Metallization of Fluid Nitrogen and the Mott Transition in Highly Compressed Low-Z Fluids

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Electrical conductivities are reported for degenerate fluid nitrogen at pressures up to 180 GPa (1.8 Mbar) and temperatures of ~7000 K. These extreme quasi-isentropic conditions were achieved with multiple-shock compression generated with a two-stage light-gas gun. Nitrogen undergoes a nonmetal-metal transition at 120 GPa, probably in the monatomic state. These N data and previous conductivity data for H, O, Cs, and Rb are used to develop a general picture of the systematics of the nonmetal-metal transition in these fluids. Specifically, the density dependences of electrical conductivities in the semiconducting fluid are well correlated with the radial extent of the electronic charge-density distributions of H, N, O, Cs, and Rb atoms. These new data for N scale with previous data for O, as expected from their similar charge-density distributions.

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Dense hydrogen and oxygen have recently been shown to undergo Mott transitions from semiconducting to metallic fluids at 100 GPa pressures and several 1000 K [1,2]. Their metallic state is that of the minimum conductivity of a metal, as is that of fluid Cs and Rb which undergo similar transitions at comparable temperatures [3]. Fluid H, O, Rb, and Cs are all strong-scattering metals which reach metallic conductivities of $\sim 1000\ (\Omega\text{-cm})^{-1}$, when the ratio of the size of these atoms to the average distance between them is ~0.3. They all have essentially the same value of electrical conductivity because the minimum conductivity of a metal scales weakly with the number of conduction electrons per atom and the density of metallization [4].

It is important to understand the properties of low-*Z* elements at high pressures because they are very important scientifically and, potentially, technologically. For example, if solid monatomic nitrogen could be synthesized to be metastable at ambient, it might be a clean energy source [5]. Electrical conductivities of N, O, and H are important for understanding generation of magnetic fields in the deep interiors of giant planets in this solar system and in the ~100 extrasolar planets which have been discovered recently [6]. Obtaining extreme conditions of pressure and temperature enables investigation of condensed matter at conditions which have only recently become accessible [7] but have been sought for decades [8]. Fluid hydrogen in the isotopic form of deuterium and tritium is the fuel in inertial confinement fusion [9]. Metallic fluid hydrogen might provide a possible route to the synthesis of novel metastable materials such as solid metallic hydrogen [10].

The purpose of this Letter is to address the systematics of the approach to metallization within the semiconducting phase and to demonstrate for the first time that electrical conductivity in the semiconducting phase is strongly correlated with the radial extent of the electronic charge-density distribution of the atom. This issue has received relatively little experimental attention because there are few disordered, elemental systems which are essentially monatomic and undergo the nonmetal-metal transition. To our knowledge, the only simple fluids observed do this are N along with O, H, Cs, and Rb. Fluid iodine also undergoes a nonmetal-metal transition at ~3 GPa [11], but the densities have not been reported. For this reason electrical conductivities of nitrogen were measured at 100 GPa pressures to test the prediction of our simple picture of the semiconducting phases of this unique ensemble of fluids at extreme conditions. The conductivities of nitrogen scale essentially as those of oxygen, as expected. These experiments also yield a simple explanation for why the simple Herzfeld criterion [12] yields calculated metallization densities of monatomic H and Cs which are in excellent agreement with experiment.

Dense fluid nitrogen is probably monatomic and highly degenerate in these experiments. While the pressures in the nitrogen experiments are determined to within 1% by measurement of impactor velocity, the densities and temperatures are calculated by simulating each experiment using the nitrogen equation of state described previously [13]. Calculated densities ranged from 2.9 to 4.2 g/cm^3. Temperatures were in the range 6000 to 8000 K. These are estimated from the hydrodynamic simulations and previous single and double shock-temperature measurements [13]. We used the fact that the majority of the final temperature in a shock reverberation experiment is deposited on the first and second shocks. For nitrogen, we typically get four reverberations until we reach the final pressure. Since our second shock pressures in each of the experiments lay in the same range as the previously measured double shock temperatures [13], for our final temperature, we estimated a second shock temperature based on the previous measurements and added a representative amount for the final two reverberations.

N_2 dissociates when $k_B T_d / E_d \sim 0.1$, where k_B is Boltzmann's constant, T_d is the temperature of dissociation, and $E_d\sim$ is the dissociation energy at 0 K [14]. At a density of 3 g/cm^3, $E_d \sim 3$ eV [15] and thus $k_B T/E_d \sim 0.2$, which suggests that nitrogen is completely dissociated. In addition, the calculated dissociation fraction of N_2 molecules is 0.4 at 2.9 g/cm^3 on the 5000 K isotherm [16]. Because of the higher densities and temperatures reached in these experiments, the dissociation fraction will be substantially higher. Again, this suggests that all the N_2 molecules are dissociated, which is the assumption we make for both N and O. Total dissociation of N_2 is remarkable in view of the fact that the dissociation energy of the triple bond of the N_2 molecule is 9.8 eV. It is also quite probable that H_2 is totally dissociated, given that the calculated H_2 dimer lifetime is $\sim 10^{-14}$ s at conditions in these experiments [17,18]. Similarly, expanded Cs and Rb undergo a nonmetal-metal transition in a fluid composed primarily of monomers with a relatively low concentration of dimers [19]. Thus, in the following considerations, we assume that all five fluids are monatomic and consider their atomic wave functions. While there might be some relatively low concentration of dimers in these fluids, their concentration should be sufficiently low so that the basic conclusion is unchanged.

The nitrogen results reported here used multiple-shock compression [20,21] to reach 80 to 180 GPa at $\sim$7000 K. At the maximum density of 4.2 g/cm^3, the free-electron Fermi energy of N with three valence electrons per atom is 24 eV, large compared to the temperature of 0.6 eV. Similarly, the free-electron Fermi energies of H and O are 19 and 29 eV at a density of 0.64 and 4.75 g/cm^3, respectively. Thus, metallic fluid N, O, and H are highly degenerate.

The electrical conductivity of nitrogen was measured using two different circuits depending on the expected value of the conductivity. For conductivities below 1 $(\Omega\text{-cm})^{-1}$, a charged capacitor is discharged through the sample which is initially an insulator and becomes conducting after shock compression [22]. The measured resistance is converted to a conductivity using an experimentally determined geometric factor. This method loses sensitivity when resistances fall below a few Ohms. For conductivities above 1 $(\Omega\text{-cm})^{-1}$, a constant current supply flows through the parallel combination of a known shunt resistor and the sample with two voltage probes [21]. Sensitivity is maximized by choosing the shunt resistor equal to the expected sample resistance at high pressure. For conductivities of 10^2 up to 10^4 $(\Omega\text{-cm})^{-1}$ the same circuit and four voltage probes are used on the sample because of possible contact resistances. In these experiments, shunt resistances of a few 0.1 Ω were used and voltages of 0.3 to 1.3 V were measured with currents of $\sim$5 A.

The electrical conductivity of nitrogen to 180 GPa is shown in Fig. 1. The electrical conductivity of nitrogen is very similar to those of hydrogen [1] and oxygen [2]. From 80 to 120 GPa, nitrogen is semiconducting and can be described by the same exponential form used to describe the semiconducting state in fluid hydrogen [21]. The electrical conductivity of nitrogen reaches minimum metallic conductivity at $\sim$120 GPa. The conductivity above the transition, 1000 $(\Omega\text{-cm})^{-1}$, is essentially pressure and temperature independent. Metallic conductivity is expected to increase only a factor of $\sim$2 at higher pressures up to several TPa [23]. Except for slightly different transition pressures to the metallic fluid, the electrical conductivity of all three are essentially the same. The slight differences in the conductivity in the semiconducting region is attributed to the different thermal history and mobility gap of each material.

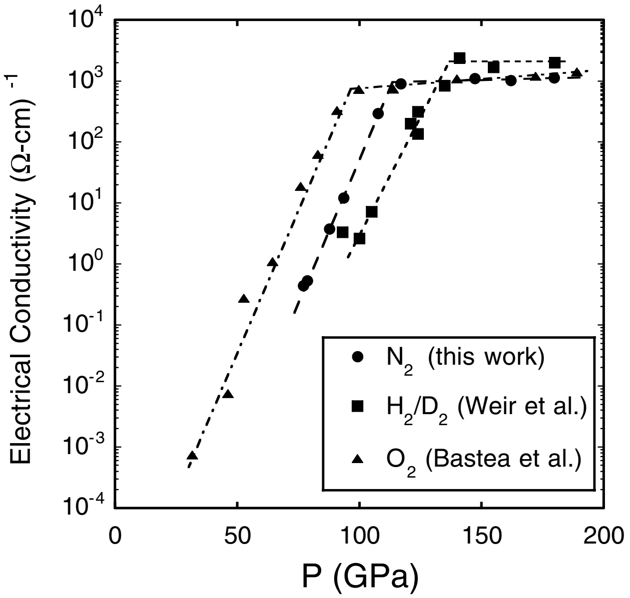

FIG. 1. The electrical conductivity of fluid N, H, and O plotted as a function of multiple shock pressure. Minimum metallic conductivity is reached at 100, 120, and 140 GPa for oxygen, nitrogen, and hydrogen, respectively. Compression factors over intial liquid densities are 3.6, 4.2, and 9.1 for these three fluids, respectively.

The electrical conductivity of nitrogen, hydrogen [1], and oxygen [2] is plotted versus $D^{1/3}a^*$ [24] in Fig. 2. For a^*, we used the empirical values of Slater [25] except for hydrogen. For hydrogen, we used the exact value of the Bohr radius. The scaled electrical conductivity curves for N and O almost coincide and reach metallic transition at $D^{1/3}a^* \sim 0.34$. For comparison, the scaled electrical conductivity curves for H [1], Rb, and Cs [3] are also shown in Fig. 2. For these monovalent elements, the metallic transition occurs at $D^{1/3}a^* \sim 0.38$. By scaling the electrical conductivity of N and O with a^*, we show that the behavior of both materials is identical. Furthermore, we find that there is a general trend that polyvalent atoms like N and O reach metallization at lower values of the scaled density than monovalent atoms like H, Rb, and Cs.

The general systematics for the electrical conductivities of N, H, O, Cs, and Rb in the semiconducting region can be explained on the basis of their relative radial

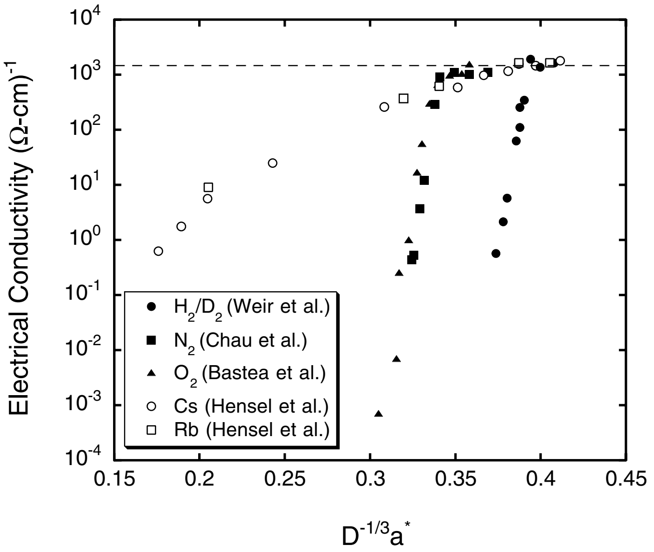

FIG. 2. The electrical conductivity of N, H, O, Cs, and Rb plotted versus the scaled density $D^{1/3}a^*$, where $D^{-1/3}$ is the average distance between atoms and a^* is the size of the atom.

charge-density distributions. The valence charge-density distributions [26] for N, H, O, Cs, and Rb are shown in Fig. 3(a). For purposes of comparison, the charge-density distributions for each element have been shifted so that the peak in each distribution lies at $r = 1$ bohr. For N and O, whose valence shell is in a p orbital, the charge distribution has been spherically averaged. From Fig. 3(a), elements that semiconduct at lower relative densities (pressures of 0.01 GPa), Rb and Cs, have the largest radial extent of the charge distributions. Not very much compression is required to have sufficient overlap of the valence electrons between adjacent atoms to delocalize. Hydrogen has the smallest radial extent and requires the highest pressure (~ 140 GPa) to reach metallization. However, the scaled electrical conductivity curves of H, Rb, and Cs all metallize at a common value of the scaled density, $D^{1/3}a^* \sim 0.38$. The charge densities of N and O have a radial extent comparable to that of H; the free atom sizes of H, N, and O are very close. However, N and O have three and four valence electrons, respectively, and thus have a higher charge density at a given radius than H. As a result, N and O reach metallization at a slightly lower value of the scaled density, 0.34 rather than 0.38. Effectively, the amount of overlap between the valence shell of adjacent atoms determines the transition to a metallic state (delocalized electrons). This simple picture illustrates the physical basis for the Mott criteria, $D_m^{1/3}a^* = \text{const}$, used previously to understand the nonmetal to metal transition in hydrogen and oxygen. The constant in the Mott criteria depends, not surprisingly, on the valence of the atom. This simple model, based on atomic wave functions, readily estimates the metallization densities for monatomic fluids and shows that the metallization process depends systematically on the electronic structure. In this discussion, we have not included other factors such as hybridization of wave functions, different scattering mechanisms, and other details which are likely important. Also, we have used ambient pressure atomic wave functions in this analysis in the same spirit as Mott.

Besides the Mott picture, we can examine the metallization process from the Herzfeld-Goldhammer picture [12]. In the Herzfeld-Goldhammer picture, compressing a system with average polarizability, α, and molar density, D, results in a dielectric catastrophe and a transition to a metallic state when $\frac{4\pi}{3}\alpha D = 1$. Since α is considered to be constant, this equation defines metallization density. The different radial extents of the charge-density distributions are consistent with the large differences in electronic polarizabilities of these atoms and the approach to

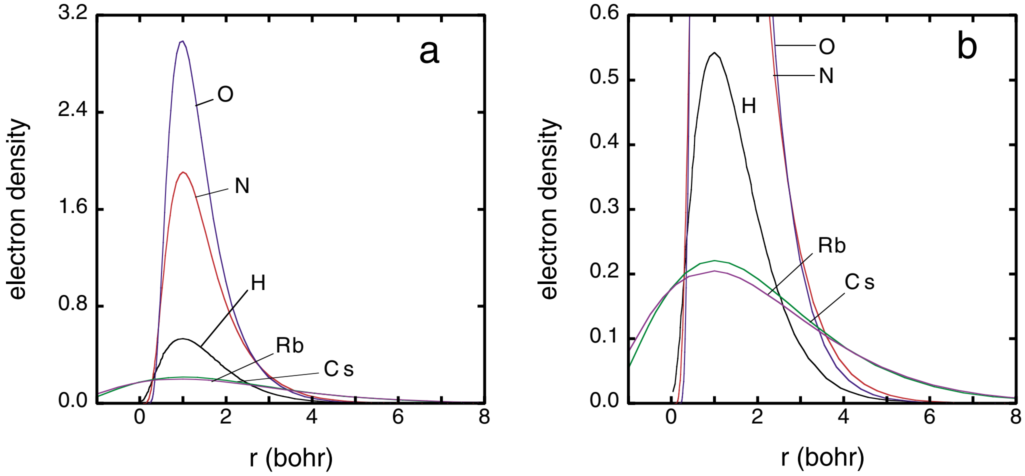

FIG. 3 (color online). (a) The valence electron densities ($4\pi r^2\psi^*\psi$) of N, H, O, Rb, and Cs are plotted as a function of r. The charge-density distributions are plotted, for comparison purposes, with the peak of the distribution centered at 1. (b) The data in (a) plotted on a different scale.

a metallic state within the Herzfeld-Goldhammer picture. The average electronic polarizability for H, N, O, Rb, and Cs are 0.667, 1.10, 0.802, 47.3, and 59.6 (in units of 10^{-24} cm^3) [27], respectively. So for H, we get a metallization density of 0.60 mol/cm^3 which is consistent with the experimental value of 0.64 mol/cm^3 [1]. The polarizability is larger for the large atoms, Rb and Cs, because the outer electrons are screened from the nucleus by the large electronic core. Thus the outer electrons see a relatively lower Coulomb force and, hence, respond much more to an applied electric field than electrons within more tightly bound atoms. The electron in the hydrogen atom sees the unscreened Coulomb force of the proton and is tightly bound. In this way, an electric field causes a larger polarizability of a large atom relative to that of a small one.

We have demonstrated that the electrical conductivities in the semiconducting regime and metallization of dense fluids are correlated with radial variations in the charge-density distributions of the respective atoms. The behavior of the electrical conductivity of dense fluid nitrogen was shown to be nearly identical to that of oxygen, as predicted by this simple picture. While the original observation of a metallic transition in dense fluid hydrogen was unexpected, this nonmetal to metal transition occurs systematically in a number of different fluids. The only requirement for this transition is a fluid that is compressed sufficiently for the valence shell of adjacent atoms to overlap. Also, while each of these dense fluid systems might have some small fraction of dimers, we argue that the transition to a metallic fluid is dominated by the monatomic species and that a similar effect is expected for the diatomic species. We expect that a larger number of fluid systems have an identical nonmetal to metal transition. For example, CO, which is isoelectronic to N_2, is expected to behave like nitrogen and oxygen, while Cl_2, F_2, and Br_2 are expected to behave like H, Cs, and Rb.

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[1] S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996).

[2] M. Bastea, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **86**, 3108 (2001).

[3] F. Hensel and P. P. Edwards, Phys. World **4**, 43 (1996).

[4] Minimum metallic conductivity $\sigma_{\min}$ is derived from the Drude model: $\sigma = \frac{ne^2\tau}{m}$, where n is total number of electrons per unit volume, e is charge of an electron, τ is relaxation time for scattering of electrons at Fermi level, and m is electron mass. In the strong-scattering Ioffe-Regal limit, the minimum electron mean free path λ for metallic conduction is the average distance between nearest neighbors, so that $\tau = \frac{\lambda}{\nu_F}$ and $\lambda = D_m^{-1/3}$, where ν_F is Fermi velocity and D_m is atom density at metallization. For z conduction electrons per atom, $\sigma = \sigma_{\min} = z^{2/3}e^2/3\hbar D_m^{-1/3}$, where $\hbar = \frac{h}{2\pi}$ and h is Planck's constant. Assuming that z is the number of electrons in the outermost unfilled atomic shell, then $z = 1$, 3, and 4 for H($1s^1$), N($2p^3$), and O($2p^4$), respectively. For H, N, and O, $z^{2/3}/D_m^{-1/3} = 1.3 \pm 0.3$ Å. Thus, $\sigma_{\min}$ is expected to be within $a \sim 2$ for all three. For H, $\sigma_{\min}$ is calculated to be 5000 $(\Omega\text{-cm})^{-1}$, in good agreement with experiment, 1000 $(\Omega\text{-cm})^{-1}$.

[5] M. I. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, Nature (London) **411**, 170–174 (2001).

[6] G. W. Marcy and R. P. Butler, Publ. Astron. Soc. Pac. **112**, 137 (2000).

[7] W. J. Nellis, A. A. Louis, and N. W. Ashcroft, Philos. Trans. R. Soc. London A **356**, 119 (1998).

[8] E. Wigner and H. B. Huntington, J. Chem. Phys. **3**, 764 (1935).

[9] J. Lindl, Phys. Plasmas **2**, 3933 (1995).

[10] W. J. Nellis, Philos. Mag. B **79**, 655 (1999).

[11] V. V. Brazhkin, S. V. Popova, R. N. Voloshin, and A. G. Umnov, High Press. Res. **6**, 363 (1992).

[12] K. F. Herzfeld, Phys. Rev. **29**, 701 (1927).

[13] W. J. Nellis, H. B. Radousky, D. C. Hamilton, A. C. Mitchell, N. C. Holmes, K. B. Christianson, and M. van Tiel, J. Chem. Phys. **94**, 2244 (1990).

[14] W. J. Nellis, Phys. Rev. Lett. **89**, 165502 (2002).

[15] M. Ross, J. Chem. Phys. **86**, 7110 (1987).

[16] S. Mazevet, J. D. Johnson, J. D. Kress, L. A. Collins, and P. Blottiau, Phys. Rev. B **65**, 014204 (2002).

[17] T. J. Lenosky, J. D. Kress, and L. A. Collins, Phys. Rev. B **56**, 5164 (1997).

[18] Since the typical atomic collison times are of order 10^{-14} s while our diagnostic resolution time is of order 10^{-9} s, the fluid is in thermal equilibrium and we cannot distinguish between a liquid and a glass.

[19] F. Hensel, E. Marceca, and W. C. Pilgrim, J. Phys. Condens. Matter **10**, 11 395 (1998).

[20] V. E. Fortov, V. Ya. Ternovoi, S. V. Kvitov, V. B. Mintsev, D. N. Nikolaev, A. A. Pyalling, and A. S. Filimonov, JETP Lett. **69**, 926 (1999).

[21] W. J. Nellis, S. T. Weir, and A. C. Mitchell, Phys. Rev. B **59**, 3434–3449 (1999).

[22] A. C. Mitchell and W. J. Nellis, J. Chem. Phys. **76**, 6273–6281 (1982).

[23] D. J. Stevenson and N. W. Ashcroft, Phys. Rev. A **9**, 782 (1974).

[24] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford, London, 1971), p. 133.

[25] J. C. Slater, J. Chem. Phys. **41**, 3199 (1964).

[26] F. Herman and S. Skillman, in *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963), Chap. 6.

[27] T. Miller, in *CRC Handbook of Physics and Chemistry*, edited by David R. Lide and H. P. R. Frederikse (CRC Press, New York, 1998), pp. 10-201 and 10-202.