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Metal-Insulator Transition in Solid Hydrogen[*]

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The transition between compressed molecular hydrogen and metallic hydrogen is investigated from the point of view of a metal-insulator transition. By studying how the electronic states in metallic hydrogen change when nearest-neighbor protons are moved closer together it is found that the transition should occur at a pressure in the neighborhood of 3 Mbar. The metastability of metallic hydrogen at low pressures is investigated and it is found that at zero pressure and temperature metallic hydrogen would last only a fraction of a second.

I. INTRODUCTION

There is at present great interest in the possibility of producing metallic hydrogen in the laboratory. In this connection it is important to have some estimate of what pressure is needed to produce metallic hydrogen and whether metallic hydrogen would be metastable at low pressures. Estimates of the pressure needed to make metallic hydrogen vary all the way from 0.25 to 20 Mbar.[1,2] In this paper we will discuss the transition between compressed molecular hydrogen and metallic hydrogen from the point of view of a metal-insulator transition. This point of view allows us to estimate the transition pressure in a simple way and also to investigate whether metallic hydrogen is metastable at low pressures.

Our method is based on calculating the distortion of the electronic wave functions in metallic hydrogen as nearest-neighbor protons are moved closer together. That is, metallic hydrogen with protons regularly spaced in a bcc or hcp array will be perturbed by decreasing the separation of nearest neighbors while keeping the over-all density constant (see Fig. 1). If the protons are moved only a little or if the density is high enough, moving the protons will produce only a small change in the electronic wave functions. However, if the protons are moved substantially closer together and if the density is low enough the change in the electronic wave functions can be large. We might ask if the change in the electronic wave functions can be so large that the wave functions become localized around pairs of protons. The localized electrons would of course not be free to move and hence in this case the perturbed metal would be an insulator. If we approximate the electronic wave

functions in the metal by plane waves, then the criterion for electrons becoming localized can be approximated by the condition that an electron of average energy forms a bound state in the potential near two protons that have been moved closer together.

In the normal metal, where a cell contains only one proton, it is energetically favorable for an electron to be unbound. However, in the perturbed metal where there are two protons in a cell it may be energetically favorable for an electron to become localized. In other words, the decrease in potential energy due to the attraction of an extra proton may more than compensate for the increase in kinetic energy of the localized electron. The
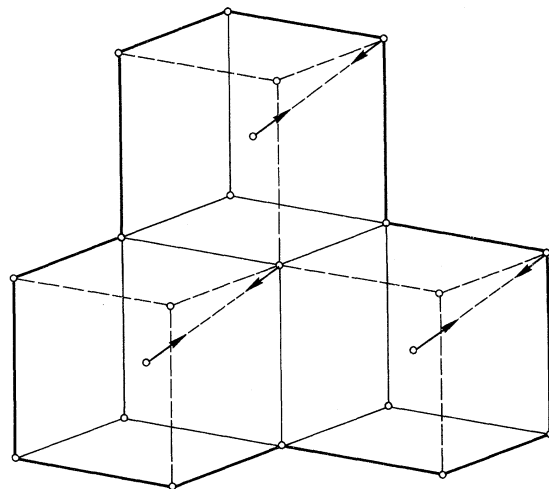

FIG. 1. Displacement of nearest-neighbor protons in a body-centered-cubic structure.

tendency to form a bound state in the perturbed metal will be greater at low densities than at high densities, because as the density is raised changes in kinetic energy become relatively more important compared to changes in potential energy. By solving the Schrödinger equation for an electron moving in the potential near two protons that have been moved closer together we can calculate, as a function of density, the energy of the bound state. By comparing this bound-state energy with the average energy of an electron in the metal we can determine at what density a given displacement of the protons will turn the metal into an insulator.

For the purposes of estimating at what pressure compressed molecular hydrogen turns into metallic hydrogen we should consider displacements of the protons such that the separation of the photons in the perturbed metal is approximately equal to the separation of the protons in a hydrogen molecule, namely $1.4a_0$. In Sec. II some simple approximations are introduced for estimating the density at which such displacements cause electrons to become localized. This gives an estimate for the transition pressure which is consistent with present experimental knowledge of the equation of state of compressed molecular hydrogen.

In Sec. III we will study the question of whether metallic hydrogen is metastable at low pressures. Using the method developed in Sec. II we can calculate, as a function of pressure, what displacements of the protons in metallic hydrogen would cause electrons to become bound. The probability per unit time for attaining these displacements at zero temperature can be estimated from the Debye temperature. Thus we are able to estimate from the Debye temperature how long it would take a sample of metallic hydrogen at zero temperature and low pressure to switch to the insulating form.

II. TRANSITION PRESSURE

In order to estimate the pressure below which metallic hydrogen is unstable against formation of compressed molecular hydrogen we must first calculate the binding energy of an electron in the potential near two protons separated by $1.4a_0$. As in the Wigner–Seitz approximation[3] for a normal metal we will assume that the motion of different electrons is correlated in such a way that this potential goes to zero as one approaches neighboring pairs of protons. In estimating the energy of an electron bound to a pair of protons in the perturbed metal we will consider first the situation at pressures $\lesssim 1$ Mbar and then the situation at higher pressures.

At pressures less than about 1 Mbar the total volume of two Wigner–Seitz cells in the unper-

turbed metal will be sufficiently large compared to the volume occupied by a hydrogen molecule so that the potential seen by an electron in the perturbed metal will be similar to the potential seen by an electron in a hydrogen molecule. As an approximation we will assume that the potential an electron sees in the neighborhood of two protons separated by $1.4a_0$ differs from that in a hydrogen molecule only in that the potential is zero outside a certain sphere centered on the pair of protons. The radius of this sphere will be chosen so that the volume of the sphere is equal to twice the volume of a Wigner–Seitz cell in the unperturbed metal. The change in bound-state energy of an electron from that in a hydrogen molecule will be determined by the value of the electron wave function outside the sphere. Since the volume of the sphere is large compared to the volume of a hydrogen molecule we need only concern ourselves with the exponential tail of the electron wave function. Thus for simplicity we will assume that the bound-state wave function is an exponential function:

$$\psi(r) = (\pi a^3)^{-1/2} e^{-r/a} , \qquad (1)$$

where r is the distance from a point halfway between the two protons separated by $1.4a_0$. The expectation values of the electron kinetic energy, electron-proton attraction, and electron-electron repulsion will approximately agree with accurate numerical calculations for a hydrogen molecule[4] if we choose $a = 0.97a_0$. If we use the wave function (1) with $a = 0.97a_0$ and first-order perturbation theory to calculate the change in the bound-state energy in the perturbed metal from that in a hydrogen molecule, we obtain the bound-state energies (for $r_s > 1.5a_0$) shown by the solid line in Fig. 2.

As the pressure is increased the size of a Wigner–Seitz cell decreases. At a pressure of 20 Mbar the radius of a sphere containing the volume of two Wigner–Seitz cells becomes comparable to a Bohr radius. Thus at pressures > 20 Mbar the bound-state energy of an electron in the perturbed metal is small. Hence, we may approximate the bound-state wave function by a function of the form

$$\psi(r) = (C_1/R) e^{-r/b-r/R}, \quad r < R$$

$$= (C_2/r) e^{-r/b}, \qquad r > R \qquad (2)$$

where R is the radius of the sphere containing the volume of the two Wigner–Seitz cells. Continuity of the wave function at $r = R$ requires $C_1 = eC_2$; the absolute values of C_1 and C_2 are fixed by the normalization condition $\int |\psi|^2 d^3x = 1$. The constant b will be approximately related to the bound-state energy E_b by
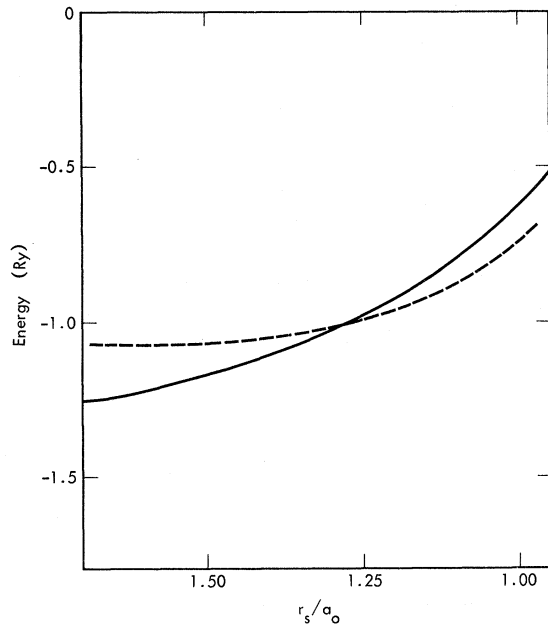
FIG. 2. Bound-state energy in perturbed metallic hydrogen (solid line). Average energy of an electron in metallic hydrogen (dashed line). The abscissa r_s is related to the density n by $\frac{4}{3}\pi r_s^3 = 1/n$.

$$b \simeq 2\pi\hbar/(2mE_b)^{1/2} , \tag{3}$$

where m is the electron mass. In order to estimate the bound-state energy one may use the wave function (2) to calculate the expectation value of the kinetic energy and electron-proton potential energy. In order to take into account electron-electron correlation we will assume that the electron-electron repulsion energy is $e^2/2R$. Taking the sum of these energies and using Eq. (3) then gives us an estimate of the bound-state energy at high pressures. By joining the results for high pressure and the results for low pressure we obtain the curve for bound-state energy vs density shown in Fig. 2.

In order to determine at what density electrons in the perturbed metallic hydrogen would actually become localized we must compare the bound-state energies just calculated with the energies of the metallic electrons. We will first look at the energies of the electrons in the unperturbed metal. Because of the simple nature of metallic hydrogen the energies of electrons in unperturbed metallic hydrogen can presumably be calculated fairly accurately using the Wigner–Seitz approximation.[3] In Fig. 2 the dashed line shows the average energy of an electron in metallic hydrogen according to calculations[5] based on the Wigner–Seitz approximation. If the energies of the electrons in the perturbed metal were the same as in the unperturbed metal, then the perturbed metal would become an insulator at a density

where the two curves in Fig. 2 cross. This density corresponds to a pressure of 3 Mbar. This, of course, is only a rough estimate of the transition pressure because of the crude nature of our approximations and because the transition in reality also involves a change in density. An accurate calculation of the transition pressure would necessitate calculating when the Gibb's energy of compressed molecular hydrogen becomes equal to the Gibb's energy of metallic hydrogen. Nevertheless, our estimate of the transition pressure is consistent with present experimental knowledge of the equation of state of compressed molecular hydrogen at high pressures.[6,7]

III. METASTABILITY

We now turn to the question of the metastability of metallic hydrogen at pressures below the transition pressure. We will restrict our attention in the following to the situation for zero temperature. That is, we will study the stability of metallic hydrogen with respect to the zero-point vibrations. From the considerations of Sec. II it is evident that by moving two protons closer together than they are in the normal metal some of the electrons in the metal can become localized. The fraction of electrons that can be bound depends on both the displacement of the protons and the pressure. As one lowers the pressure the fraction of electrons that become localized because of a given displacement of the protons increases. Thus it is possible that at low pressures the electrons in metallic hydrogen can become localized as a result of the zero-point vibrations. In order to investigate this effect we will first study how the binding energy of an electron in a modified cell depends on the separation of the two protons when the pressure is low.

In Sec. II we found that if pairs of protons are moved to a separation of $1.4a_0$ an average electron will become bound at a pressure of ~ 1 Mbar. We will now calculate what separation of two protons would cause an average electron to become bound at a pressure of 1 atm. If we use a trial wave function

$$\psi(r) = (\pi a^3)^{-1/2} e^{-r/a}, \tag{4}$$

then the binding energy of the electron may be written in the form

$$E = (1/a^2 - 2\alpha/a + 2\beta/a)\,\text{Ry} , \tag{5}$$

where α is a measure of the electron-proton attraction and β is a measure of the electron-electron repulsion. The constant α is determined by the separation of the two protons; in fact

$$\alpha \approx 2 - 0.6\,[(r_s - \delta)/a]^2 , \tag{6}$$

where δ is the assumed displacement of each pro-

TABLE I. Bound-state energy as a function of proton separation at zero pressure.

Proton separation (a_0)	Probability	Bound-state energy (Ry)
2.0	9×10^{-10}	0.92
1.8	4×10^{-12}	1.01
1.6	6×10^{-15}	1.13

ton towards the other proton. We will assume that $\beta = \frac{1}{2}$. At 1 atm pressure the radius of a cell in metallic hydrogen is $r_s = 1.68a_0$. The corresponding binding energies in the modified cell for several displacements δ calculated using Eqs. (6) and (7) are shown in Table I. Since the average energy of an electron in metallic hydrogen at zero pressure is -1.06 Ry, we see that an average electron will become localized for proton separations $\lesssim 1.7a_0$.

In order to estimate how many electrons are bound at any given time we must know the probability for attaining various displacements δ. At zero temperature the probability for attaining various displacements is determined by the zero-point motion. The average displacement of a proton due to zero-point motion can be estimated for the Debye temperature. Indeed, using the Debye model for the vibration of a solid, we have the mean-square displacement of a proton in a given direction as follows:

$$\langle \delta^2 \rangle = \tfrac{3}{8} (\hbar/M\omega_D),\qquad(7)$$

where M is the proton mass and ω_D is related to the Debye temperature Θ_D by

$$\hbar\omega_D = k\Theta_D.\qquad(8)$$

The Debye temperature of metallic hydrogen at low pressure has been estimated to be on the order of 2000 °K.[5,8] This gives a root-mean-square displacement of $0.17a_0$. In order to calculate the probability for attaining various displacements we must know the shape of the interatomic potential.

In the harmonic approximation to the interatomic potential we would obtain the probabilities from a Gaussian distribution. From Table I we see that we need a displacement of about $5(\langle \delta^2 \rangle)^{1/2}$ for each of two neighboring protons in order that the protons be close enough to cause an average electron to be bound. The probability for this to occur according to a Gaussian is $\sim (6 \times 10^{-7})^2 = 4 \times 10^{-13}$. On the other hand, the frequency of vibration corresponding to a Debye temperature of 2000 °K is $2\pi\omega = 3.6 \times 10^{15}$ sec^{-1}. This means that in about 10^{-3} sec a given sample of metallic hydrogen at atmospheric pressure would convert to the insulating form. Actually, this is probably a considerable overestimate of the time that metallic hydrogen would last at low pressure. In the first place, the harmonic approximation fails for large displacements. Second, electrons on the surface which are unstable for smaller displacements would start a chain reaction when they become localized. In any case metallic hydrogen at atmospheric pressure would last only a fraction of a second. A similar conclusion has recently been reached by Salpeter.[9]

As the pressure is increased the displacement of the protons necessary to cause the wave function of an average electron to become localized decreases. At the same time the Debye temperature increases, causing the mean-square displacement of the protons to decrease as the pressure is increased. If one uses the variation of Debye temperature with pressure calculated in Ref. 5 then one finds that the ratio of the displacement of the protons necessary to localize the wave functions to the mean-zero-point displacement of the protons decreases only very slowly with pressure. Indeed, one finds that the pressure must be very high (~ 1 Mbar) in order that the metallic hydrogen have a long lifetime.

ACKNOWLEDGMENTS

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