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Abstract

The anharmonic interactions between librational waves in solid hydrogen are found to lead to significant perturbations in the single-libron spectrum. This large anharmonicity is also responsible for two-libron processes whose frequencies and Raman intensities are calculated. Our results for the one- and two-libron spectra are in excellent agreement with, and hence explain, the optical data.

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however, still remain to be delineated in detail before the phenomena reported here can be properly analyzed and understood.

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OBSERVATION OF LIBRON-LIBRON INTERACTIONS IN SOLID HYDROGEN*

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The anharmonic interactions between librational waves in solid hydrogen are found to lead to significant perturbations in the single-libron spectrum. This large anharmonicity is also responsible for two-libron processes whose frequencies and Raman intensities are calculated. Our results for the one- and two-libron spectra are in excellent agreement with, and hence explain, the optical data.

Ever since Dyson's famous paper in 1956 on spin-wave interactions in a ferromagnet,¹ great efforts have been made to observe these interactions. However, since long-wavelength spin waves interact only very weakly, this has been a difficult experimental problem, and only in the last few years has the optical observation² of two-magnon states in antiferromagnets³ shown unequivocally the existence of these interactions. The existence of anharmonicity in phonon systems is also documented,⁴ but here the fundamental interactions are less well known and hence many calculations⁵ use anharmonic force constants which are not evaluated from a microscopic point of view. In contrast, in solid hydrogen the relevant orientational interactions between molecules are determined from first principles,⁶ and hence the associated anharmonic force constants are well known. Furthermore, since these anharmonic interactions are large,⁷ the orientational excitations in solid hydrogen constitute a unique many-body system.

The elementary excitations of this system are the small librational motions of the molecules about their equilibrium orientations. In the orientationally ordered phase [which occurs for the pure ($J=1$) solid below about 3°K for H₂ and 4°K for D₂] the fcc crystal consists of four interpenetrating simple-cubic sublattices, each of which consists of molecules oriented along one of the various [111] directions.^{8,9} Since there are four molecules per unit cell, each of which can librate in two perpendicular directions, the librational excitation (libron) spectrum has eight branches.¹⁰⁻¹⁴ In this approximation the effects

of zero-point phonon motion and phonon-libron interactions are taken into account only insofar as they renormalize the orientational interactions,^{15,16} of which the quadrupole-quadrupole interactions scaled by the parameter¹⁰⁻¹⁶ Γ are the most important. From the symmetry of the four-sublattice structure, space group $T_h^{(6)}$, one expects at $k=0$ one twofold degenerate and two threefold degenerate libron energies.

These elementary excitations have been observed directly via Raman scattering of light.¹⁷ However, the interpretation of this spectrum has been unclear for two reasons. First, there were observed five lines in the Raman spectrum instead of three as predicted from theory. Second, the calculated libron energies did not agree very well with any reasonable assignment of the observed lines. Accordingly, a distortion to a lower symmetry structure was suggested.¹⁷ From x-ray work¹⁸ a similar distortion has been suggested for solid N₂. However, the distortion in solid N₂ has not been confirmed by subsequent optical data,¹⁹ and hence its existence is uncertain. For solid hydrogen, a distortion is not a plausible explanation of the spectrum, because it must be supposed to produce rather large splittings in the Raman spectrum. Recently Nakamura²⁰ has suggested that the extra lines may be due to two-libron processes. However, the mechanism he proposed relied on the zero-point disorder in the orientational system, and consequently the intensity associated with this process was very small.

Here we propose a mechanism for a two-libron absorption which can account for these two extra

lines. In addition, we have calculated the effect of anharmonic libron-libron interactions on the single-libron spectrum and find excellent agreement with the three lowest lines in the observed Raman spectrum.

The simplest and physically most transparent way to study the effect of libron-libron interactions on the single-libron spectrum is to construct an energy-dependent effective quadratic interaction, V_{eff} , from the anharmonic interactions:

$$V_{eff}(E) = \sum_e \{ [V_3|e\rangle(E-2E_0)^{-1}\langle e|V_3] - [V_2|e\rangle(2E_0)^{-1}\langle e|V_4] - [V_4|e\rangle(2E_0)^{-1}\langle e|V_2] \} + \sum_f \{ V_4|f\rangle(E-3E_0)^{-1}\langle f|V_4 \}. \tag{1}$$

Here $|e\rangle$ and $|f\rangle$ are intermediate states with two and three virtual librions, respectively; V_n represents the terms in the Hamiltonian involving n bosons; and E_0 is the libron energy in the mean-field approximation. As noted before,¹⁴ it is necessary to include further-neighbor interactions, in which case $E_0 \approx 21.2\Gamma$. The libron energies are found by adding the term V_{eff} to the free-libron Hamiltonian. From this calculation we find the libron energies to be 12.1 Γ , 15.2 Γ , and 21.1 Γ in contrast to the values obtained from the harmonic theory,¹⁴ viz. 13.7 Γ , 17.7 Γ , and 29.0 Γ . As can be seen, the lower two lines are not shifted very much by the libron-libron interactions, and for them perturbation theory is no doubt quite reliable. For the highest-energy line the anharmonic shift is quite large (in agreement with the data) and hence for each mode we have self-consistently determined E in Eq. (1) rather than setting it equal to E_0 . Also we have included the effects of anharmonicity on E_0 . As shown in Ref. 7, E_0 is thereby reduced by about 3.5 Γ .

In view of our results one naturally wishes to estimate higher-order effects. As explained by Coll and Harris⁷ and Harris²¹ (for the analogous case of the antiferromagnet), the expansion about the mean-field Hamiltonian is in powers of z^{-1} , where z is the effective number of nearest neighbors, here 12. Hence we estimate the uncertainty in our calculated energy shifts to be less than, say, 15%, as is indicated in Table I where the results of our calculations are fitted to the observed spectrum.

The existence of a large cubic anharmonicity is the obvious source of a two-libron Raman process. In Fig. 1 we show both the ordinary single-libron process and the two-libron process which is allowed when anharmonicity is present. The intensity, I_2 , of this process relative to that, I_1 , in the single-libron spectrum may be estimated simply as follows: The effective matrix element for the two-libron process is

$$\sum_e \langle f|V_3|e\rangle E_0^{-1} \langle e|H_{int}|i\rangle. \tag{2}$$

Here $|e\rangle$ is an intermediate state with one virtual libron and H_{int} is the photon-libron coupling responsible for the single-libron process.⁷ We thus have

$$I_2/I_1 \approx (V_3/E_0)^2. \tag{3}$$

We can relate this to the average energy shift of the libron energy due to cubic anharmonicity, ΔE_3 , since

$$|\Delta E_3| \approx V_3^2/E_0. \tag{4}$$

Using the results of Ref. 7 for ΔE_3 we thus obtain $I_2/I_1 \approx 0.2$.

The frequencies of the two-libron processes can also be estimated by a simple calculation. For the two-magnon spectrum of antiferromag-

Table I. Comparison of the observed and calculated Raman spectra. The errors quoted for the anharmonic theory indicate our estimates of the importance of higher-order effects. Relative intensities are given in parentheses. All frequencies are given in cm^{-1} .

H_2		
Anharmonic Theory	Observed	Harmonic Theory
$\Gamma = 0.52 \text{ cm}^{-1}$	(See Ref. 18)	$\Gamma = 0.44 \text{ cm}^{-1}$
6.3±0.2 (1.0)	6.2±1 (1.0)	6.2 (1.0)
7.9±0.2 (0.33)	8.0±1 (0.34)	8.0 (0.32)
11.0±1.0 (0.05)	11.3±1 (0.12)	13.0 (0.04)
16.6 (0.31)	16.8±1	None
20.6 (0.05)	21.0±2	None
D_2		
Anharmonic Theory	Observed	Harmonic Theory
$\Gamma = 0.73 \text{ cm}^{-1}$	(See Ref. 18)	$\Gamma = 0.64 \text{ cm}^{-1}$
8.8±0.3 (1.0)	8.8±1 (1.0)	8.8 (1.0)
11.1±0.3 (0.33)	11.2±1 (0.18)	11.3 (0.32)
15.4±1.3 (0.05)	15.1±1 (0.05)	18.6 (0.04)
23.3 (0.31)	22.5±1	None
29.0 (0.05)	29.9±2	None

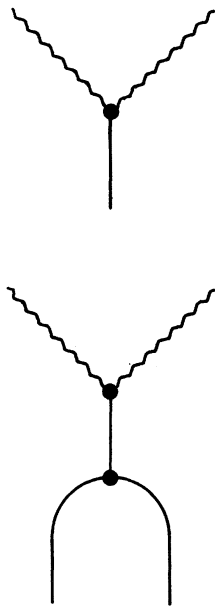


FIG. 1. The one- (top) and two- (bottom) libron Raman process in solid hydrogen. The wavy lines represent incoming and outgoing photons which create a single libron via H_{int} (see Ref. 7). The cubic libron-libron interaction gives rise to the second-order two-libron process shown above.

nets it has been shown²² that a localized picture wherein the two excitations are not allowed to separate (as in the Ising model) is qualitatively correct in that the peak in the two-magnon density of states was found to coincide with the sharp energy level obtained in the localized model. This result occurs because the two magnons (or here the two librions) are always created at neighboring sites. In solid hydrogen a pair of molecules²³ has four possible two-libron states, since each molecule can librate in either of two perpendicular directions. We have calculated the frequencies and Raman intensities of these levels, assuming all other molecules to be in their mean-field ground state. However, in order to include the large ($\sim 3.5\Gamma$) shift of the libron energy due to anharmonicity, it was necessary to treat the anharmonic part of the interactions with the surrounding molecules perturbatively. This was done by using an effective potential analogous to that in Eq. (1). Within this model the two-libron energies, with approximate Raman intensities in parenthesis, were found to be 31.3Γ ($0.09I_1$), 32.6Γ ($0.14I_1$), 36.1Γ ($0.01I_1$), and 39.7Γ ($0.035I_1$). We presume that the distinctness of the lowest two states is an artifact of the localized model and hence we treat them

as a single state in the table. The two-libron state with the smallest intensity ($0.01I_1$) was ignored in the table. As can be seen, our calculations are in striking agreement with the optical data.

Our conclusions are (a) the intensity and energy of the two-libron processes can explain the two "extra" lines in the Raman spectrum; (b) a distortion to a structure of lower symmetry is implausible; (c) the anharmonicity has a significant effect on the single-libron spectrum and taking it into account leads to excellent agreement between the three lowest lines in the Raman spectrum and the calculated single-libron modes; (d) the values of the quadrupolar coupling constant used to fit the Raman data²⁴ (viz. $\Gamma = 0.52 \text{ cm}^{-1}$ for H_2 and $\Gamma = 0.73 \text{ cm}^{-1}$ for D_2) are larger than obtained using the harmonic theory and hence more nearly agree with other determinations of Γ (for a tabulation see Ref. 14); and (e) the cross section for the inelastic scattering of neutrons should display two-libron effects quite prominently. In addition such experiments will yield estimates of nonquadrupolar interactions.⁷

Papers including detailed calculations of the anharmonicity effect and a comparison between the experimental values of Γ and those calculated using the phonon renormalization^{15,16} will be published.

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²⁴The Raman experiments were done on samples containing a small percentage of $J=0$ molecules. Taking this into account will increase the value of Γ by a few percent.

PHOTOEMISSION FROM AMORPHOUS SILICON*

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Measurements of photoelectric yield and energy distributions from amorphous silicon films are presented. The results are consistent with an exponential tail in the density of states extending from the valence band to the Fermi level. Mild heat treatment decreases the amplitude of this tail. Tentative explanations of these observations are given.

Amorphous elemental semiconductors are particularly well suited for studying the influence of long-range order or the lack thereof on the electronic structure of materials. The absence of long-range order in amorphous materials is expected¹⁻³ to produce exponential tails in the density of states near the band gap were crystals have sharp edges. A puzzling case is presented by germanium, where an exponential tail has been observed by some authors^{4,5} by optical absorption measurements, while others⁶ report well-defined optical thresholds as in crystals. Additional support for sharp band edges comes from the measurements of photoelectric emission by Donovan and Spicer,⁷ who report energy distributions with sharp high-energy cutoffs. Thus the existence of an exponential tail in elemental amorphous semiconductors seems open to question.

We present photoemission data obtained from vapor-quenched amorphous silicon films. Samples were prepared by a sublimation technique described by Thomas and Francombe.⁸ The films, several thousand angstroms thick, were deposited onto etched single-crystal [111] silicon substrates, held at liquid-nitrogen temperature during deposition and the first experimental runs. The source material was 1- Ω -cm n -type silicon. Transmission electron-diffraction studies of samples similarly prepared in an evaporator showed the broad halos characteristic of the amorphous state.⁹ All photoemission samples

were prepared in ultrahigh vacuum and measured *in situ*; ambient pressures were in the 10^{-11} Torr range after bakeout, although this increased to 10^{-7} Torr during sample fabrication. Energy distribution curves were measured by the retarding-field method. A rotatable sample holder supported two amorphous silicon samples and a metallic (W) emitter. Energy distributions from the latter enable measurement of all electron energies with respect to the Fermi level¹⁰; this is significant in light of the results presented below.

The samples could be heated to temperatures below the crystallization temperature by electron bombardment. Effects of such mild heat treatments have been reported with regard to optical and electronic properties, ESR and conductivity in particular, and have been interpreted as a reduction in number of vacancies¹¹ or of dangling bonds.^{11,12}

Figure 1 presents the yield spectra for three representative amorphous samples, one of which was also heated. The yield is given in electrons emitted per absorbed photon; reflection of incident light was accounted for with the help of the reflectivity measured by Beaglehole and Zavetova.¹³ Also shown in Fig. 1 are yields for cleaved¹⁴ and for annealed Si crystals¹⁵ reported by Allen and Gobel. There are several features to be noted:

(1) The yield of all amorphous samples is higher than for crystals. This is expected since