Critical Behavior in the Hydrogen Insulator-Metal Transition

R. J. HEMLEY AND H. K. MAO

The vibrational Raman spectrum of solid hydrogen has been measured from 77 to 295 K in the vicinity of the recently observed insulator-metal transition and low-temperature phase transition at 150 gigapascals (1.5 megabars). The measurements provide evidence for a critical point in the pressure-temperature phase boundary of the low-temperature transition. The result suggests that below the critical temperature the insulator-metal transition changes from continuous to discontinuous, consistent with the general criteria originally proposed by Mott for metallization by band-gap closure. The effect of temperature on hydrogen metallization closely resembles that of the lower pressure insulator-metal transitions in doped V_2O_3 alloys.

THE USE OF HIGH PRESSURES TO alter the chemical and physical properties of materials is central to condensed-matter science. This is because pressure has a fundamental effect on chemical bonding, or more generally the electron distribution, in a material. For electrical insulators, the most dramatic effect in this regard is the pressure-induced transition from insulating to metallic forms. The prototype system for understanding the eventual transition of all materials to metallic states under pressure is solid hydrogen, which forms an insulating diatomic molecular solid under ambient pressures but is predicted to become metallic at sufficiently high pressures (*1*). Indeed, the determination of the pressure of the insulator-metal transition in hydrogen and characterization of its high-density metallic forms have been major problems in condensed-matter physics for over half a century (*1*). Recent developments in the diamond-anvil cell have opened these problems to experimental investigation by static high-pressure techniques (*2–6*). Optical measurements of hydrogen to pressures above 250 GPa indicated that metallization occurs by a band-crossing mechanism in the molecular solid (*3*). Very recent measurements of infrared reflectivity have established the onset of metallization at 295 K occurs at 150 GPa (*4*). The results are consistent with theoretical predictions that the solid transforms to a molecular metallic form before transforming to a dissociated monatomic metal (7).

Spectroscopic measurements carried out on hydrogen to pressures above 150 GPa have revealed several additional phenomena. Vibrational Raman spectra of the intramolecular stretching mode (vibron) in H_2 and D_2 at high pressure demonstrate that a discontinuous transition occurs in the molecular solid at low temperatures (77 K) in the pressure range of the onset of metallization (*2, 4*). Recent measurements of the lattice phonon and rotational bands have further established that the transition occurs with at most only minor changes in crystal structure (*6*). This result indicates that the transition is largely electronic in origin; that is, it appears to involve principally changes in the molecular bonding. This interpretation in turn has lent support for the hypothesis that the vibron discontinuity is associated with the insulator-metal transition (*3, 4*). Measurements of the vibron, however, show no sign of a discontinuity as the material passes through the insulator-metal transition at 295 K (*5*). Detailed assignment of the vibron transition and its connection with the insulator-metal transition therefore have not yet been established. In the present study we report extended measurements of the temperature dependence of the molecular vibron from 77 to 295 K in the pressure range of this transition. The results provide evidence for a critical point in the vibron discontinuity below room temperature. We suggest that insulator-metal transition changes from continuous to discontinuous behavior at the critical temperature. The temperature effect observed for hydrogen appears to parallel that of the low-pressure insulator-metal transitions in the $(Cr,V)_2O_3$ alloys.

The experiments were performed with high-pressure Raman scattering techniques similar to those described previously (*2–6*). We used diamond-anvil cells with single bevel anvils with central flats of 50 to 100 μm (*5, 6*). This contrasts with the 25- to 50-μm flats used in our 200- to 300-GPa hydrogen studies (*2–4*). As a result, sample sizes were 10 to 20 times larger than those of the earlier studies and allowed for the measurement of higher precision spectra. We used a composite gasket consisting of T-301 stainless steel with a 300-μm rhenium insert in which a 30- to 50-μm hole was drilled to contain the sample. Pressures were determined with the ruby fluorescence technique (*8*). Both low- and high-frequency Raman spectra and the ruby fluorescence spectra were measured on the same point in the sample (that is, without moving the diamond-anvil cell) in order to obtain an accurate measurement of the pressure for each hydrogen Raman measurement. All ruby spectra remained sharp at high pressure because of the hydrostatic nature of the hydrogen, the sparseness of the ruby in the sample, and the fact that the samples remained thick (>1 to 2 μm) at the sample-gasket interface at the maximum pressures.

Representative spectra of the vibron of hydrogen at 77 K and 295 K at 158 GPa are shown in Fig. 1. The transition is apparent in the 77 K spectrum. The appearance of two bands at the indicated pressures arises from two phases in the sample volume probed by the laser beam (*4, 9*). The frequency shift at high pressure at the two temperatures is shown in Fig. 2. The remarkable gap in the vibron frequency as a function of pressure is clearly evident, as noted in previous low-temperature measurements (*2, 4*). At 295 K, on the other hand,

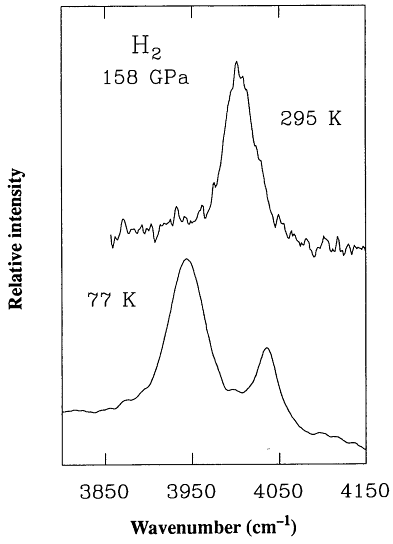

Fig. 1. Raman spectra of the intramolecular H-H stretching vibration (vibron) in solid hydrogen at 158 GPa and 77 and 295 K. A sloping background signal has been subtracted from the high-temperature spectrum. The estimated random errors in pressure and temperature are ±1 GPa and ±2 K (low temperature).

Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015.

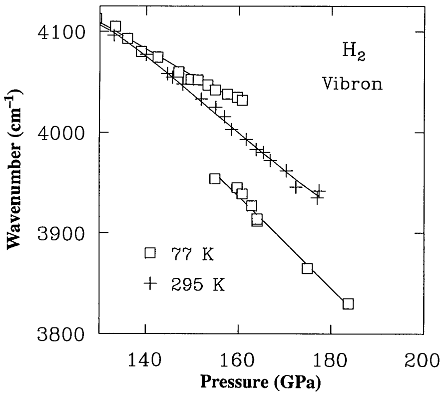

Fig. 2. Vibron frequencies versus pressure at 77 and 295 K.

the vibron shifts continuously through the gap to at least 177 GPa.

One explanation for the different behavior exhibited at the two different temperatures is the possibility that the transition shifts to significantly higher pressures with increasing temperature. This interpretation is in fact suggested by the results of recent Raman measurements by Lorenzana *et al.* (*9*) to 130 K. To examine this question we performed extended measurements of the vibron spectrum in the vicinity of the transition as a function of temperature. The magnitude of the discontinuity decreases significantly with increasing temperature; in addition, we confirm that the transition shifts to higher pressures. For example, $\Delta\nu \approx 100$ cm^{-1} at 77 K, with $P_{tr} = 152$ GPa, decreasing to $\Delta\nu \approx 35$ cm^{-1} at 130 K with $P_{tr} = 165$ GPa, as noted previously (*9*). We have successfully followed the transition to higher temperatures and pressures, and find that above 150 K and 170 GPa the splitting between the two bands is significantly less than the bandwidth of the peaks. In fact, only one band is resolved, with a bandwidth that is comparable to that observed for each peak at lower temperatures. This behavior was observed in numerous temperature and pressure cycling: in each case at temperatures between 150 and 200 K only one Raman peak was observed within the present resolution (10 cm^{-1}).

We interpret this behavior as evidence for the disappearance of the vibron transition at a critical point (critical end point) in a solid-solid transition. In other words, the phase transition is discontinuous below, and continuous above, a critical temperature T_c. The behavior is analogous to critical phenomena in a single component liquid-vapor transition or an immiscibility gap in a two-component system (*10*). If we extend this analogy further, there should be an excluded zone (two-phase region) in a plot of temperature versus vibron frequency. The results of such a plot for a range of pressures near the phase transition (150 to 170 GPa) are shown in Fig. 3. At 77 K the vibron frequency jumps from 4030 to 3960 cm^{-1} with increasing pressure; vibron frequencies between the values are not observed at 77 K. The two-phase region decreases to 4025 to 3990 cm^{-1} at 130 K and could not be observed above ~150 K. At higher temperatures all frequencies between 3900 and 4050 cm^{-1} could be observed by varying the pressure. Although a small splitting of several wave numbers in the vibron peak at higher temperatures cannot be ruled out, the large temperature dependence of the lower frequency vibron suggests that $\Delta\nu$ decreases rapidly to zero above 130 K (Fig. 3).

The evidence for a critical point in this transition has important consequences for the assignment of the transition. As discussed above, vibrational spectroscopic data are consistent with the assignment to metallization itself; however, other transitions could not be ruled out. The very important constraint in this regard is the evidence from the lattice-mode spectra for the lack of any major crystallographic structural changes accompanying the transition. Mott (*11*) has shown that band overlap must be accompanied by a discontinuity in volume and conductivity as a result of electron correlation. Such a discontinuity may only occur in the zero temperature limit and hence should terminate in a critical point at finite temperature (*11*). Later theoretical studies have shown that there may be a series of transitions to intermediate states at low temperature (*12*). The appearance of a discontinuity, lack of crystallographic transition, and the evidence for critical behavior, together with our measurements of infrared reflectivity at higher temperature (*5*), thus fit an isostructural insulator-metal transition driven by band-gap closure.

This result is shown in the pressure-temperature (P-T) phase diagram in Fig. 4. The phase line corresponding to the low temperature vibron discontinuity has a weakly positive Clapeyron slope, in agreement with previous measurements (*13*). We propose that the discontinuous behavior observed below 140 to 160 K is driven by band overlap, which gives rise to the metallic [or semimetallic (*3*)] phase. At high temperatures (295 K) the insulating (semiconducting) phase continuously transforms to the metal at 149 ± 10 GPa (*5*). The critical point constitutes the lower temperature bound on the continuous transformation. The evidence that the critical pressure exceeds 165 GPa indicates that the high-temperature boundary has a weakly negative slope, which implies that the high-pressure metallic phase has a higher entropy. Although there may be a contribution from thermally excited carriers, the high plasma frequencies obtained from Drude-model fits to the reflectance spectra (*5*) suggest that the band gap has in fact closed. Whether or not the metallic phase below T_c is distinct, and the possibility of additional low-temperature states (*14*), must await measurements of the temperature dependence of the dielectric properties at these pressures. We note that Raman measurements have failed to reveal any significant changes in vibrational properties in scanning temperature between these two regions (*15*).

It is interesting to note the similarity between the insulator-metal transition for hydrogen and that of $(Cr,V)_2O_3$ alloys, which have been studied extensively since

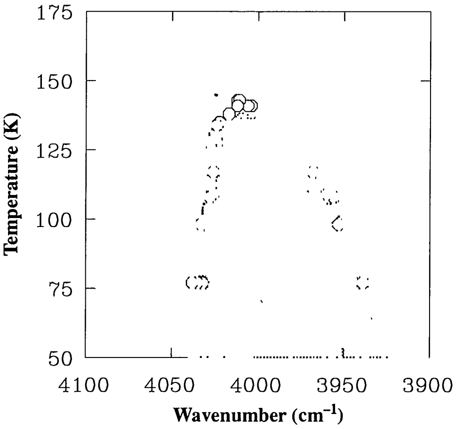

Fig. 3. Frequency-temperature plot in the vicinity of the vibron discontinuity. The squares are results reported by Lorenzana *et al.* (*9*). The shaded area is the proposed two-phase region.

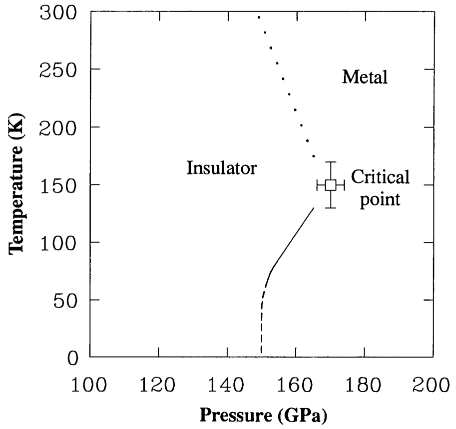

Fig. 4. Proposed P-T phase diagram for hydrogen in the vicinity of the insulator-metal transition. The solid line shows the phase boundary between the low-pressure insulating phase and low-temperature metallic phase below the critical temperature T_c. The region of the continuous transition from the insulator to the metal at high temperature above T_c is shown by the dotted line. The dashed line is the low-temperature phase boundary obtained by Lorenzana *et al.* (*9*). The possibility of additional transitions in this temperature range [see (*12, 14*)] needs to be examined by direct measurements.

the late 1960s. V_2O_3 with 3.75% Cr, for example, undergoes an insulator-metal transition under pressure and has a weakly positive Clapeyron slope, which terminates in a critical point at 1.25 GPa and 390 K (*16*). Structural studies have shown that the transition below T_c is isostructural and is associated only with a discontinuous change in lattice parameter. Furthermore, the conductivity first decreases with increasing temperature above T_c but then increases. This behavior was interpreted as a reentrant metallization that is continuous at high temperature with a negative Clapeyron slope (metallic phase above T_c) (*17*). This again may be similar to the behavior of hydrogen in the high-temperature, continuous metallization regime (*18*). Finally, we point out there is also recent evidence for analogous critical phenomena associated with pressure-induced isostructural insulator-metal transitions in other classes of materials (*19*).

REFERENCES AND NOTES

1. V. L. Ginzburg, *Key Problems in Physics and Astrophysics* (Mir, Moscow, 1978).
2. R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).
3. H. K. Mao and R. J. Hemley, *Science* **244**, 1462 (1989).
4. R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **63**, 1393 (1989).
5. H. K. Mao *et al.*, *ibid.* **65**, 484 (1990).
6. R. J. Hemley, H. K. Mao, J. F. Shu, in preparation.
7. E. Wigner and H. B. Huntington [*J. Chem. Phys.* **3**, 764 (1935)] originally predicted that hydrogen should transform to a monatomic metal under pressure. More recent theoretical studies have proposed that the molecular solid becomes metallic prior to this transition: D. E. Ramaker, L. Kumar, F. E. Harris, *Phys. Rev. Lett.* **34**, 812 (1975); C. Friedli and N. W. Ashcroft, *Phys. Rev. B* **16**, 662 (1977); B. I. Min, H. J. F. Jansen, A. J. Freeman, *ibid.* **33**, 6383 (1986); T. W. Barbee, A. Garcia, M. L. Cohen, J. L. Martins, *Phys. Rev. Lett.* **62**, 1150 (1989).
8. H. K. Mao, J. Xu, P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986); R. J. Hemley *et al.*, *Phys. Rev. B* **39**, 11820 (1989).
9. H. Lorenzana, K. A. Goettel, I. F. Silvera, *Phys. Rev. Lett.* **63**, 2080 (1989).
10. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, New York, 1971).
11. N. F. Mott, *Proc. Phys. Soc. A* **62**, 416 (1949); *Philos. Mag.* **6**, 287 (1961); *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).
12. D. Jerome, T. M. Rice, W. Kohn, *Phys. Rev.* **158**, 462 (1967); B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **4**, 755 (1968), and references therein.
13. We have found that extrapolation of the data obtained in the lower temperature range by Lorenzana *et al.* (*9*) also suggests that the vibron discontinuity may vanish at ~150 K. These authors did not discuss this result and its implication for critical behavior, however, possibly because their measurements were limited to lower temperatures and because they did not interpret the vibron transition as being associated with metallization.
14. We cannot yet rule out, for example, the possible formation of an excitonic insulator (*12*) stable at low temperatures over a narrow pressure interval as the band gap closes. The transition to such a phase (or phases) is also expected to exhibit critical behavior. Experimental verification of theses states appears incomplete, however (*19*).
15. The low-frequency rotational (or librational) bands (<400 cm^{-1}) have a weak dependence on temperature at these pressures. These results suggest the possibility of minor orientational transitions at higher temperatures that are distinct from the vibron transition (R. J. Hemley and H. K. Mao, in preparation).
16. D. B. McWhan and J. P. Remeika, *Phys. Rev. B* **2**, 3734 (1970); A. Jayaraman *et al.*, *ibid.*, p. 3751.
17. J. M. Honig and J. Spalek, *Proc. Indian Natl. Acad.* **52**, 232 (1986); J. Spalek, A. Datta, J. M. Honig, *Phys. Rev. Lett.* **59**, 728 (1987).
18. The metallization need not be strictly reentrant if there is a single high-pressure metallic phase. Although there may be a close parallel between the insulator-metal transition in hydrogen and in the doped V_2O_3 systems, we point out that there is evidence for three low-temperature phases in the latter [anti-ferromagnetic insulator, paramagnetic insulator, and paramagnetic metal (*16, 17*)]. The presence of the magnetic impurities and non-stoichiometry in the V_2O_3 alloys are likely to make insulator-metal transitions in this system more complex.
19. See for example, J. Neuenschwander and P. Wachter, *Phys. Rev. B* **41**, 12693 (1990), and references therein.
20. We thank J. Shu and M. Hanfland for help with the experiments, and N. W. Ashcroft for useful discussions. This work was supported by the NSF (grants EAR-8610086, EAR-8720320, and DMR-8912226), NASA (grant NAGW1722), and the Carnegie Institution of Washington.

25 May 1990; accepted 5 July 1990

Diffraction from Polymerized Membranes

FARID F. ABRAHAM AND DAVID R. NELSON

Flexible polymerized membranes in a good solvent are expected to exhibit a remarkable low-temperature flat phase, characterized by a diverging bending rigidity, vanishing elastic constants, and large fluctuations both parallel and perpendicular to the surface. A theory of the equilibrium structure factor provides a good fit to extensive molecular dynamics simulations of simplified "tethered surface" models of these materials. These results show how information about the size, thickness, and internal structure of polymerized membranes can be extracted from diffraction experiments.

TWO-DIMENSIONAL POLYMERIZED networks appear naturally in a biological context (*1*), and can be made artificially by, for example, modifying traditional methods of polymer synthesis, or by polymerizing ampiphillic bilayers or monolayers (*2*). A dilute solution of flexible sheet-like macromolecules prepared in this way should have properties which are strikingly different from conventional linear polymer chains. Polymer chains in a good solvent crumple into a fractal object whose characteristic size or "radius of gyration" R_g varies as a nontrivial power of the linear dimension L, $R_g \sim L^{3/5}$ (*3*). Linear polymers fold up on scales larger than a "persistence length" which is typically only a few monomer units in size. The statistical mechanics of two-dimensional polymer networks (*4*) has attracted intense theoretical interest, in part because, unlike linear polymers, they are expected to exhibit a low-temperature flat phase with an *infinite* persistence length. The flat phase arises because the resistance to in-plane shear deformations leads to an anomalous stiffening of the surface in the presence of thermal fluctuations (*5*). This flattening results from a delicate interplay between geometry and statistical mechanics which has no analog in conventional polymer solutions.

The simplest model of polymerized membranes is a "tethered surface," composed of hard spheres of diameter d each tied to six near neighbors to form a planar triangulated network; the network is then equilibrated at a finite temperature by allowing it to bend and possibly crumple in three dimensions. Although the first simulations of such tethered surfaces were interpreted in terms of a high-temperature crumpled phase (*4*), extensive simulations of much larger surfaces with a very similar potential revealed that these objects were in fact flat (*6, 7*), with very large fluctuations in the direction parallel to the average surface normal (see Fig. 1).

The elastic properties of this flat phase are embodied in an unusual long wavelength Hamiltonian which describes the energy of in-plane and out-of-plane phonon modes. In-plane phonon displacements $\mathbf{u}(x_1, x_2)$ and an out-of-plane displacement $f(x_1, x_2)$ are defined by the equation

$$\mathbf{r}(x_1, x_2) = m_0[(x_1 + u_1)\hat{\mathbf{e}}_1 + (x_2 + u_2)\hat{\mathbf{e}}_2 + \mathrm{f}(\hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2)] \tag{1}$$

which gives the three-dimensional position vector $\mathbf{r}(x_1, x_2)$ of an atom in the membrane as a function of internal membrane coordinates x_1 and x_2 attached to the monomers. These internal parameters multiply orthogonal unit vectors $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ which span a flat zero temperature reference state (typically, a hexagonal piece of triangular lattice in computer simulations) of characteristic linear dimension L. Distances will be measured in units of d, the average spacing between nearest neighbor monomers in the reference

---

F. F. Abraham, IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099.
D. R. Nelson, Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138.