Order Parameter and a Critical Point on the Megabar-Pressure Hydrogen-*A* Phase Line

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We present experimental evidence that a critical point, also reported by Hemley and Mao, exists for the hydrogen-*A* phase line at a pressure of 173(4) GPa and 151(15) K. We give an interpretation of this critical point in terms of its relationship to a low-pressure disordered insulating phase and a possible metallic phase at high pressure. We interpret the temperature dependence of the vibron frequency of the H-*A* phase as a measure of one of the two order parameters characterizing this phase.

The phase diagram of solid molecular hydrogen has recently been explored experimentally in the megabar-pressure regime[1,2] (1 Mbar = 100 GPa). Hemley and Mao[1] reported spectroscopic evidence of a transition in H_2 at 77 K and about 145 GPa, which they interpreted as a transition to the orientationally ordered state, seen at lower pressures.[3] Lorenzana, Silvera, and Goettel[2] determined the phase line of this transition in the (P,T) plane and showed that the transition was to a new phase that exists only for pressures above about 150 GPa, independent of the ortho-para concentration. They named this the hydrogen-*A* phase (H-*A*) and presented evidence[4] that it is orientationally ordered. Evidence is mounting that the H-*A* phase is metallic. From measurements of dielectric properties of high-pressure hydrogen, Eggert, Goettel, and Silvera[5] estimated the pressure for band-gap closure in H_2 and proposed that the new H-*A* phase is the molecular metallic form of H_2. Recent room-temperature measurements of reflectivity seem to support this conclusion.[6] Here we report two new results: (1) an interpretation of the temperature dependence of the vibron frequencies in terms of the order parameter of the H-*A* phase, and (2) a determination of a thermodynamic critical point for the H-*A* phase line at 173(4) GPa and 151(15) K. We present a picture in which, below the critical point, shown in Fig. 1, H_2 undergoes a first-order phase transition to a metallic state in entering the H-*A* phase. Above the critical point, we expect a continuous transformation from a disordered insulator to an ordered metal. Results pertaining to a critical point have also been reported elsewhere.[7]

Hydrogen was compressed to a maximum pressure of 167 GPa in a diamond-anvil cell (DAC), over the temperature range of 5–150 K. The experimental procedure has been described elsewhere.[2] Most of the vibron measurements reported in this article are for 77-K equilibrium hydrogen, so that the ortho concentration is approximately 0.5, with small deviations to higher concentrations due to thermal excursions of relatively short duration. Some lower-temperature measurements were for samples which had converted to parahydrogen. However, we observed no shift in the vibron frequencies greater than 5 cm^{-1} while these samples converted to equilibri-

um at 77 K, and conclude that this has not affected our results.

The H-*A* phase line was determined earlier from a discontinuity in the frequency of the internal vibrational mode, the vibron.[2] Above the $T=0$ K critical pressure for the H-*A* phase, the phase line can be traversed by changing the temperature at constant pressure. As the temperature is raised, the low-pressure vibron gains intensity at the expense of the H-*A* vibron. In Fig. 2, we show vibron spectra for a pressure of 164 GPa, as the transition temperature is crossed. Lorenzana, Silvera, and Goettel[2] also found that the H-*A* transition exhibits little hysteresis and takes place at a sharply defined temperature and pressure. They explained the observed coexistence of the two vibron peaks over a limited range in both temperature and pressure as arising from pressure gradients.

Our determination of the order parameter and the critical point is based on a study of the Raman-active vibrons. At a constant pressure we found that the frequency of the H-*A* peak demonstrated little temperature dependence, until near the phase transition, where it changed markedly. By contrast, the low-pressure vibron
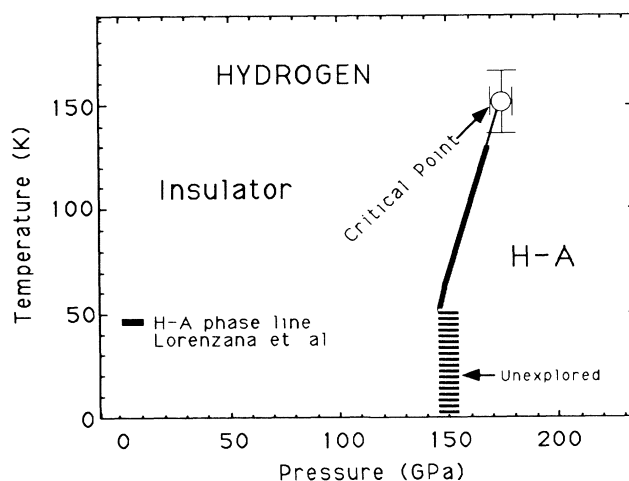

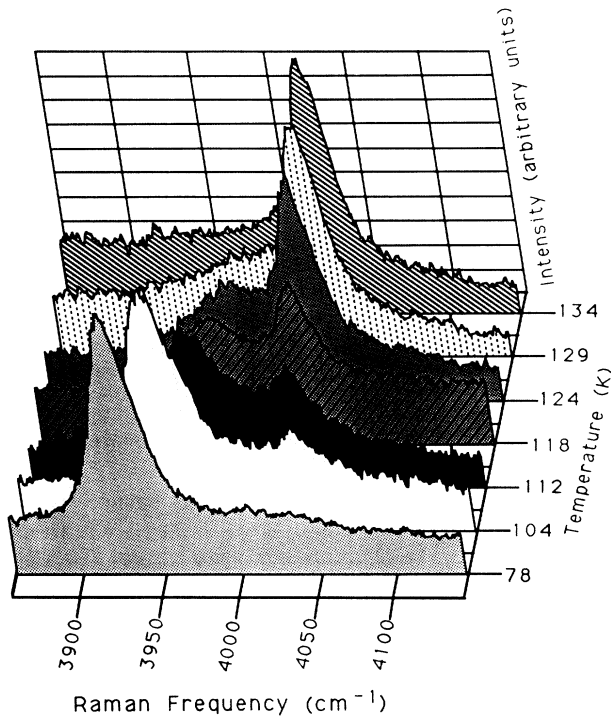FIG. 1. Proposed phase diagram for the H-*A* phase showing the critical point.

FIG. 2. Spectra showing the thermal behavior of the vibron near the H-A transition in solid H_2 at a pressure of 164 GPa. The low-frequency peak is the H-A vibron.
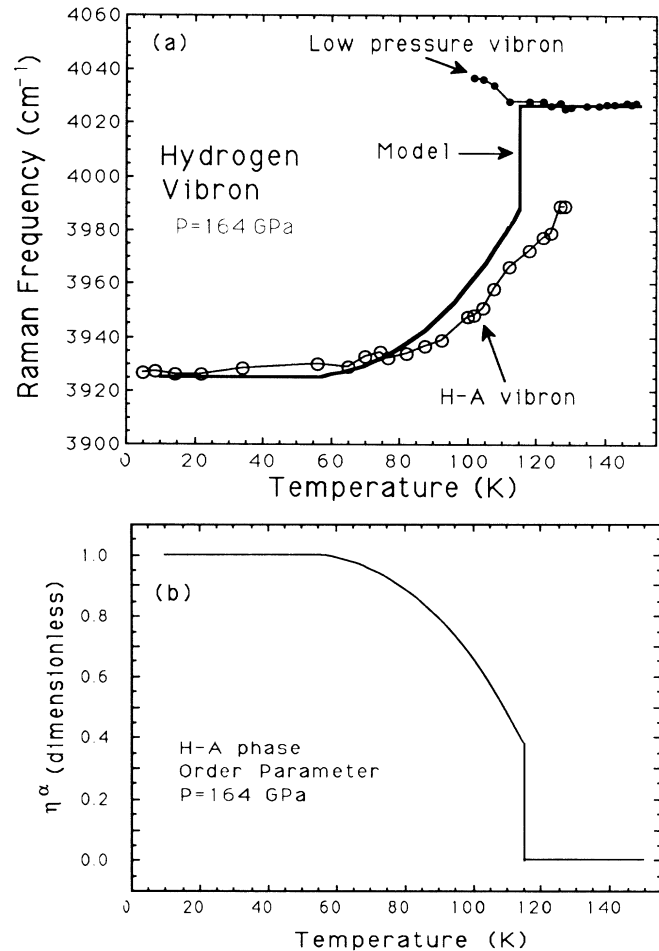

FIG. 3. (a) Temperature dependence of the vibrons from liquid-helium temperature to 145 K at a constant pressure. The model line is the temperature dependence in the absence of a pressure gradient. (b) The order parameter for the metallic phase, extracted from (a).

remained relatively constant with changing temperature. In Fig. 3(a), we plot the peak frequencies of both the low-pressure and the H-A vibron, which shows this temperature dependence, as well as the vibron discontinuity. As discussed in Ref. 2 a pressure distribution in the sample can distort the spectrum. We have used a model of a sharply defined transition pressure, with the sample having a linear pressure gradient, to remove this distortion:[2] The heavy line in Fig. 3(a) is the curve which reproduces our data when it is convolved with the pressure distribution.

We introduce a model which assumes that the H-A phase is metallic and has two coupled order parameters. At the transition into the H-A phase, bonding electrons on the H_2 molecules are transferred into band states and become itinerant. The weakening of the bond and the shielding of the Coulomb forces results in a reduction in the vibron frequency, as is observed.[8] The order parameter for the metallic phase is the free-carrier density n. It has also been shown that above the H-A phase line the molecules are orientationally disordered and within the H-A phase they are ordered.[4] The simplest order parameter to describe orientational ordering is

$$\sigma(P,T) = \left[\frac{4\pi}{5}\right]^{1/2}\frac{1}{N}\left[\frac{1}{x_o}\sum_i^{\text{ortho}}\langle Y_{20}^o(\omega_i)\rangle\right.$$

$$\left.+\frac{1}{x_p}\sum_i^{\text{para}}\langle Y_{20}^p(\omega_i)\rangle\right], \qquad (1)$$

where x_c is the ortho $(c=o)$ or para $(c=p)$ concentration, Y_{20}^c is a spherical harmonic of angular argument ω_i, $\langle\rangle$ implies a thermal average, and N is the number of molecules. It has been shown in general by Ashcroft,[9] and in particular by Garcia et al.[10] for the hcp structure, that the valence-conduction band gap is much smaller in the ordered than in the disordered phase, so that ordering favors metallization. Thus, the picture of the phase transition is one in which the order parameters n and σ are coupled; a first-order phase transition takes place and n discontinuously takes on a finite value. Silvera has proposed a model Hamiltonian which may be capable of explaining the observations in terms of a three-state Potts model describing the molecular orientations, in which the free-carrier charge density plays the role of an external field.[11]

In light of the arguments presented above, we propose

to write the vibron frequency in either phase as

$$v_{vib}(P,T) = v_{dis}(P) - [n(P,T)/n(P,0)]^{\alpha} v_n(P)$$

$$\equiv v_{dis} - \eta^{\alpha}(P,T) v_n , \quad (2)$$

where v_{dis} is the vibron frequency in the disordered phase, η is the normalized order parameter for the metal, and v_n scales the frequency shift. The exponent α is an unknown constant, presumably of order unity, which must be determined from a detailed theory of electronic structure. Here we have assumed that the vibron shift arises only from charge transfer; a small shift could also arise from the change in the interactions when the crystal orientationally orders, but we ignore this. Following this analysis, we see from Fig. 3 that in the low-pressure phase v_{vib} has no temperature dependence, as η is zero; this agrees with experiment, after the effect of the pressure distribution is removed. At the H-A phase line, η discontinuously changes and then further increases as the temperature is lowered. This additional temperature dependence we interpret as arising from an increase in the orientational order parameter σ, which results in increased band overlap or increased n.[12] Thus, from Fig. 3(a) and Eq. (2), we can plot the experimental normalized order parameter, shown in Fig. 3(b).

In studying the dependence of η on the critical pressure P_c or T_c, we have observed an unexpected result: The vibron discontinuity, $\eta(P_c, T_c) v_n(P_c)$, continuously decreases towards zero with increasing pressure and temperature. At 77 K, the phase transition occurs at 153 GPa, and the frequency discontinuity is 93 cm^{-1}; by 164 GPa, the discontinuity is about 36 cm^{-1}. This is demonstrated in Fig. 4. Figure 5 shows a plot of $\eta^{\alpha} v_n$ at the phase transition as a function of pressure. A linear extrapolation of this curve to zero frequency yields a critical pressure for the discontinuity going to zero at 173(4) GPa. Extrapolating the phase line determined by Lorenzana, Silvera, and Goettel,[2] the corresponding transition temperature is 151(15) K. Thus, the H-A phase line terminates in a critical point.

A complementary method for extracting the (P, T) point where the two vibron frequencies merge is as follows. From the temperature studies, we were able to ascertain that at a constant pressure $v_{vib}(P,T) - v_{dis}(P)$ decreased with increasing temperature, near the critical temperature. Although the transition from the H-A phase to the low-pressure phase occurs before the discontinuity goes to zero in our measurements, the curves can be extrapolated to extract a temperature $T_{\eta=0}$ at which $\eta(P_c, T_c)$ would be zero. The results of these extrapolations are consistent with the first method, although less precise as we did not have as much data. As a consequence we use the first method for the determination of the critical point.

Because our understanding of high-pressure hydrogen is developing very rapidly, there are a number of uncertainties in the behavior and unexplored regions of the phase diagram. It is useful to present a critical, albeit somewhat repetitive, discussion of these recent developments. The H-A phase was shown to be a unique phase that exists only at megabar pressures. An earlier proposal of a high-pressure phase diagram by Silvera[13] showed a phase line similar to that for H-A which was the metallic molecular phase, and it has been argued that H-A is indeed this phase.[5,8] Mao, Hemley, and Hanfland[6] presented spectroscopic evidence consistent with H-A having the hcp structure. Garcia et al.[10] show that an orientationally ordered hcp phase, rather than a disordered phase, favors metallization;[14] they predict a critical pressure of 180(20) GPa at $T=0$ K. Lorenzana, Silvera, and Goettel[4] reported that in crossing the H-A line in temperature, the rotational bands exhibit severe line broadening and apparent disappearance of intensity. This was interpreted as evidence for an orientational ordering transition, consistent with the picture of the me-
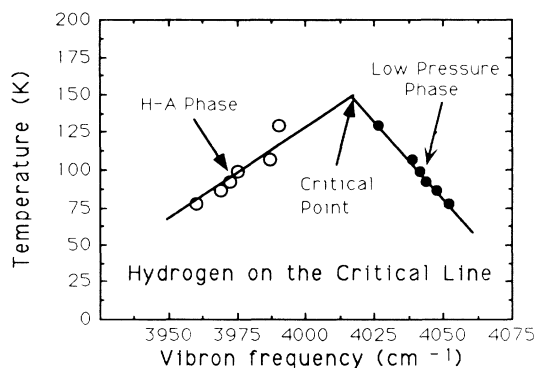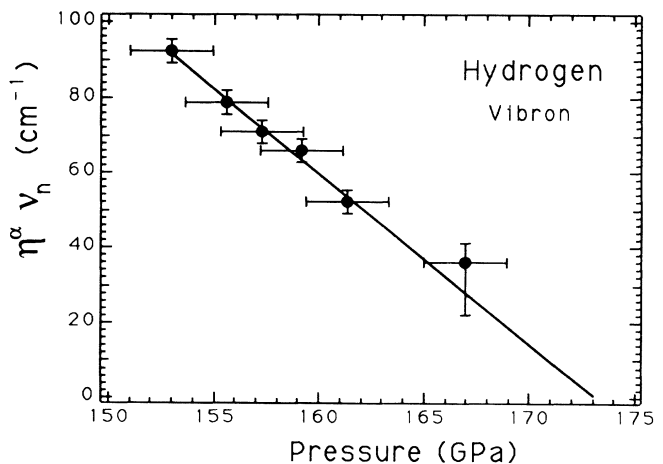

FIG. 4. The vibron frequencies at the critical pressure and temperature as a function of temperature. The solid lines are straight-line fits and extrapolations of the data points.

FIG. 5. The vibron frequency discontinuity at the H-A phase transition as a function of pressure. The line is a linear fit that predicts that the discontinuity will be zero at 173(4) GPa.

tallic state being ordered.

The positive slope of the H-A phase line (Fig. 1) is an indication that the anisotropic interactions responsible for orientational ordering increase with pressure, as expected. An extrapolation of the H-A line to room temperature implies a critical pressure of about 205–220 GPa. However, the H-A line terminates in a critical point. Mao, Hemley, and Hanfland[6] have reported an onset of Drüde-type reflectivity at room temperature, above 149 GPa. Extrapolating to the critical point of the H-A line yields a negative slope, which may indicate that the free charge carriers are thermally excited. A statistical-mechanical theory for this critical region would be useful for a comparison to experiment. While no definitive proof for the H-A phase being the molecular conducting state exists at this time,[15] we believe that it is indeed metallic, given all of the work discussed above, and it is useful to interpret current results in terms of such a picture.

We return now to the interpretation of the critical point shown in the phase diagram, Fig. 1. We have already discussed the scenario below this point. Above the critical-point temperature, with increasing pressure, we believe that the sample transforms continuously from an orientationally disordered insulator to an ordered metal. The evidence presented here for the critical point at high pressures shows that the phase diagram of H_2 is more intricate than had been previously anticipated. Further characterization of H_2 in the critical region of the phase diagram remains an important and exciting prospect for future research.

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

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[8]I. F. Silvera, J. H. Eggert, K. A. Goettel, and H. E. Lorenzana, II, in Proceedings of the Archimedes Workshop, Catania, Italy, 28–31 May (to be published).

[9]N. W. Ashcroft, Phys. Rev. B **41**, 10963 (1990).

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[12]In this description we ignore the effects of thermal excitation of the electrons.

[13]I. F. Silvera, in *Simple Molecular Systems at Very High Density*, edited by A. Polian and P. Loubeyre (Plenum, New York, 1989), p. 33.

[14]N. W. Ashcroft, Phys. Rev. B **41**, 10963 (1990).

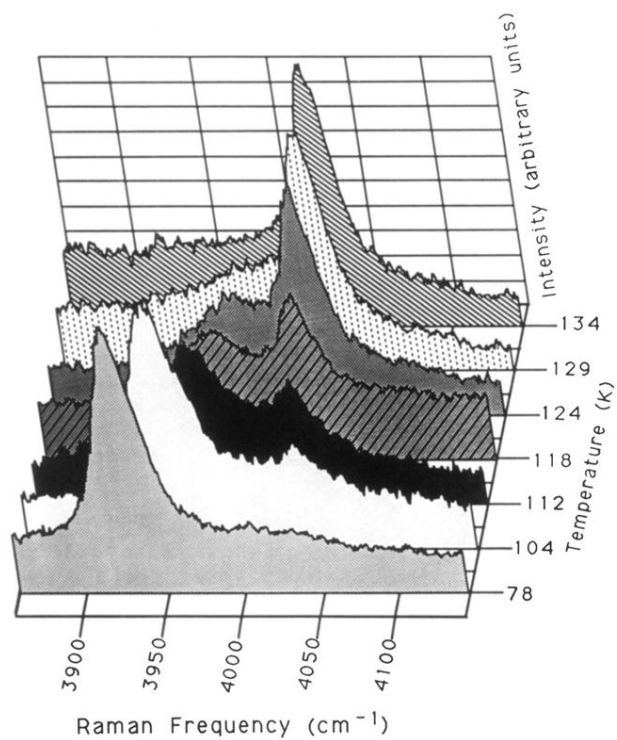[15]See Ref. 7 for a discussion of criteria for the insulator-to-metal transition.

FIG. 2. Spectra showing the thermal behavior of the vibron near the H-*A* transition in solid H_2 at a pressure of 164 GPa. The low-frequency peak is the H-*A* vibron.