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Universal behaviour of nonmetal–metal Mott transitions in fluid H, N, O, Rb, and Cs

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Abstract

The systematics of Mott transitions in low- Z and alkali fluids H, N, O, Rb, and Cs are discussed. Such transitions have only been obtained in elemental, monatomic, and disordered systems by using high pressures and temperatures. By finding elements which undergo this transition, it is possible to test Mott's ideas in systems which are relatively simple. For fluid H, N, and O, 100 GPa pressures and ~ 2000 K temperatures are required and were achieved by dynamic shock compression. For fluid Rb and Cs, 0.01 GPa and ~ 2000 K are required and were achieved statically by Hensel *et al.* Despite the fact that these two groups of elements at ambient conditions are so different chemically and that pressures required to observe this transition differ by a factor of 10^4 for the two groups, the metallic conductivities are essentially the same for all five and the density dependences of their semiconductivities are determined systematically by the radial extents of the electronic charge-density distributions of the various atoms. The latter observation provides a physical understanding for the Herzfeld criterion of metallization. It is the tuning of both high pressure and temperature which permits these two apparently different classes of elements at ambient conditions to become quite similar in nature at extreme conditions.

1. Introduction

One major goal of high-pressure research is to identify important scientific problems which can only be investigated with high pressures. The purpose of this paper is to describe one such problem; namely, the systematics of the Mott transition [1] from a semiconducting or nonmetallic state to a metallic state in elemental fluid H, N, O, Rb, and Cs. A Mott transition is one in which a system is an insulator at $T = 0$ K or a nonmetal (semiconductor) at $T > 0$ K when the atoms are relatively far apart; the system becomes metallic when the atoms approach sufficiently close to one another that sufficient overlap of wavefunctions on adjacent atoms occurs that an electron delocalizes. A Mott transition can also be induced

by varying composition to vary electron density. Previous to the discovery of the elemental systems considered here, Mott transitions were observed only in compounds, such as SmB_6 or SmS , which become metallic under pressure, or $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$, which becomes metallic on varying the composition x [2]. It would be very useful to test Mott's ideas with simple systems which are elemental, monatomic, and undergo nonmetal–metal transitions at conditions which can be achieved in a laboratory.

Near ambient conditions, the elements under consideration here certainly do not undergo Mott transitions. The alkali metals melt to metallic liquids and the low- Z diatomics are insulators. It is the tuning of both high pressure and temperature which permits these two apparently different classes of elements at ambient conditions to become quite similar in nature at extreme conditions.

A pressure can be considered 'high' if its application results in a significant change in a physical or chemical property [3]. In the case of Cs and Rb, pressures of only ~ 0.01 GPa are required to induce Mott transitions. In the case of H, N, and O, pressures of ~ 100 GPa are required. Since both pressure ranges cause nonmetal–metal transitions, both can be considered 'high', even though they differ in magnitude by a factor of 10^4 .

The temperatures required in both cases are also high, $T \sim 2000$ K. As discussed below, the appropriate pressures and temperatures are achieved by static compression and heating in the case of Cs and Rb and by dynamic compression and heating in the case of H, N, and O. Metallization occurs when the thermal energy $k_B T \sim E_g$, where k_B is Boltzmann's constant and E_g is the mobility gap. While ~ 2000 K is hot to our senses, these metallic fluids are actually relatively cool in the sense that they are electronically degenerate. That is, their temperatures T in the metallic state are less than their respective Fermi temperatures T_F . For example, in the case of hydrogen, $T/T_F \sim 0.01$.

2. Experimental pressures and temperatures

In this section we describe briefly the two different experimental methods used to achieve the desired pressures and temperatures. In the case of Cs and Rb, Hensel *et al* [4] used a relatively large-volume press to achieve static pressures and temperatures of ~ 0.01 GPa and 2000 K, respectively. Because thermal transport times are much less than experimental lifetimes, sample temperature equilibrates to a value determined by an external heater. The liquid–vapour critical points of Cs and Rb are achieved at these pressures and temperatures. At densities lower than the critical density, these alkalis enter a two-phase region in which liquid and vapour are in equilibrium along their saturation curves. Liquid Cs and Rb are semiconductors along their saturation curves. At their critical points these fluids become metallic and remain so at higher densities. Electrical conductivities were measured as densities were varied continuously by pressures in the 0.01 GPa range. The great experimental challenges here are dealing with the extremely corrosive nature of hot alkali fluids under pressure and controlling thermodynamic conditions near the critical point.

In the case of H, N, and O, extreme conditions of ~ 100 GPa and \sim several 1000 K were achieved by dynamically compressing cryogenic liquid H_2 , N_2 , or O_2 near atmospheric pressure with a reverberating shock wave. A compressible liquid sample was contained between two relatively incompressible Al_2O_3 anvils. In this way the initial shock pressure incident from the first anvil decreases by a factor of ~ 30 in magnitude on entering the liquid. This shock transits through the sample thickness and is then reflected off the second anvil; the shock then reverberates in the sample between the two anvils until pressure equilibrates at the initial shock pressure in the anvil [5]. This pressure history consists of a relatively weak initial shock followed by a series of very weak shocks. This history is well approximated by an isentrope

starting from the weak first shock. This total process is termed a quasi-isentrope. This process achieves lower temperatures and higher pressures and densities than can be achieved with a single shock. For example, a reverberating shock in liquid H₂ achieves 200 GPa, a density of tenfold compressed liquid H₂, and a temperature of 2500 K. A single shock achieves 20 GPa, fourfold compressed liquid H₂, and 4000 K.

A quasi-isentropic compression typically requires 50 ns to complete and peak pressure is then maintained for 100 ns. Since the time between atomic collisions is 10⁻⁵ ns and the time resolution is 1 ns, the fluid is in thermal equilibrium. Because thermal transport times are much longer than experimental lifetimes, this process is adiabatic and temperature increases. The experimental lifetimes are also much shorter than required for high-temperature hydrogen to diffuse into the walls of its holder. Thus, this dynamic process compresses and heats a sample in thermal equilibrium and essentially none of the sample is lost by mass diffusion. The densities and temperatures achieved are such that a low-*Z* liquid sample is compressed to a fluid and the diatomic molecules dissociate into a monatomic state. The challenges in this experiment are maintaining a 20 m long two-stage gun which launches a metal plate at velocities up to ~6 km s⁻¹, cryogenic sample holders, fast electronics, and x-radiography.

These two very different techniques produce a unique set of elemental, disordered, and essentially monatomic fluids, all of which undergo nonmetal–metal transitions with the same Mott physics. These fluids are excellent examples showing the fact that it is the density and temperature which a given application of pressure achieves which is important, rather than the pressure itself. As shown below, these nonmetal–metal transitions stem from the wavefunctions of the outermost electrons of the respective atoms and the strong scattering of electrons which are delocalized. The nature of these atomic wavefunctions also provides insight into the Herzfeld criterion of metallization.

3. Systematics

Mott transitions have been observed in the nominally nonmetallic elements hydrogen, oxygen, and nitrogen when compressed to ~100 GPa pressures and temperatures of several 1000 K [6–8]. The metallic states in these dense fluids are in the strong-scattering electronic regime close to the minimum conductivity of a metal, as are fluid caesium and rubidium which similarly undergo nonmetal–metal transitions at comparable temperatures, though at substantially lower pressures of ~0.01 GPa [9]. These systems are said to be strong-scattering because the mean free path of a conduction electron is the average distance between adjacent atoms. All five of these elements have metallic conductivities of ~1000 Ω⁻¹ cm⁻¹ when the ratio of the size of the isolated atom to the average distance between them is ~0.3. Remarkably, all of these chemically diverse elements have essentially the same value of metallic conductivity since the minimum conductivity of a metal scales weakly with the number of conduction electrons per atom and the density of metallization. That is, for a metallic fluid with *z* conduction electrons per atom, the minimum metallic conductivity is given by $\sigma_{\min} = (z^{2/3}e^2)/(3\hbar D_m^{-1/3})$, where *e* is the charge of an electron, $\hbar = h/2\pi$, *h* is Planck's constant, and *D_m* is the atom density at metallization. For H, N, O, Rb, and Cs, *z* = 1, 3, 4, 1, and 1, respectively. These are the numbers of electrons in the unfilled outermost electron shells. The fact that metallic conductivity is essentially the same for the fluid elements hydrogen, nitrogen, oxygen, rubidium and caesium illustrates the similar nature of these two apparently disparate groups of elemental fluids, the alkalis and the low-*Z* elements, near their nonmetal–metal transition densities.

The measured electrical conductivities of fluid hydrogen, nitrogen, and oxygen are plotted versus dynamic pressure in figure 1. At these extreme conditions all three of these chemical elements are probably monatomic [8]. Comparable conductivities for hydrogen were measured

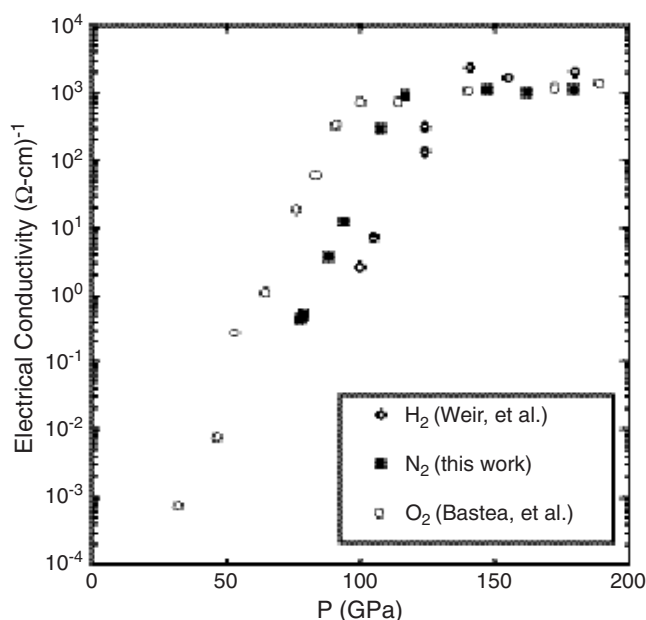


Figure 1. Electrical conductivities of fluid O, N, and H plotted versus pressure produced by a reverberating shock wave. Minimum metallic conductivity is reached at 100, 120, and 140 GPa for oxygen, nitrogen, and hydrogen, respectively. Compression factors over initial liquid densities are 3.6, 4.2, and 9.1, respectively.

under similar conditions generated with high explosives [10]. As shown in figure 1, these three fluids are semiconducting below 140, 120, and 100 GPa, respectively, and have essentially the same minimum metallic conductivity at higher pressures up to 180 GPa. At metallization, liquid hydrogen, nitrogen, and oxygen are compressed by factors of 9.1, 4.2, and 3.6 with respect to the initial liquid density, which correspond to free-electron Fermi energies of 19, 24, and 29 eV, respectively.

In contrast to the metallic regime in which all five elements have essentially the same conductivities, the corresponding density dependences of their conductivities within the semiconducting regime vary substantially. Conductivity data for fluid Cs, Rb, O, N, and H are plotted versus $D^{1/3}a^*$ in figure 2, where D is the number density of atoms, $D^{-1/3}$ is the average distance between atoms, and a^* is their effective size, usually taken as the effective Bohr radius of the outermost (valence) electrons. For H, $a^* = a_B$, the Bohr radius. $D^{1/3}a^*$ is thus the ratio of the size of an atom to the average distance between two adjacent atoms. Importantly, these density dependences within the semiconducting regime are strongly correlated with the radial extent of the electronic charge-density distributions of the respective atoms [8].

The charge-density distributions of Cs and Rb, shown in figure 3 along with those of H, N, and O, have relatively large radial extents because the Coulomb force between the outermost electron and the nucleus is highly screened by the large, filled inner-electron core. On the other hand, the charge-density distribution of H has a relatively small radial extent because the Coulomb force of the nucleus is unscreened and, thus, the electron is tightly bound to the proton. In the case of N and O, the filled inner $1s^2$ and $2s^2$ shells provide some screening of the nuclear Coulomb force and they have larger charge densities than the H electron because N and O have three and four outermost electrons, respectively. As a result, N and O metallize

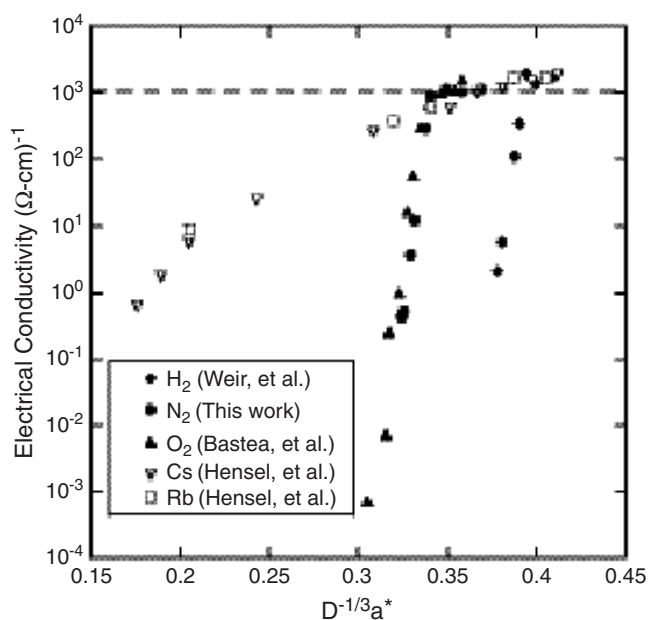


Figure 2. Electrical conductivities of Cs, Rb, N, O, and H plotted versus the scaled density $D^{1/3}a^*$, where $D^{-1/3}$ is the average distance between atoms and a^* is the size of the atom.

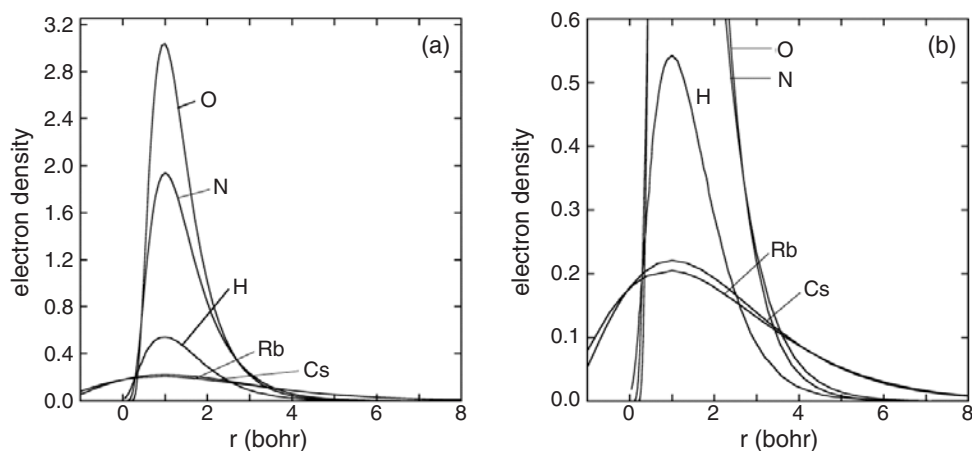


Figure 3. (a) Valence electron charge densities ($4\pi r^2\psi^*\psi$) of H, N, O, Rb, and Cs plotted versus radial distance r . For purposes of comparison of radial extents, charge densities have been shifted radially so that the maximum of each curve is at 1 bohr. (b) Data from (a) on an expanded scale.

at a somewhat smaller value of $D^{1/3}a^*$ than does H, 0.34 versus 0.38. Cs and Rb also reach the metallic state at $D^{1/3}a^* = 0.38$, but their conductivities increase at much less compression than that of H because their charge densities have a much larger radial extent relative to that of H.

The degree to which conduction electrons are bound to their ionic core also yields a simple explanation for the relative magnitudes of the polarizations of these atoms and, thus, a simple rationalization of the Herzfeld–Goldhammer criterion for metallization density [11]. In this

picture, compressing a system with electronic (atomic) polarizability, α , results in a dielectric catastrophe and a concomitant electronic transition to the metallic state when $\frac{4\pi}{3}\alpha D_m = 1$. Since α is usually considered to be the free-atom value, this simple equation defines the metallization density of any chemical element. In particular, the Herzfeld–Goldhammer criterion, which depends only on the polarization of the free (isolated) atom, yields calculated metallization densities of monatomic monovalent H and Cs which are in excellent agreement with experiment. The different radial extents of the electronic charge-density distributions are also consistent with the large differences in electronic polarizabilities of these atoms, which for H, N, O, Rb, and Cs are 0.667, 1.10, 0.802, 47.3, and $59.6 \times 10^{-24} \text{ cm}^3$, respectively. The polarizability is larger for the larger atoms, Rb and Cs, because the outer electrons are strongly screened from the nucleus by the large electronic core. Thus, the outer 5s and 6s valence electrons of Rb and Cs, respectively, respond much more to an applied electric field than electrons which are more tightly bound, such as for H. In this way, an electric field causes a larger polarizability of these large atoms relative to that of a small one. The small value of α for atomic hydrogen necessitates the very high elemental densities required for the transition to metallic hydrogen. In contrast, the large polarizabilities for atomic rubidium and caesium ensure that these elements metallize at densities commensurate with ambient pressures on our planet.

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References

- [1] Mott N F and Davis E A 1971 *Electronic Processes in Non-Crystalline Materials* (London: Oxford University Press)
- [2] Mott N F 1980 *High Pressure Science and Technology* ed B Vodar and Ph Marteau (Oxford: Pergamon) pp 1–7
- [3] Drickamer H G 1980 private communication
- [4] Hensel F, Marceca E and Pilgrim W C 1998 *J. Phys.: Condens. Matter* **10** 11395
- [5] Nellis W J, Weir S T and Mitchell A C 1999 *Phys. Rev. B* **59** 3434
- [6] Weir S T, Mitchell A C and Nellis W J 1996 *Phys. Rev. Lett.* **76** 1860
- [7] Bastea M, Mitchell A C and Nellis W J 2001 *Phys. Rev. Lett.* **86** 3108
- [8] Chau R, Mitchell A, Minich R and Nellis W J 2003 *Phys. Rev. Lett.* **90** 245501
- [9] Hensel F and Edwards P P 1996 *Phys. World* **4** 43
- [10] Fortov V E, Ternovoi V Ya, Kvitov S V, Mintsev V B, Nikolaev D N, Pyalling A A and Filimonov A S 1999 *JETP Lett.* **69** 926
- [11] Herzfeld K F 1927 *Phys. Rev.* **29** 701