azimuthal propagation velocities with the theoretical slab-model value (in both magnitude and direction), as well as by the occurence of large but finite parallel wavelengths, evidenced by the zero amplitude at the center of the machine. Use of the measured value of the wavelength yields a computed growth rate close to the maximum theoretical growth rate, if one identifies the radial extension of the mode with a radial wavelength.

Further results concerning the experimental and theoretical aspects of this work will be published elsewhere.

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Libron Spectra of Oriented Crystals of Paradeuterium and Orthohydrogen in the Ordered State

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New Raman spectra obtained in large oriented crystals of paradeuterium and orthohydrogen give an unambiguous identification of the single-libron modes and remove all former reservations in assigning the $Pa3$ structure to the orientationally ordered phase.

The most direct experimental information concerning the properties of the spin-wavelike excitations called librons in solid hydrogen has been provided by the Raman scattering results.[1,2] However, the extraction of quantitative information has been hampered by the fact that the number of features observed (four or more) was not consistent with the three one-libron modes (E_g, $T_g^{(1)}$, $T_g^{(2)}$) predicted on general grounds for the $Pa3$ structure. A number of possible explanations were proposed. The first was that $Pa3$ was indeed the proper space group for the crystal and the extra features arose from two-libron excitations,[1] but this suffered from the fact that no three lines could be chosen to give simultaneous agreement for the intensities and frequen-

cies predicted by then current theories.[3] The second explanation proposed a trigonal distortion of the $Pa3$ structure to one of lower symmetry, $R\bar{3}$, which partially lifted the degeneracy of the two T_g modes and allowed a reasonable fit to be made by theory. On the other hand, spectra obtained for the $J=0\rightarrow 2$ transition of the small fraction of molecules having $J=0$ cast considerable doubt on the latter explanation since the number of features expected for the $R\bar{3}$ structure is eight, whereas only four were observed.[2] It was at this time that James[4] predicted the existence of metastable orientational orders quite different from $Pa3$, but the splitting of the $J=0\rightarrow 2$ transition calculated from James' results corresponded very poorly with experiment.[5] Nakamura and Miyagi[6] recalculated the libron spectrum giving consideration to the effects of zero-point librational motion. They assigned the lowest three lines to single-libron excitations and the higher-lying features to two-libron processes even though the frequency fit was poor and the theoretical intensity for the two-libron scattering was too low. Coll and Harris[7] also recalculated the libron spectrum for both the $Pa3$ and the $P4_2/mnm$ structure (one of the metastable structures predicted by James) and included anisotropic interactions other than electric quadrupole-quadrupole (EQQ). They found poor agreement for the $P4_2/mnm$ structure, but using the previous suggestion of split T_g modes presented a remarkably good fit for the $Pa3$ structure by assigning all of the lines to one-libron processes. Recently, however, Coll et al.[8] have again calculated the libron spectrum for an undistorted $Pa3$ structure this time neglecting all interactions except EQQ, but taking into account the effect of libron-libron interactions which cause significant shifts in the predicted frequencies and also give rise to two-libron scattering. They then obtained a good fit to the frequency ratios, but this time assigned the lowest three observed lines to one-libron processes and the high-frequency band to two-libron scattering. The present Raman scattering results, obtained in what were effectively single crystals of known orientation rather than the polycrystalline samples of previous investigations, provide an identification of the libron modes which to a good approximation is independent of the assumptions concerning the form of the anisotropic interactions and depends only on the symmetry of the crystal.

The experimental procedures for growing the crystals and obtaining the Raman spectra have been described elsewhere.[2] The frequencies have been measured to a much greater accuracy by a different procedure. A spectral comb was generated with a Fabry-Perot etalon illuminated by a white light source. A 20-Hz chopper alternately fed the Raman light and the calibration light into the spectrometer. The photomultiplier output was separated by two gated integrators and recorded simultaneously with a two-pen recorder (see Fig. 1).

The reason for our current success in obtaining large single crystals of the hcp phase is not clear, but there were several minor changes in the procedure and apparatus.[2] These included the following: (1) The level of nonhydrogen con-

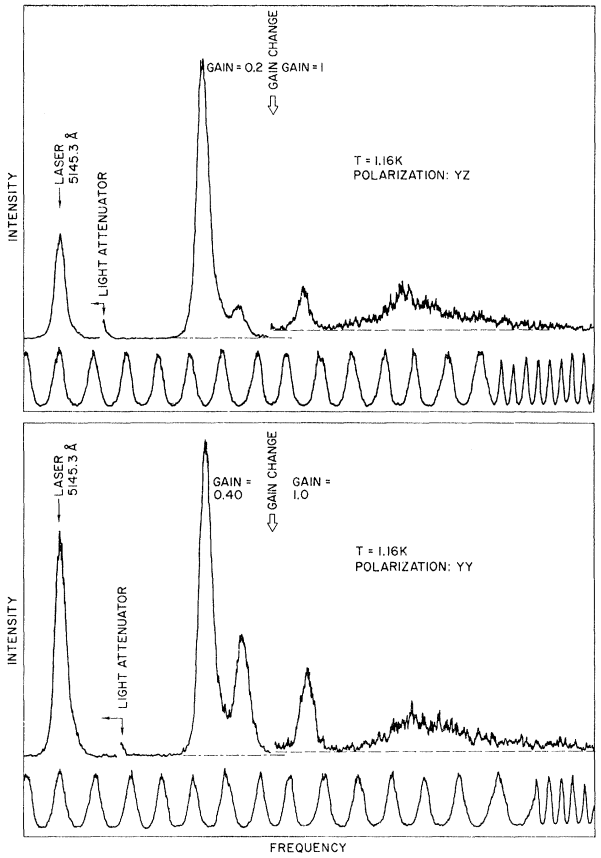

FIG. 1. Spectra of 98.8% paradeuterium for YZ and YY polarizations. Ordinates of both spectra are directly relatable by the indicated gain factors. Note the change in baseline with change in gain. The laser light was attenuated near 5145.3 Å to enable recording of the frequency fringes without saturating the electronics. The fringe spacing is 2.057 cm^{-1}. A linear frequency axis could not be shown because of the nonlinearity of the spectrometer drive as indicated by the irregularity of fringe spacing. The width of the laser line is an indication of the instrumental resolution.

taminants in the samples was reduced, (2) a first-surface dielectric reflector replaced the second-surface metallic mirror formerly used, and (3) the copper heat conductor at the bottom surface was tapered in an attempt to reduce the area over which nucleation occurred.

Growth takes place in the birefringent hcp phase and observation of the crystals between crossed polarizers clearly showed the presence of grain boundaries in nonsingle-crystal samples. The direction of the c axis was determined after growth by the polarization properties of the Raman-active optical phonon of the hcp phase.[9] The samples discussed in this Letter had no apparent grain boundaries or visible cracks and were assumed to be single crystals. The angle between the c axis and the axis of the scattering tube (Z or vertical direction) was determined to be less than 14°. The actual angle could be considerably less than this upper bound which was arrived at through consideration of the signal/noise ratio of the optical-phonon polarization intensity ratios.

The transition from the hcp to fcc phase apparently takes place by a sliding of hexagonal layers relative to one another which requires that the original hcp c direction becomes one of the [111] directions of the cubic phase.[10] In this case, a consideration of the geometry shows that from a single crystal of the hcp phase only two cubic crystallites can result, and they are related by a rotation of $2\pi/6$ about the original c direction. Given the location of the molecular centers in the fcc phase, there are two ways in which orientational order can lead to the $Pa3$ structure resulting in a second type of domain analagous to a magnetic domain.

Spectra were taken for right-angle scattering as a function of the polarization of the incident and scattered light beam, and also of the angle ψ through which the sample is rotated about an axis coincident with the laser beam. The intensities for the various combinations of incident and scattered light polarizations are labeled by expressions such as XY, YY, etc., in which the letters give the electric-field direction of the incident and scattered light, respectively. A right-handed laboratory coordinate frame is used with the Z axis coincident with the laser beam, and the X axis along the direction of propagation of detected light.

Figure 1 shows sample spectra obtained in para-D_2 at 1.16 K for the YY and YZ polarizations. The first notable feature is the strong dependence of the intensity of the three lowest lines on the output polarization, in contrast to

Table I. Frequencies and intensities as a function of polarization of the libron modes. The intensities are normalized such that the total intensity of the E_g mode summed over all polarizations is equal to 2.0. The intensities of the $T_g^{(1)}$ mode for the XZ and YZ polarizations are significantly less accurate than the rest of the intensities because of the close proximity of a strong E_g mode. Theoretical values are given in parenthesis. The experimental values of the frequencies are accurate to 0.1 cm^{-1}.

Mode	Frequency Expt.(cm^{-1})	Theory[8]	$\Gamma_{eff}(cm^{-1})$
	p-D_2(98.8%)		
E_g	9.00	12.1Γ	.744
$T_g^{(1)}$	11.17	15.2Γ	.735
$T_g^{(2)}$	15.38	21.1Γ	.729
	o-H_2(96.7%)		
E_g	6.53	12.1Γ	.540
$T_g^{(1)}$	8.23	15.2Γ	.541
$T_g^{(2)}$	11.29	21.1Γ	.535

Mode	Intensity (Relative) XY	XZ	YY	YZ
	p-D_2(98.8%)			
E_g	.36	.67	.35	.62
	(.333)	(.667)	(.333)	(.667)
$T_g^{(1)}$	.13	.077	.130	.064
	(.146)	(.0733)	(.220)	(.0733)
$T_g^{(2)}$	.028	.017	.030	.014
	(.0223)	(.0111)	(.0336)	(.0111)
Two-libron	.078	.103	.095	.082

a much weaker dependence for the high-frequency band. Although it is not very pronounced for the spectra shown, the shape of the high-frequency band changes significantly as a function of polarization.

We next note that to within experimental error there was no dependence of the intensities on the angle ψ for the XY and XZ combinations (corresponding spectra were not taken for the YY and YZ combinations). Previous calculations of Raman intensities of the libron modes for a polycrystalline sample in which the [111] directions of the crystallites were oriented along the incident light beam[1] showed that in fact there should not be any dependence of the intensities on the angle ψ of such a crystallite. This result also holds for a sample containing the types of domains already discussed and is consistent with the experimental observations. The theoretical dependence of the intensities on polarization is given in Table I along with the experimental observations for para-D_2. The calculated values were obtained using standard polarizability theory,[1] but normalized to the recent powder-average results of Coll et al.[8] in order to take account of anharmonic effects. These values are essentially identical to results derived from expressions given by Nakamura and Miyagi[6] for a single crystal.[11] Note that as required by their common transformation properties, the $T_g^{(1)}$ and $T_g^{(2)}$ modes have identical polarization properties although different total intensities. The theoretical and experimental intensities agree quite well except perhaps for the YY component of the $T_g^{(1)}$ mode. In order to see whether this discrepancy was significant, for each mode the theoretical intensities summed over the four polarization combinations were adjusted to equal the corresponding experimental quantities. This procedure allows one to compare better the experimental and theoretical polarization dependencies which are properties of the crystal symmetry, while suppressing theoretical information on the relative mode intensities which is model dependent. The resultant fit, shown in Fig. 2, is very good except for the $T_g^{(1)}$ mode where the deviations may be outside of experimental error. Due to the circumstance that the $T_g^{(1)}$ mode is much weaker than the E_g mode with which it overlaps, the discrepancy is not considered to be significant as far as the identification of the modes is concerned. Converted to equivalent strengths for a powder, the experimental mode intensities are 1 : 0.256 : 0.060 to

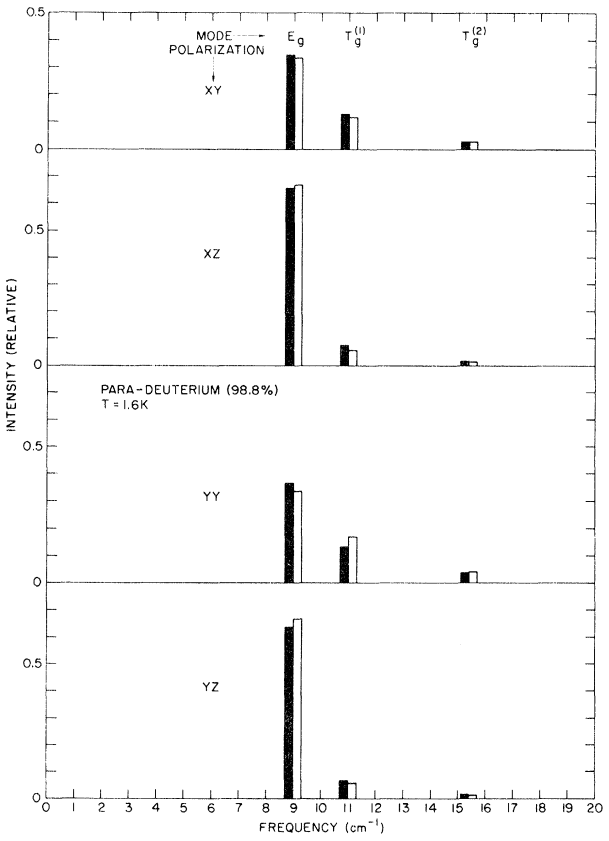

FIG. 2. Bar graph of experimental (solid bars) and theoretical (open bars) intensities for the E_g, $T_g^{(1)}$, and $T_g^{(2)}$ modes. See text for a discussion of normalization.

be compared with the results of Coll et al.,[8] 1 : 0.33 : 0.05, and Nakamura and Miyagi,[6] 1 : 0.318 : 0.042. It has also been possible to identify the $J = 0 \rightarrow 2$ impurity transitions in terms of the $Pa3$ structure.[5]

Frequencies of the one-libron lines accurate to 0.1 cm^{-1} are also given in Table I for 98.8% para-D_2 and 96.7% ortho-H_2, and compared with the recent anharmonic theory of Coll et al.[8] The agreement for frequency ratios is very good and leads to values of $\Gamma_{\text{eff}} = 0.736$ and 0.539 cm^{-1} for D_2 and H_2, respectively. Miyagi and Nakamura[12] have suggested that the libron frequencies scale directly with the concentration of the $J = 1$ species. However, this has not been taken into account in the comparison.

Although the polarization properties of libron scattering were also obtained in oriented crystals of ortho-H_2, they have not been included in Table I as the spectra were not as complete as for para-D_2, the signal-to-noise ratio was poorer, and the lines were not as well resolved. To within experimental error, however, the results

were the same as for para-D_2.

In summary, these new Raman spectra for oriented crystals give an unambiguous identification of the single-libron modes and remove all former reservations in assigning the $Pa3$ structure to the orientationally ordered phase of pure orthodydrogen and paradeuterium.

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[12]H. Miyagi and T. Nakamura, to be published.

Evidence for the Dissociation of Close Pairs Produced in Platinum at Temperatures Above Stage I*

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Experimental data are interpreted as evidence that with increasing irradiation temperature above Stage I in metals there is an increasing probability that close pairs will dissociate. The dissociated partners contribute to the damage produced during elevated-temperature irradiations in the same way as free defects produced otherwise.

When a close Frenkel pair is produced at a high temperature there is a significant probability that the interstitial will jump away from its vacancy partner towards a more stable position. Let E_r be the activation energy required for an interstitial to make a jump closer to its vacancy partner towards possible recombination. Similarly, let E_d be the activation energy for the interstitial to jump away from its partner towards possible dissociation. The respective probability for each type of jump at temperature T is proportional to $N_r \exp(-E_r/kT)$ or $N_d \exp(-E_d/kT)$, where N_r and N_d are the number of equivalent sites associated with either type of jump. The fraction of interstitial jumps towards dissociation then is

$$f_d = \frac{N_d \exp(-E_d/kT)}{N_d \exp(-E_d/kT) + N_r \exp(-E_r/kT)}. \quad (1)$$

If $E_d - E_r \equiv \Delta E$ and $N_r/N_d \equiv \gamma$ then,

$$f_d = [1 + \gamma \exp(\Delta E/kT)]^{-1}. \quad (2)$$

For many metals the low-temperature recovery-rate spectra are known for several types of irradiations, and in some cases values of E_r have been measured for particular types of close pairs. On the other hand, no values for E_d, and hence ΔE, have been measured. Since values of ΔE are unknown, we assume $\Delta E \simeq 0.2E_r$, and using a typical value for E_r of 0.1 eV the following values for f_d are obtained with Eq. (2):

T (°K)	f_d
30	0.00033
100	0.09
300	0.26
1000	0.44
∞	0.50

A value of $\gamma = 1$ was used to calculate the above examples. Values of γ less than 1 are more realistic and would enhance dissociation, reducing the temperature required to produce a given