

Metallization of Solid Hydrogen at Megabar Pressures: A First-Principles Quasiparticle Study

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Quasiparticle calculations have been performed for the band gap of solid molecular hydrogen in the hcp structure. The calculations predict that the orientationally ordered phase undergoes metallization due to an indirect band overlap at the volume $V=2.50$ cm³/mol, and the orientationally disordered phase at $V=1.89$ cm³/mol, which correspond to metallization pressures of 151 and 300 GPa, respectively. A quantitative relation between the degree of orientational order and the metallization volume is obtained.

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Solid hydrogen is an insulating molecular crystal at low pressures. Upon application of high enough pressures it is expected to eventually become a metal.¹ Both the metallization pressure and the mechanism that leads to metallization are subjects of debate and intensive current experimental studies.¹⁻⁷

In this paper we report calculations for the pressure-induced metallization of solid molecular hydrogen in the hexagonal-close-packed (hcp) structure. The metallization pressure is obtained from the closure of the band gap. We make use of a recently developed first-principles quasiparticle method⁸ that permits the calculation of band gaps of semiconductors and insulators within a typical accuracy of 0.1 eV. According to our calculations, the hcp orientationally ordered phase metallizes at a molar volume of $V=2.50$ cm³/mol, and the hcp orientationally disordered phase at $V=1.89$ cm³/mol. The metallization of both phases is due to indirect band overlap. The use of recently proposed extrapolations of experimental equations of state^{9,10} places the above transitions at 151 and 300 GPa, respectively, for the fully ordered and disordered phases. We also obtain a quantitative relation between the degree of orientational order and the metallization volume. The present results should be relevant to the current experimental search for the metallization of solid hydrogen at megabar pressures.

Although relatively accurate data are available at low pressures, only limited experimental data on the structural properties of solid hydrogen are available at high pressures. X-ray diffraction¹⁰ shows that the hcp structure is stable at 300 K for pressures up to 26 GPa. Above this pressure, x-ray data are not available, but optical experiments give clues on the possibility of phase transitions. Three indications of possible transitions have been observed: (1) At 8 K, the roton bands in Raman spectra of parahydrogen disappear above 110 GPa;¹¹ this was tentatively identified as an orientational ordering transition.¹¹ This interpretation has been questioned by other authors.¹² At 77 to 295 K, the roton bands persist at least up to 160 GPa, with no sign of an observable discontinuous orientational transition.^{12,13} (2) At pres-

ures near 150 GPa, a discontinuity in the vibron frequency in Raman spectra as a function of pressure^{3,14} indicates another phase transition, to the so-called hydrogen-*A* phase. (3) A recent experiment has been performed on reflectance spectra of solid hydrogen for pressures between 140 and 180 GPa.⁵ An observed increase in the low-frequency reflectivity for pressures above 150 GPa was associated with a transition to a metallic phase. A fit by the Drude model was then used to deduce a metallization pressure at 149 ± 10 GPa.⁵ A similar procedure has been successfully applied to analyze the metallization of solid xenon,¹⁵ but the experimental evidence for the metallization in solid hydrogen is less complete.

Several previous theoretical investigations^{7,16-19} have studied the possibility of metallization of solid molecular hydrogen by band overlap. However, most of these studies¹⁶⁻¹⁸ have assumed cubic structures which might not be the relevant ones since, according to a recent calculation¹⁹ using the local-density approximation²⁰ (LDA), the hcp structure has a lower enthalpy in the megabar range as compared to cubic structures. A most recent study on the metallization of hcp molecular hydrogen is given in Ref. 7, in which two different calculations were performed: (1) A LDA calculation resulted in a metallization pressure of 95 GPa for the orientationally ordered hcp hydrogen. (2) A calculation using the $X\alpha$ approximation²¹ fitted to reproduce the optical gap at atmospheric pressure resulted in a metallization pressure of $180(\pm 20)$ GPa for the same structure. Those results are considered as lower and upper bounds for the metallization pressure, with the LDA value certainly underestimating the correct band-gap-closure pressure.^{7,22} Such a large uncertainty arises because the LDA typically provides a good description of ground-state properties of solids but fails in quantitatively describing the excitation spectra. For a quantitative study on metallization by band overlap, the inclusion of many-electron effects in calculating the quasiparticle band gap is necessary.²²

The method used in the present work has been described in Refs. 8 and 23. The electronic excitation en-

ergies are obtained by solving⁸

$$(T + V_n + V_H)\psi_{nk}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_{nk})\psi_{nk}(\mathbf{r}') = E_{nk}\psi_{nk}(\mathbf{r}), \quad (1)$$

where T is the kinetic-energy operator, V_n is the potential due to the nuclei, V_H is the Hartree potential, Σ is the electron self-energy operator, and E_{nk} and ψ_{nk} are, respectively, the quasiparticle energies and wave functions. Σ is taken to be the first term in an expansion in the screened Coulomb interaction,

$$\Sigma_{GW} = \frac{i}{2\pi} \int d\omega e^{-i\delta\omega} G(\mathbf{r}, \mathbf{r}', E - \omega) W(\mathbf{r}, \mathbf{r}', \omega), \quad (2)$$

where the dressed electron Green's function G is given by

$$G(\mathbf{r}, \mathbf{r}', E - \omega) = \sum_i \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')}{(E - \omega) - E_i - i\delta_i} \quad (3)$$

and $W = v\epsilon^{-1}$ is the screened Coulomb interaction. In the present approach, the static dielectric response matrix ϵ (including full local-field effects) is obtained from first principles²² within the random-phase approximation and extended to finite frequency through a generalized plasmon-pole model.⁸ For the external potential due to the hydrogen nuclei, we use the exact Coulomb potential. Since the molecular hcp insulating phase is nonmagnetic, spin-polarization effects are not considered.

The calculations were carried out to convergence to a numerical accuracy of 0.03 eV in the band gap. A plane-wave cutoff energy of 45 Ry was used for the wave functions. The calculations for the orientationally disordered phase were performed within the spherical approximation^{7,24} in which the potential of the nuclei is averaged isotropically over all possible molecular orientations. This approach is equivalent to considering the $J=0$ rotational state disregarding the rotational coupling between molecules and the Debye-Waller factor.⁶ We use an intramolecular separation of 1.40 a.u., obtained from LDA total-energy calculations.¹⁸ We also use a c/a ratio of 1.58,⁷ obtained from extrapolation of x-ray-diffraction data¹⁰ (the use of the c/a ratio of 1.56 predicted¹⁹ by LDA only increases the band gap by 0.1 eV). Our calculations result in metallization volumes; to convert those to metallization pressures, we made use of extrapolations of recent experimental equations of state (EOS).^{9,10} The difference between the two extrapolations will be assumed as the uncertainty in the EOS.

At low pressures, the experimental absorption spectra of solid hydrogen^{25,26} yield a band gap of 14.5 ± 1 eV. Our quasiparticle calculations give, at zero-pressure molar volume,²⁷ a minimum band gap of 15.4 and 15.3 eV for the orientationally ordered and disordered phases, respectively. This is in contrast with the corresponding LDA values⁷ of 8.4 and 8.3 eV. At low pressures, the effect of orientational disorder of the H_2 molecules on the band structure is small. At high pressures, however,

this effect is very large, as we shall see below.

In Fig. 1(a) we show the quasiparticle energy bands for solid hydrogen in the orientationally ordered hcp structure at molar volume $V = 2.524$ cm³/mol, close to the calculated metallization volume. The bands corresponding to occupied (quasihole) and unoccupied (quasielectron) states are, respectively, below and above the Fermi level (dashed line). The band structure is shown between the Γ point and the K point [see Fig. 1(a)]. The system has an indirect minimum gap with the valence-band maximum at about $\frac{2}{3}$ of the distance between Γ and K and the conduction-band minimum at Γ . The energy dispersion of the bottom of the conduction band is highly anisotropic. As a result, the Fermi surface for electrons at small band overlap is extremely flat with the semiaxis along the c direction being about 5 times smaller than along the a - b directions. The Fermi surface for holes consists of six pockets centered on the valence-band maxima. Using an ellipsoidal approximation for the Fermi surfaces and extrapolating the band overlap from the

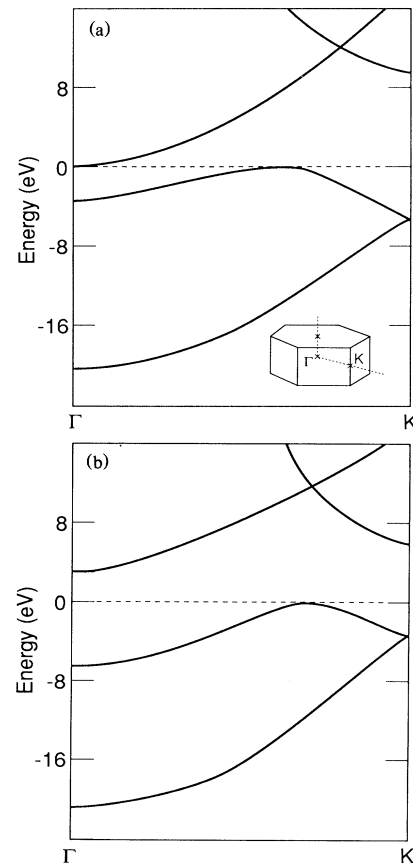


FIG. 1. (a) Quasiparticle energy bands for solid hydrogen in the orientationally ordered hcp structure at molar volume $V = 2.524$ cm³/mol. The Fermi level (dashed line) is the origin of the energy scale. (b) The same as (a) but for the orientationally disordered hcp phase.

insulating phase, we have estimated the variation of the density of carriers with pressure close to the metal-insulator transition. For instance, at 177 GPa, the estimated carrier density (electrons or holes) is $5 \times 10^{20} \text{ cm}^{-3}$.

Figure 1(b) shows the quasiparticle energy bands for the orientationally disordered structure at the same volume as in Fig. 1(a). The main effect on the band structure caused by the orientational disorder is that the band gap increases near Γ and decreases near the surface of the Brillouin zone. This results in a larger minimum gap (by an increase of 3.1 eV). The effect of order-induced decrease of the band gap,⁶ also obtained in LDA band-structure calculations,⁷ originates from a reduction of the potential form factors for relevant reciprocal-lattice vectors.⁶ Our results further show that, unlike the minimum band gap, dielectric screening does not change significantly with the orienting of the molecules. This arises because the dielectric response is related to an "average energy gap"²⁸ rather than to the minimum gap. The average gap is less affected by disorder than the minimum gap due to the opposite effects of disorder on the quasiparticle energies at the surface and at the center of the Brillouin zone (see Fig. 1). This indicates that attempts to relate the average gap to the minimum gap²⁹ should proceed with care.

In Fig. 2 we show the variation of the calculated minimum band gaps with volume. The closure of the band gap with pressure has its origin on the character of the band extrema: Being a solid of closed-shell molecules, the top of the valence band consists primarily of antibonding combinations of Σ_g (intramolecular bonding) orbitals, and the bottom of the conduction band consists basically of bonding combinations of Σ_u (intramolecular antibonding) orbitals. As the distance between molecules decreases, the increase of the overlap between molecular orbitals makes the intermolecular bonding states decrease in energy relative to the antibonding states, which gives rise to the gap closure. The

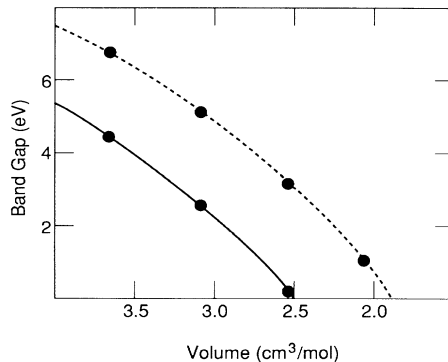


FIG. 2. Variation of the calculated minimum band gap with volume for the orientationally ordered phase (—) and for the orientationally disordered phase (---).

theoretical metallization volumes are 2.50 and 1.89 cm^3/mol for the orientationally ordered and disordered phases, respectively. The use of recent extrapolations for experimental EOS,^{9,10} including a vibron correction of -9 GPa ,⁹ places the metallization at $151 (\pm 6) \text{ GPa}$ for the ordered phase and close to 300 GPa for the disordered phase. Our estimate of the uncertainty for the transition pressure in the ordered phase comes from a typical uncertainty of 0.1 eV in the quasiparticle band gap⁸ and an uncertainty of $\pm 3 \text{ GPa}$ in the EOS. It was not possible to estimate the uncertainty in the disordered phase because of the lack of data for the vibron correction at 300 GPa and because of the spherical model employed. Our calculated metallization volumes apply also to solid deuterium; the only difference is that one has to use a different EOS. The use of the extrapolated EOS for deuterium of Ref. 9 places the metallization at 196 GPa for the ordered phase and at 399 GPa for the disordered phase.

We have also investigated the effect of partial orientational disorder due to the librational motion of the molecules. We modeled partial disorder by assuming a homogeneous proton density for polar angles (relative to the c axis) smaller than a given θ_0 and equal to zero otherwise. We then calculated the band gap as a function of the order parameter $\langle Y_{20} \rangle$ (the average value of the spherical harmonic Y_{20} over a given proton density, normalized to 1 at perfect ordering). Considering that the band gap is almost linear with V^{-1} and is insensitive to disorder at high volumes, we obtained that the metallization volume is approximately given by

$$V_{\text{met}} = V_{\text{ord}} + [a(1 - \langle Y_{20} \rangle)^2 + (1 - a)(1 - \langle Y_{20} \rangle)](V_{\text{dis}} - V_{\text{ord}}), \quad (4)$$

where $a=0.32$ best fits our results, and V_{ord} and V_{dis} are the calculated metallization volumes for the ordered and disordered phases, respectively. Equation (4) shows that partial disorder shifts the metallization transition to pressures above that of the perfectly ordered structure due to the increase of the band gap. For instance, a change in $\langle Y_{20} \rangle$ from 1 to 0.86 (which corresponds to $\theta_0=25^\circ$) shifts the metallization pressure by 10 GPa.

In a recent experimental study of solid hydrogen,⁵ a qualitative change in the infrared-reflectance spectra at 295 K for pressures between 142 and 158 GPa was ascribed to a metal-insulator transition. This finding would imply, from our results, that the metallic phase has an order parameter $\langle Y_{20} \rangle$ close to unity. However, there is also a recent observation of rotational (or librational) bands in Raman spectra at 295 K for pressures up to 160 GPa,¹³ which may be interpreted as the H_2 molecules still having large rotational or librational motions. Our calculations indicate two circumstances that could favor metallization: First, low temperatures favor ordering transitions in both hydrogen¹¹ and deuterium,³⁰ and therefore should favor metallization at

lower pressures. Also, the larger atomic mass of deuterium makes it ordered³⁰ at a lower pressure than hydrogen.¹¹ Therefore, our results suggest that deuterium should become a metal at a larger critical cell volume. However, the metallization pressure of solid deuterium may still be higher than that of hydrogen because of the difference in the equations of state.⁹

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¹For a review, see F. Siringo, R. Pucci, and N. H. March, *High Pressure Res.* **2**, 109 (1989).

²H. K. Mao and R. J. Hemley, *Science* **244**, 1462 (1989).

³H. E. Lorenzana, I. F. Silvera, and K. E. Goettel, *Phys. Rev. Lett.* **63**, 2080 (1989).

⁴J. H. Eggert, K. A. Goettel, and I. F. Silvera, *Europhys. Lett.* **11**, 775 (1990); **12**, 381 (Addendum) (1990).

⁵H. K. Mao, R. J. Hemley, and M. Hanfland, *Phys. Rev. Lett.* **65**, 484 (1990).

⁶N. W. Ashcroft, *Phys. Rev. B* **41**, 10963 (1990).

⁷A. Garcia, T. W. Barbee, III, M. Cohen, and I. F. Silvera, *Europhys. Lett.* **13**, 355 (1990).

⁸M. S. Hybertsen and S. G. Louie, *Phys. Rev. Lett.* **55**, 1418 (1985); *Phys. Rev. B* **34**, 5390 (1986).

⁹J. van Straaten and I. F. Silvera, *Phys. Rev. B* **37**, 1989 (1988).

¹⁰H. K. Mao, A. P. Jephcoat, R. J. Hemley, L. W. Finger, C.

S. Zha, R. M. Hazen, and D. E. Cox, *Science* **239**, 1131 (1988).

¹¹H. E. Lorenzana, I. F. Silvera, and K. E. Goettel, *Phys. Rev. Lett.* **64**, 1939 (1990).

¹²R. J. Hemley, H. K. Mao, and M. Hanfland, in *Proceedings of the Archimedes II Workshop on Molecular Solids under Pressure, Catania, Italy, 1990*, edited by R. Pucci (Elsevier, New York, 1990).

¹³R. J. Hemley, H. K. Mao, and J. F. Shu, *Phys. Rev. Lett.* **65**, 2670 (1990).

¹⁴R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).

¹⁵K. A. Goettel, J. H. Eggert, and I. F. Silvera, *Phys. Rev. Lett.* **62**, 665 (1989); R. Reichlin, K. E. Brister, A. K. McMahan, M. Ross, S. Martin, Y. K. Vohra, and A. L. Ruoff, *Phys. Rev. Lett.* **62**, 669 (1989).

¹⁶D. E. Ramaker, L. Kumar, and F. E. Harris, *Phys. Rev. Lett.* **34**, 812 (1975).

¹⁷C. Friedli and N. W. Ashcroft, *Phys. Rev. B* **16**, 662 (1977).

¹⁸B. I. Min, H. J. F. Jansen, and A. J. Freeman, *Phys. Rev. B* **33**, 6383 (1986).

¹⁹T. W. Barbee, III, A. Garcia, M. Cohen, and J. L. Martins, *Phys. Rev. Lett.* **62**, 1150 (1989).

²⁰W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

²¹J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

²²H. Chacham, X. Zhu, and S. G. Louie (to be published).

²³M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **35**, 5585 (1987).

²⁴D. M. Wood and N. W. Ashcroft, *Phys. Rev. B* **25**, 2532 (1982).

²⁵A. Gedanken, B. Raz, and J. Jortner, *J. Chem. Phys.* **59**, 2752 (1973).

²⁶K. Inoue, H. Kanzaki, and S. Suga, *Solid State Commun.* **30**, 627 (1979).

²⁷A. Driessen and I. F. Silvera, *J. Low Temp. Phys.* **54**, 361 (1984).

²⁸S. H. Wemple and M. DiDomenico, Jr., *Phys. Rev. B* **3**, 1338 (1971).

²⁹J. van Straaten and I. F. Silvera, *Phys. Rev. B* **37**, 6478 (1988).

³⁰I. F. Silvera and R. J. Wijngaarden, *Phys. Rev. Lett.* **47**, 39 (1981).