

Solid Oxygen and Hydrogen

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Solid Hydrogen: The Ideal Analog of an Antiferromagnet*

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A physically meaningful analogy is drawn between the ordering and dynamical behavior of molecular rotations in solid hydrogen and the ordering and dynamical behavior of magnetic spin systems. In solid hydrogen the magnitude J of the rotational angular momentum is a good quantum number. Molecules having $J=1$ resemble spin one magnetic moments, whereas those with $J=0$ are "non-magnetic." Solid solutions of these two species are analogs of magnetic alloys. The thermodynamic properties, in particular the order parameter, the specific heat, and the nuclear magnetic resonance properties are similar to those of magnetic systems. As for the dynamics, the small librations about the ground state are analogs of spin waves, and the interactions between the librational excitations are similar to, but larger than, the usual spin-wave interactions. This circumstance enables the direct observation of the two-libron spectrum and also leads to large anharmonic shifts in the single-libron spectrum.

I. INTRODUCTION

The analogy between spin waves in magnetic systems and molecular rotations in solid hydrogen, while only qualitative, is nevertheless very direct and physically revealing. The purpose of this paper is to develop this analogy in detail. We shall discuss several properties of solid hydrogen with respect to which it is truly an ideal "magnetic" system.

This paper is aimed at "magneticians" and it is hoped that the analogy mentioned above will provide a readily understandable and esthetically pleasing introduction to molecular rotations in solid hydrogen. Accordingly, although familiarity with concepts of magnetism is taken for granted, no prior knowledge of solid hydrogen will be assumed. The necessary background material is presented in Sec. II. The analogy between solid hydrogen and magnetic systems is described more fully in Sec. III, and in Secs. IV and V this analogy is used to discuss the static and dynamic properties of solid hydrogen. Section VI contains concluding remarks.

II. PROPERTIES OF HYDROGEN MOLECULES

The purpose of this section is to review some of the fundamental properties of hydrogen molecules.

First let us discuss the rotational motion of a free hydrogen molecule. The hydrogen molecule is very nearly a rigid rotator, and as such its orientational wavefunctions are the spherical harmonics $Y_J^M(\theta, \varphi)$, where θ and φ are the angular coordinates of the molecular axis. Since $Y_0^0(\theta, \varphi)$ is a constant, we see that ($J=0$) molecules are to all intents and purposes spheres, rather than dumbbells, as one might have thought! Thus, an orientational potential will not affect these molecules, and they are analogous to nonmagnetic ions. Molecules with $J=1$ have three

substates, $M=\pm 1$ or 0 , and thus look exactly like magnetic spins with $S=1$. They can be aligned by orientational interactions just as magnetic spins are aligned by exchange interactions.

For H_2 the Pauli exclusion principle dictates that for ($J=0$) molecules the nuclear spins of the protons are antiparallel, i.e., that their resultant nuclear spin is $I=0$, whereas for ($J=1$) molecules the nuclear spins are parallel, i.e., they have $I=1$. Molecular levels with $J>1$ are not populated at low temperature. Even in the solid J remains a good quantum number, because the anisotropic interactions between molecules are small compared to the separation between J levels. There is a continual conversion of ($J=1$) molecules into ($J=0$) molecules, since the latter have lower energy. This conversion is rather slow, as it involves a change of nuclear spin. As a result, experiments may be done on samples containing an arbitrary fixed concentration x of ($J=1$) molecules. It is clear that such an alloy is analogous to a magnetic alloy containing a concentration x of spin 1 and $1-x$ of spin 0. In contrast to the magnetic case, however, alloys in solid hydrogen involve an insignificant variation in force constants and no mass defect. In this sense solid hydrogen indeed constitutes an ideal "magnetic" alloy. A simplified phase diagram for alloys of solid H_2 is shown in Fig. 1. The phase diagram for alloys of solid D_2 is similar. For more details on these two solids, consult Refs. 7, 8, 17, and 18.

Let us now discuss the molecules in the solid. They are virtually undistorted from free molecules.¹ They interact mainly via weak long range forces such as van der Waals interactions.^{1,2} It is these forces which determine such bulk properties as the compressibility or the cohesive energy. The orientational interactions are weaker and are mainly due to the interaction between the static electric quadrupole moments of the

molecules.² Thus a reasonable model of the orientational state of solid hydrogen includes only electrostatic quadrupole-quadrupole (*EQQ*) interactions on a rigid lattice.

To understand these interactions it is useful to compare them to the more familiar dipole-dipole interactions. Whereas the latter are scaled by μ^2/R^3 , where μ is the dipole moment and R the separation, the *EQQ* interactions are scaled by e^2Q^2/R^5 , where eQ is the quadrupole moment of the hydrogen molecule. The *EQQ* interaction \mathcal{H}_{EQQ} is of the form²

$$\mathcal{H}_{EQQ} = \sum_{i < j} \Gamma(R_{ij}) f(\omega_i, \omega_j), \quad (1)$$

where $\Gamma(R) = 6e^2Q^2/25R^5$ is the *EQQ* coupling constant and $f(\omega_i, \omega_j)$ is a function of order unity of the orientations ω_i and ω_j of the interacting molecules. In order to visualize the *EQQ* interaction we show in Fig. 2 the interaction of two linear quadrupoles compared to that of two dipoles. Note that whereas two dipoles have highest and lowest energy when they are parallel or antiparallel, the *EQQ* energy is minimized when the molecules are perpendicular to one another and is maximized when they are parallel to one another.

These properties enable us to make several important observations about the ordering of molecular axes in solid hydrogen. First, we can estimate the ordering temperature, T_λ , to be roughly of order $kT_\lambda \sim z\Gamma_0$, where z is the number of nearest neighbors and $\Gamma_0 \equiv \Gamma(R_0)$, where R_0 is the nearest-neighbor separation. In this regard Γ_0 is analogous to the exchange integral J in magnetic systems. It is worth noting, however, that while J is a phenomenological parameter which is normally not calculated from first principles, Γ_0 is so calculable, since the quadrupole moment of the hydrogen molecule has been evaluated rather accurately.³ Thus, any many-body effects, such as phonon renormalizations,⁴ which alter the value of Γ_0 are potentially observable. Moreover, knowing the microscopic interactions as a function of separation enables one to calculate further neighbor interactions,⁵ which are nonnegligible, since $\Gamma \sim R^{-5}$. Finally, since it is impossible to construct a close-packed lattice in which all pairs of molecules are perpendicular, the lowest-energy configuration of a lattice of quadrupoles is not obvious. However, Nagai and Nakamura⁶ found that the classical ground state for an fcc lattice is one in which there are four sublattices. All molecules on a given sublattice are parallel and point along one of the four different $[111]$ directions. We shall refer to this state as the "Néel state."

FIG. 1. The simplified phase diagram of solid H₂. The orientationally disordered (ordered) phase has hcp (fcc) structure.

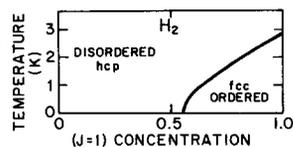
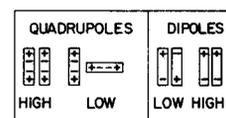


FIG. 2. The high- and low-energy configurations for linear quadrupoles (left) and for dipoles (right).



In conclusion we note a few of the bulk properties of solid hydrogen. It crystallizes in an hcp lattice at about 14 K and is a very compressible solid: even moderate pressures produce significant increases in Γ_0 . As indicated in Fig. 1, the order-disorder transition is accompanied by a change in crystal structure.^{7,8} However, for simplicity we shall ignore the influence of lattice structure on this transition.

III. SOLID HYDROGEN AS A MAGNETIC ANALOG

In this section we describe the analogy between the ordering and dynamical motion of spins in magnetic systems and the ordering and dynamical motion of molecular axes in solid hydrogen. In later sections this analogy is used as a physical basis for understanding the properties of solid hydrogen.

Let us first consider the ordering processes in the two systems. In the magnetic case the alignment of spins at high temperature is essentially random. Similarly, the alignment of the molecular axes in solid hydrogen is essentially random at temperatures well above the order-disorder transition. In both cases there is a transition temperature where the alignment has anomalous behavior. For the magnetic case the order parameter σ is simply the sublattice magnetization:

$$\sigma(T) = \langle S_z \rangle_T, \quad (2)$$

where $\langle \rangle_T$ indicates a thermal average, whereas in solid hydrogen the order parameter is defined by

$$\sigma(T) = \langle 3 \cos^2\theta - 1 \rangle_T, \quad (3)$$

where θ is the angle between the molecular axis and the preferred axis of alignment. Schematic diagrams of the temperature dependence of the order parameter are presented in Fig. 3. For hydrogen in the "paramagnetic" regime $\sigma(T)$ does not vanish, in contrast to the magnetic case.

The analogy described above also applies to dynamical properties. In magnetic systems the elementary excitations are spin waves in which the spins perform small oscillations about their equilibrium orientation. Likewise in solid hydrogen there exist librational waves^{9,10} in which the molecular axes perform small torsional oscillations about their equilibrium orientations. These ideas suggest that such torsional oscillations (called librations) might be viewed as optical phonons. As we have noted, however, the total angular momentum J of a molecule in the solid is a good quantum number, and hence J is analogous to the spin quantum number in magnetic systems. The fact that there are

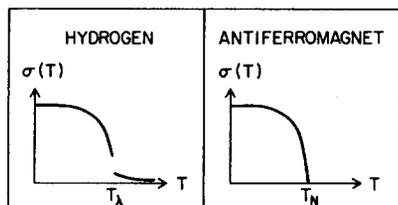


FIG. 3. The temperature dependence (schematic) of the order parameter for solid hydrogen (left) and for an antiferromagnet (right).

$2J+1$ rotational states in which the molecule can "rotate" suggests intuitively an analogy with the precessional motion of a spin within its $2S+1$ quantum states.

IV. STATIC "MAGNETIC" PROPERTIES OF SOLID HYDROGEN

In this section we treat in detail the analogy between solid hydrogen and magnetic systems with regard to their static properties, viz. the order parameter, the specific heat, and the properties of isolated pairs of "magnetic" molecules.

A. The Order Parameter

Let us discuss the long-range order parameter. We have seen in Fig. 3 the qualitative similarity between the ordering of magnetic systems and of molecular rotations. It is interesting that the order parameter is measured via nearly identical NMR techniques in the two cases. In magnetic systems the nuclear spins interact with the electron spins via the hyperfine interaction $A\mathbf{I}\cdot\mathbf{S}$, where \mathbf{I} is the nuclear spin and A is a constant. The hyperfine field the nuclear spin sees is simply $A\langle\mathbf{S}\rangle_T$, since fluctuations in \mathbf{S} are too rapid for the nuclear spin to follow. Thus, measurement of ν_T , the NMR frequency at temperature T leads to a determination of $\sigma(T)$ ¹¹:

$$\sigma(T)/\sigma(0) = \nu_T/\nu_0. \quad (4)$$

A similar method can be used for solid hydrogen.¹² Consider first a nonrotating H_2 molecule. The hyperfine field, H_{hf} , at one of the protons is given by

$$H_{\text{hf}} = H_0 \pm H_d, \quad (5)$$

where H_0 is the applied magnetic field and H_d is the dipolar field due to the other proton in the molecule:

$$H_d = (\mu/a^3) (3 \cos^2\theta_n - 1), \quad (6)$$

where μ is the proton magnetic moment, a the distance between protons in the molecule, and θ_n the angle between H_0 and the molecular axis. Since the choice of sign in Eq. (5) depends on the orientation of the nuclear spin of the other proton relative to H_0 , one expects two NMR frequencies. In the solid the molecule

rotates too rapidly for the nuclear spin to follow, and as a result we set

$$H_d = (\mu/a^3) \langle 3 \cos^2\theta_n - 1 \rangle_T, \quad (7)$$

so that H_d is proportional to $\sigma(T)$.

This method is not ideal for solid H_2 , because the NMR lines are severely broadened by the random dipolar interactions between protons in different molecules. For D_2 the hyperfine field is relatively larger than the intermolecular dipolar interaction, and hence more precise measurements can be made in this case. Thus, Maraviglia *et al.*¹³ were able to determine the critical index for σ as a function of T . Since σ is the analog of the magnetization, one writes

$$\sigma(T) \sim (T_\lambda - T)^\beta, \quad T \rightarrow T_\lambda^-, \quad (8)$$

and the experimental result is $\beta = 0.33 \pm 0.06$. This value is close to those for magnetic and other systems.¹⁴

Above the ordering temperature the separation of the two NMR lines is smaller than their width, and hence $\sigma(T)$ is determined,¹⁵ albeit rather inaccurately, via the temperature-dependent contribution to the NMR linewidth.¹²

It is also interesting to study the order parameter of $(J=0)-(J=1)$ alloys. At zero temperature the concentration dependence of the order parameter and of the transition temperature T_λ (see Fig. 1) are similar. In this behavior solid hydrogen resembles an antiferromagnetic alloy in which magnetic spins are randomly replaced by nonmagnetic ions. This replacement weakens the resistance of the spins to zero-point fluctuations. Thus, as the concentration x of magnetic spins decreases, σ decreases, until at some critical value of concentration $x = x_c$ long-range order disappears. Analogous behavior occurs in solid hydrogen for the same reason. Due to zero-point fluctuations the true ground state of the orientational system in solid hydrogen differs from the "Néel state" in which each molecule is aligned in its molecular field. As $(J=1)$ molecules are replaced by "nonmagnetic" $(J=0)$ molecules, the fluctuations increase, just as in the magnetic case. The results of Ref. 16 represent an ideal case, since, as noted above, the absence of mass defects, etc. makes solid hydrogen an ideal magnetic alloy.

B. The Specific Heat and $(\partial p/\partial T)_V$

We first consider the relation between the specific heat at constant volume C_V and $(\partial p/\partial T)_V$. On dimensional grounds we write the rotational free energy F in terms of a function ϕ of Γ_0/kT :

$$F = kT\phi(\Gamma_0/kT). \quad (9)$$

Within the spirit of the rigid lattice approximation the free energy depends on the volume only through the volume dependence of the E_{QQ} coupling constant Γ_0 . It then follows that there is a contribution to the pressure due to molecular rotation. In fact, one can

derive from Eq. (9) the relation^{17,18}

$$(\partial P/\partial T)_V = -(\partial \ln \Gamma_0/\partial V) C_V \equiv \gamma_{\text{rot}} C_V/V, \quad (10)$$

where γ_{rot} is a "rotational" Grüneisen constant. Since $\Gamma_0 \sim R^{-5}$, we see that γ_{rot} should be about 5/3. Of course, in this relation p and C_V refer only to orientational contributions. They may be determined from the total pressure and total specific heat by subtracting off the lattice contributions which are measured separately in the pure ($J=0$) solid.

In principle the same technique can be applied to magnetic systems. In practice the separation of lattice and magnetic contributions is usually difficult. An important exception is solid He³, which is an ideal Heisenberg antiferromagnet with a Néel temperature of order 10^{-3} K. There the "exchange" Grüneisen constant analogous to γ_{rot} in Eq. (10) is very large, and it is possible to effectively measure the high-temperature specific heat for $T \gg T_N$ very precisely.¹⁹

Let us now consider the high-temperature orientational specific heat of solid hydrogen. The calculations, based on high-temperature expansions in the parameter (Γ_0/kT) , are similar to those for magnetic systems where the comparable parameter is (J/kT) . It was found,²⁰ using a series of four terms in (Γ_0/kT) , that a Padé approximate fits the data for both D₂²¹ and H₂²² reasonably well. As in magnetic systems,²³ the "high-temperature" regime (where the first term is dominant) corresponds to surprisingly large values of T/T_λ .

Due to the difficulty in subtracting off the lattice specific heat, high-temperature determinations of J have usually involved measurement of the magnetic susceptibility. In solid hydrogen the analogous quantity is the electric polarizability, α . For an H₂ molecule α is anisotropic, having the value α_{\parallel} or α_{\perp} depending on whether the applied electric field \mathbf{E} is parallel or perpendicular to the molecular axis \hat{n} . For general orientations we have

$$\alpha = \frac{1}{3}\alpha_{\parallel} + \frac{2}{3}\alpha_{\perp} + \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})(3 \cos^2 \theta_{\mathbf{E}} - 1), \quad (11)$$

where $\theta_{\mathbf{E}}$ is the angle between \mathbf{E} and \hat{n} . Thus, in principle measurement of the polarizability yields $\langle 3 \cos^2 \theta_{\mathbf{E}} - 1 \rangle_T$, which is proportional to the order parameter.

C. Pair Interactions

Since solid hydrogen is such an ideal magnetic alloy, the strength of pair interactions between ($J=1$) molecules determined at very low ($J=1$) concentration is relevant to the entire range of concentration. In contrast, the interactions vary with composition in the mixed rare-earth garnets.²⁴ The same problem occurs in more severe form for Jahn-Teller systems,²⁵ since there the concentration dependence of the strains is crucial. Accordingly, it would be delightful if the energy levels of an isolated pair of ($J=1$) molecules surrounded only by "nonmagnetic" ($J=0$) molecules could be observed directly using optical or resonance techniques,

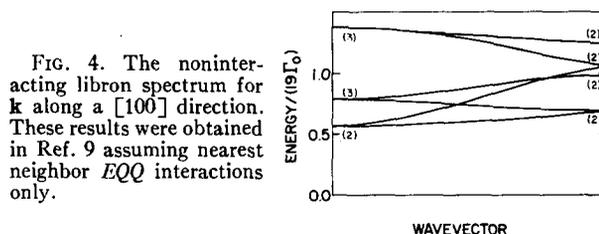


FIG. 4. The noninteracting libron spectrum for \mathbf{k} along a [100] direction. These results were obtained in Ref. 9 assuming nearest neighbor EQQ interactions only.

as Birgeneau *et al.*²⁶ have done for the analogous magnetic case (see Note added in proof).

An alternative method is to measure the thermodynamics properties of an isolated pair of ($J=1$) molecules. This has been done both by $(\partial p/\partial T)_V$ ^{17,18} and by NMP²⁷ measurements. As we have said, the former is essentially equivalent to the specific heat. The NMR measurement determines the order parameter, which for a pair of ($J=1$) molecules is $\langle 3 \cos^2 \theta_p - 1 \rangle_T$, where θ_p is the angle between one of the molecular axes and the vector connecting the two molecules. Since the energy levels of a pair of ($J=1$) molecules are well known, it is easy to calculate the specific heat and the order parameter as a function of the variable (Γ_0/kT) . By fitting the experimental data^{18,27} to such calculations the value of Γ_0 for H₂ was found to be about 0.57 cm^{-1} . The fact that the lattice is not rigid probably explains the discrepancy between this value and that (0.698 cm^{-1}) predicted for a rigid lattice using the first-principles calculations of the quadrupole moment eQ .

Experiments on very dilute ($J=1$) hydrogen can also be used to determine the "single-ion" crystalline field. In the hcp lattice the crystalline potential is of the form

$$V = V_c(J_z^2 - \frac{2}{3}) \quad (12)$$

which would remove the threefold rotational degeneracy of a ($J=1$) molecule even in the absence of EQQ interactions. It can be shown that at temperatures which are large in comparison to the magnitude of the crystalline field energy, the dipolar field H_d appearing in Eq. (5) is proportional to V_c , which scales the crystalline field. Using the approach, Hardy and Gaines²⁸ have determined that $|V_c/k|$ is of order 10^{-2} K. Thus the crystalline field is only important at extreme dilution when the EQQ interactions become weak.

V. DYNAMICAL PROPERTIES

Let us see how the analogy we have been describing leads to an understanding of the dynamical properties of solid hydrogen. We consider the following dynamical properties: (1) the libron spectrum, (2) the specific heat of librations, and (3) the nuclear spin-lattice relaxation time T_1 .

A. The Libron Spectrum

The elementary excitation spectrum for rotations in solid hydrogen is analogous to that of an anisotropic

antiferromagnet. In both systems the approximate ground state is one in which each spin or molecule is aligned in its own molecular field. In the simple antiferromagnet there are two spins per unit cell and hence two spin deviation operators per unit cell. As a result the antiferromagnetic spin-wave spectrum has two branches. For solid hydrogen, as we have seen, the "Néel state" is one wherein each unit cell contains four molecules, each of which can librate in either of two perpendicular directions. Hence the librational wave (libron) spectrum has eight branches.^{9,10} For the antiferromagnet the presence of an anisotropy energy destroys the rotational invariance and leads to a gap in the spin-wave spectrum. For solid hydrogen the *EQQ* interactions are already very anisotropic, and hence the libron spectrum has a large energy gap. The non-interacting libron spectrum calculated in Ref. 9 is shown in Fig. 4.

Let us now discuss the interaction between the elementary excitations. Ever since Dyson's famous paper²⁹ on this subject in 1956, great efforts have been made to observe spin-wave interactions. They are usually small, and in particular they vanish in the zero-wave vector limit and, for the ferromagnet, in the zero-temperature limit. For the antiferromagnet at zero temperature they lead to small apparent changes³⁰ in the exchange constant J . However, since J is a phenomenological parameter, it is hard to verify this renormalization experimentally. The interactions between librations is a larger and experimentally more accessible effect for several reasons. First, since the *EQQ* interaction is not rotationally invariant, the zero-wave vector librations are not perfect modes, and hence libron-libron interactions do not vanish in the zero-wave vector limit. Second, the effects of zero-point motion lead to renormalizations in Γ_0 , a parameter which is not only calculable from first principles, but also observable independently in other ways. Finally, the cubic anharmonic term in the *EQQ* interaction is fortuitously very large.³¹

Now we discuss the effect of libron-libron interactions on the single-libron spectrum. It is instructive to recall the results for magnetic systems. We note that in the random phase approximation (RPA) each spin precesses in the average uncorrelated field of its neighbors. As a result, the spin-wave energy $\epsilon_{\mathbf{k}}$ is scaled by $\langle S_z \rangle$. Thus for an antiferromagnet at zero temperature the RPA gives

$$\epsilon_{\mathbf{k}}/\epsilon_{\mathbf{k}}^0 = \langle S_z \rangle / S, \quad (13)$$

where $\epsilon_{\mathbf{k}}^0$ is the spin-wave energy in the absence of zero-point motion and $\langle S_z \rangle$ is the average of S_z in the true ground state. Due to zero-point motion $\langle S_z \rangle = S(1-\delta)$, so that

$$\epsilon_{\mathbf{k}}/\epsilon_{\mathbf{k}}^0 = 1 - \delta < 1. \quad (14)$$

A similar argument holds when the RPA is used to treat the libron spectrum in solid hydrogen. Here

$\langle S_z \rangle / S$ is replaced by $\langle \sigma \rangle / \sigma^0$, where σ^0 is the value of the order parameter in the molecular field ground state, i.e., in the "Néel state," and $\langle \sigma \rangle$, the value of the order parameter in the true ground state, is smaller than σ^0 due to zero-point motion.

The above results are incorrect, and use of either Dyson's formalism,²⁹ Oguchi's method,³⁰ or Keffer and Loudon's physical argument³² shows that the spin-wave energy is approximately scaled by the internal energy rather than by the magnetization. Thus in place of Eq. (13) we estimate

$$\epsilon_{\mathbf{k}}/\epsilon_{\mathbf{k}}^0 \sim |E|/|E^0|, \quad (15)$$

where E is the true ground-state energy and E^0 is the energy of the Néel state. Since $|E| > |E^0|$, we see that due to zero-point motion we have

$$\epsilon_{\mathbf{k}}/\epsilon_{\mathbf{k}}^0 > 1! \quad (16)$$

The same effect occurs for the quartic libron-libron interactions in solid hydrogen, and hence they tend to increase the single-libron energy in accord with Eq. (16). However, unlike the Heisenberg Hamiltonian, the *EQQ* interaction has cubic anharmonic terms, which are large and which are completely ignored by the RPA. They lead to substantial downward shifts in the libron energies, and the net result is that the perturbed libron energies are smaller than those found using noninteracting librations.³¹ As can be seen in Fig. 5, inclusion of libron-libron interactions markedly improves the fit to the single-libron Raman spectrum.³³ In addition, the value of Γ_0 , viz. $\Gamma_0 = 0.79 \text{ cm}^{-1}$, obtained by fitting the anharmonic calculations to the observed spectrum is much closer to the theoretically expected value and agrees better with other determinations. Thus the effect on the elementary excitations of libron-libron interactions is experimentally confirmed to a much greater degree than has heretofore been possible for spin-wave interactions in magnetic systems.

Undoubtedly the best way to observe the single-libron spectrum is via the inelastic scattering of neutrons. The experiment is more difficult for solid hydrogen than for magnetic systems,³⁴ however. We note that because of its low ($J=1$) \rightarrow ($J=0$) conversion rate and larger fraction of coherent scattering solid D_2 is to be preferred over solid H_2 for such experiments. The cross section for the inelastic scattering of neutrons will provide a determination of the full frequency and wavevector-dependent "susceptibility" of librations. In this way the energy, $\epsilon_{\rho}(\mathbf{k})$, and the decay rate, $\gamma_{\rho}(\mathbf{k})$, can be determined for all the libron modes, $\rho = 1-8$. In addition, the scattering cross section will display the two-libron effects mentioned below.

Let us now consider the Raman processes^{33,35} in which a long-wavelength photon is scattered and elementary excitations are created in the system. For antiferromagnets the one-magnon process, analogous to that for librations in solid hydrogen shown in Fig. 6(b), is for-

bidden by symmetry, and hence the lowest-order process is that in which two magnons with total momentum zero are created on neighboring sites.³⁶ [See Fig. 6(a).] For solid hydrogen this process is unimportant,³⁷ but the same net effect is realized³¹ by creating a virtual libron which decays into two final-state librons due to the large cubic anharmonic terms mentioned above [see Fig. 6(c)]. Whereas the microscopic mechanism for the two-magnon process is unclear,³⁶ the matrix elements for all processes in Fig. 6 are known for solid hydrogen, since the interaction of the hydrogen molecule with photons (through its polarizability) and the cubic libron-libron interactions due to *EQQ* anharmonicity are known. The theoretical relative intensities³¹ for the Raman spectrum of solid hydrogen are in good agreement with the experiment.³³

Elliott and Thorpe³⁶ have shown that the two-magnon spectrum has a peak which is shifted from that of two noninteracting magnons by their binding energy. This binding energy can be evaluated within the Ising model, where it is the decrease in energy of two spin reversals when they are on neighboring sites. A similar calculation³¹ yields a two-libron spectrum for solid hydrogen in agreement with the Raman data.³³

B. Specific Heat of Librons

Although direct optical observation, where possible, is the most sensitive way to observe spin-wave excitations, they can also be detected via their specific heat. In the iron garnets both techniques have been used to detect the acoustic and low-lying optical spin-wave modes.^{38,39} For solid hydrogen Ramm *et al.*¹⁷ have essentially measured the libron specific heat via the technique of $\partial p/\partial T$ measurement discussed above. To fit their results they scaled the theoretically calculated density of states for noninteracting librons,¹⁰ by treating the average libron energy Δ as an adjustable parameter. Their results over a wide range of temperature and concentration, x , of ($J=1$) molecules give

$$\Delta(x) = \Delta_0(2.0x - 1.0), \tag{17}$$

where $\Delta_0 = 21.2\Gamma_0$. For $x \approx 1$ one might have expected

$$\Delta(x) = x\Delta_0. \tag{18}$$

Since solid hydrogen is truly an ideal magnetic alloy, the result in Eq. (17) poses a clear challenge to theoreticians.

FIG. 5. The Raman spectrum of orientationally ordered solid D_2 (top) compared to non-interacting libron theory (middle) and anharmonic libron theory (bottom). The heights of the lines indicate their intensity.

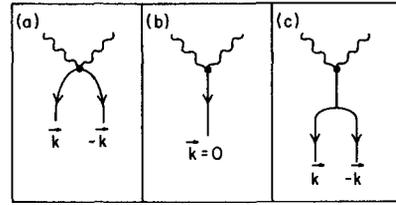
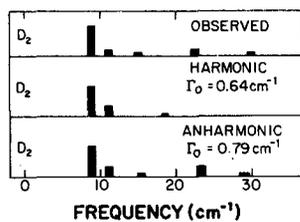


FIG. 6. Various Raman processes. Wiggly lines represent photons and plain lines magnons or librons. In (c) the three-libron vertex represents the cubic anharmonic term in the *EQQ* interaction.

C. Nuclear Spin-Lattice Relaxation Rates

The nuclear spin-lattice relaxation rate, T_1^{-1} , is a measure of the magnitude of fluctuations in the "lattice" at a frequency coincident with the NMR frequency ω_0 . This is reasonable, as spin-lattice relaxation involves converting Zeeman energy into lattice fluctuations of the same frequency. In the magnetic case the "lattice" is the magnetic spin system which is essentially always in equilibrium with the phonon bath. For solid hydrogen the "lattice" is the system of molecular rotations which is likewise in equilibrium with the phonon bath. Since $\hbar\omega_0$ is negligible in comparison to J or Γ_0 , we may say that T_1^{-1} is a measure of the zero-frequency magnetic fluctuations:

$$T_1^{-1} \sim |V|^2 g(0), \tag{19}$$

where V is the matrix element for the hyperfine interaction and $g(0)$ is the density of magnetic fluctuations.

To be more specific, in magnetic systems where the hyperfine interaction is of the form $A\mathbf{I} \cdot \mathbf{S}$, one has⁴⁰

$$T_1^{-1} = \frac{1}{2} A^2 k T \chi_{+-}''(\omega_0)/\omega_0. \tag{20}$$

Here $\chi_{+-}''(\omega_0)$ is the absorptive part of the transverse susceptibility, so that $kT\chi_{+-}''(\omega_0)/\omega_0$ is the density of transverse fluctuations. In most models this density is assumed to be either Gaussian $\sim \tau \exp(-\frac{1}{2}\omega_0^2\tau^2)$ or Lorentzian $\sim \tau/(1+\omega_0^2\tau^2)$, where τ is the correlation time. In the infinite-temperature limit a dimensional argument shows that the correlation time is roughly $\tau \sim \hbar/J$, whence $T_1^{-1} \sim A^2/J$. As the temperature decreases, τ increases, and as a result, T_1^{-1} increases, reaching a maximum at the transition temperature. Below the transition, where spin-wave modes develop, any disturbances require exciting a spin wave. But since the resonant energy of a spin wave is much larger than $\hbar\omega_0$, $\chi_{+-}''(\omega_0)/\omega_0$ must involve the nonresonant excitation of a spin wave. This process occurs infrequently, and hence T_1^{-1} decreases rapidly as the zero-temperature limit is approached.

The same qualitative features obtain for solid hydrogen. Here the hyperfine interaction contains two terms, one of the form $c\mathbf{I} \cdot \mathbf{J}$, and the other of the form $5d[\mathbf{i}_1 \cdot \mathbf{i}_2 - 3(\mathbf{i}_1 \cdot \hat{n})(\mathbf{i}_2 \cdot \hat{n})]$, where c and d are known

constants. Thus we have⁴⁰

$$T_1^{-1} = (16\pi^3/3)[c^2 g_1(\omega_0) + 9d^2 g_2(\omega_0)]. \quad (21)$$

Here $\omega_0 g_L(\omega_0)$ plays the role of a generalized susceptibility for $Y_L^M(\theta, \varphi)$ and is analogous to the usual susceptibility for the transverse spin component. Thus, since the correlation time here is of order $\tau \sim \hbar/\Gamma_0$ at high temperature, we have $g_L(\omega_0) \sim \Gamma_0^{-1}$ and hence $T_1^{-1} \sim (c^2 + d^2)/\Gamma_0$ at high temperature. As the temperature decreases τ increases, and as a result T_1^{-1} increases, until the order-disorder transition is reached. Below the transition the occurrence of low frequency fluctuations is strongly inhibited by the large libron energy gap Δ . Thus, in the ordered phase we have^{15,41}

$$T_1^{-1} \sim [(c^2 + d^2)/\Gamma_0] \exp(-\Delta/kT), \quad (22)$$

as one finds for magnetic systems when kT is less than the spin-wave energy gap.⁴²

These qualitative features have been confirmed by experiment. The increase in T_1^{-1} with decreasing temperature in the "paramagnetic" regime was observed in H_2 by Amstutz *et al.*⁴³ The anomalous increase in T_1 at the transition, indicated by Eq. (22) has been observed by Smith *et al.*⁴⁴ in D_2 .

VI. CONCLUSION

We have seen that most of the orientational properties of solid H_2 and solid D_2 in their various alloys of ($J=0$) and ($J=1$) modifications have very direct analogies with properties of magnetic systems. We have attempted to exploit this analogy in order to provide magneticians with a convenient introduction to the orientational properties of solid hydrogen. This is a worthwhile objective, because it is likely that there are valuable techniques commonly used in magnetism which have yet to be applied to solid hydrogen. From the examples discussed here we conclude that solid hydrogen is at least as ideal a system for study as the more familiar magnetic systems.

Note added in proof: Such an experiment has been reported by I. F. Silvera, W. N. Hardy, and J. P. McTague, *Bull. Am. Phys. Soc.* **15**, 1622 (1970).

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