat from sample to sample in a random way, independently of orthoconcentration, and so did the shape of the line. We believe that these variations may result from the H_2 sample's not being a perfect powder, and hence the average over the factor $1-3\cos^2\Theta_{Z,\text{H}_0}$ is not the same in different experiments. This is shown in Fig. 8. However, the temperature variation of $\delta\nu$ should not be affected. From an average of seven experiments at different orthoconcentrations $0.65<c<0.85$, we find that the limiting, low-temperature value of the splitting is $\delta\nu=165\pm5$ kHz. Assuming $J_Z{}^2=0$, the resulting value of d is $\delta\nu/3=55\pm2$ kHz. This is slightly smaller than d for the free molecule, in agreement with the observation of Reif and Purcell.[3] Alternatively, we may analyze the value of the splitting using the d for the free molecule, giving $\langle 2-3J_Z{}^2\rangle_{T=0}=1.90\pm0.07$. This compares with a value of

$$\langle 2-3J_Z{}^2\rangle_{T=0}=2(1-0.02/c+0.032c)\approx 1.98 \qquad (12)$$

predicted by Harris.[9] In the parentheses on the right-hand side of Eq. (12), the second term represents the zero-point motion[34] and the third one results from a perturbation calculation[9] that takes into account the fact that $J=1$ is not a perfect quantum number.

In two separate experiments, the low-temperature splitting for a given H_2 sample was observed at, respectively, 1.25 and 0.5°K as a function of decreasing orthoconcentration between $c=0.85$ and $c=0.63$. The line shape did not change during either experiment but $\delta\nu_{\text{obs}}$ at a given temperature was found to decrease with orthoconcentration. By extrapolating to the limiting splitting at $T=0$ using the results of Fig. 6 and by taking into account intermolecular broadening [Eq. (8)], it was found that $\delta\nu(T=0)$ decreases by $(2.5\pm1.0)\%$, which is slightly larger than that predicted from Eqs. (12) and (7), namely, 1.4% over the orthoconcentration range mentioned above.

VI. CONCLUSION

The rotational ordering in the cubic phase, as investigated by NMR, seems qualitatively understood, but the high value of the critical orthoconcentration deserves further theoretical research. The study of the rotational angular momentum $\langle J_Z{}^2\rangle$ in the cubic phase near the ordering region may be complicated by the coexistence of both hcp and cubic phases over an extended temperature range. In solid D_2, it has been shown[12] that the cubic phase can be stabilized up to higher temperatures after repeated thermal cycling through the crystalline transition. Hence a study of NMR in the cubic phase of deuterium may be promising and may avoid the difficulty of phase coexistence and also of the large ortho-para conversion one encounters in solid H_2. Such a study will be undertaken in this laboratory in the near future.

Several phenomena in H_2 ortho-para solutions are yet to be understood. One of them is that the NMR doublet, expected at intermediate orthoconcentrations at temperatures where the orientation of the $J=1$ molecules is almost complete, has not been observed. More experiments are in progress in a different cryostat to study the line shape at $c\approx0.55$ at temperatures below 0.4°K with the hope of observing this doublet.

We also hope that the information obtained so far will stimulate more theoretical research on the rotational ordering of ortho-para solutions.

ACKNOWLEDGMENTS

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Spin-Lattice Linewidths for EPR in Multilevel Systems

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The magnetic relaxation of an isolated moment via contact coupling to conduction-electron spins is considered for the case where the splitting scheme of the moment shows an effective-spin doublet plus other levels. Relaxation transitions proceeding via these other levels are considered, and it is shown that they produce significant deviations from the proportional-to-temperature linewidth obtained by considering only direct transitions within the doublet. Some results for phonon processes are also given.

I. INTRODUCTION

In treating paramagnetic resonance transitions among a few low-lying levels of an isolated magnetic ion, it is often convenient to consider these levels as being described by an "effective spin," while the remaining levels can be for some purposes ignored. However, matrix elements of the dynamic spin-lattice Hamiltonian connecting the effective spin levels to the other levels correspond to processes in which "effective spins" are not conserved in number but are destroyed and recreated. It is clear that such processes can contribute to the relaxation of the effective spin system and cannot, in general, be neglected. A well-known example is the so-called "two-step" phonon-induced longitudinal relaxation of rare-earth ions.[1,2]

In the present paper, we consider relaxation by conduction-electron spin flip of crystal-field-split moments in dilute rare-earth alloys, which have recently become of considerable interest for electron-paramagnetic-resonance (EPR) experiments.[3,4] We will show that in such systems the other-level transitions can lead to significant deviations from the proportional-to-temperature linewidth which is conventionally considered to be the "earmark" of relaxation via conduction-electron spins.[5]

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[4] C. R. Burr and R. Orbach, Phys. Rev. Letters **19**, 1133 (1967).

[5] A bottleneck in conduction-electron spin relaxation can also alter the temperature dependence of the linewidth [see, for example, A. J. Heeger, A. C. Gossard, and J. H. Wernick, J. Appl. Phys. **38**, 1251 (1967)]. These effects need not be considered here since the g value of a crystal-field doublet is normally quite different from two.