Hydrogen, the First Alkali Metal

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Abstract: We examine the density-dependent metal–nonmetal transition (MNMT) for the Group 1 elements hydrogen, rubidium and caesium. Remarkably, the experimentally observed metallization densities agree closely with those predicted from the 1927 classical theory of K. F. Herzfeld, which outlines the critical conditions necessary for the metallization of any element of the periodic system. The metallization densities of the alkali metal elements are also consistent with the quantum mechanical theory of the MNMT, as first set out by Sir Nevill Mott.

Keywords: alkali metals · hydrogen · metallic hydrogen · metallization densities · periodicity

It is now understood that the remarkable periodicity in the properties of the chemical elements[1] originates in the underlying periodicity of the electronic structure of their constituent atoms.[2] However, the unquestionable similarity of the electronic configuration of the hydrogen atom—a single electron in the valence 1 s shell—and that of the valence atomic structure of Li ($2s^1$), Na ($3s^1$), K ($4s^1$), Rb ($5s^1$) and Cs ($6s^1$), do not appear, at first sight, to be reflected in the characteristic properties of the corresponding elements under ambient conditions on this planet. Thus, based on common experience, the element hydrogen is unquestionably a nonmetal, whilst the alkali elements are undoubtedly metals. It has long been presumed, however, that hydrogen at sufficiently high density (pressure) would eventually succumb to metallization.[3] Should hydrogen be transformed into a metallic state, one would then naturally enquire whether the properties of this, the lightest metal, are indeed reminiscent of those of the established alkali metals of Group 1 of the periodic table.

The first successful measurements of the electrical conductivity of highly compressed (to 1.8 Mbar) fluid hydrogen at high temperature (4400 K)[4] lead us to question whether the observed conductivity at high pressure (Fig. 1) is indicative of a metallic form of hydrogen. The data clearly reveal a dramatic increase in the electrical conductivity of fluid hydrogen under pressure,[4] reaching a limiting value of approximately 2000 $\Omega^{-1}cm^{-1}$. However, there is a fundamental problem in defining the actual value of the conductivity which typifies the metallic state of hydrogen (and indeed any element) at the high temperatures characteristic of these experiments. The only rigorous criterion for differentiating between a metal and a nonmetal is the electrical conductivity at the absolute zero of temperature; there, metals have a finite conductivity (with the exception of superconductors, which show infinite conductivity), whilst nonmetals have zero electrical conductivity.[5–7]

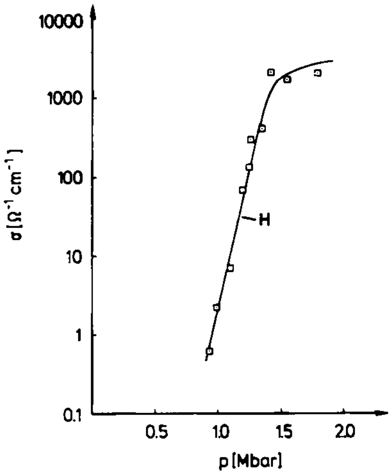

Fig. 1. The electrical conductivity of fluid hydrogen as a function of pressure (ref. [4]).

In the absence of a rigorous criterion for defining the metallicity of disordered elemental fluids at finite (high) temperature, we compare the electrical conductivity of fluid hydrogen with that of fluid alkali metal elements. There is now irrefutable evidence that the highly conducting fluid alkali metal elements can also continuously transform, upon expansion under supercritical conditions, to an elemental state having very low values of electrical conductivity. To date, the most extensive studies have been carried out on the expanded fluids of rubidium and caesium.[8] Figure 2 shows the electrical conductivity for the compressed fluid hydrogen[4] and the expanded fluids rubidium and caesium[8] measured at comparable temperatures (2000–4000 K) over a range of elemental (atom) densities (*m*). All three fluid elements undergo a density-induced, continuous transition from

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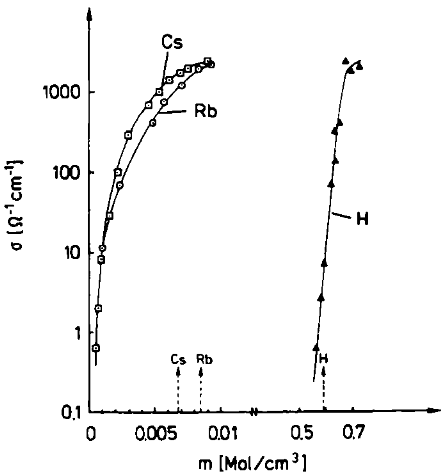

Fig. 2. The electrical conductivity of fluid caesium, rubidium and hydrogen as a function of the molar atom density m at a temperature of $kT \approx 0.15$ eV. The arrows indicate the predicted metallization densities for each element based on the Goldhammer-Herzfeld model (see text).

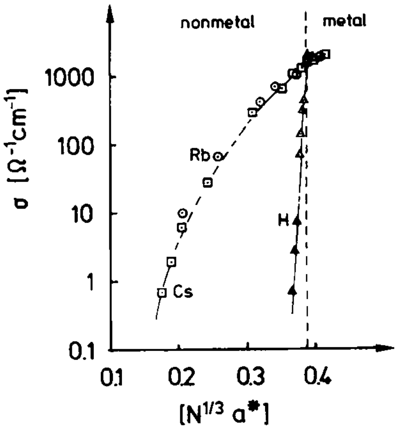

Fig. 3. The transition to the metallic state for fluid caesium, rubidium and hydrogen: the dependence of the electrical conductivity on the scaling parameter $[N^{1/3}a^*]$. The dotted line drawn at $N^{1/3}a^* = 0.38$ indicates the common metallization condition for the three alkali metal elements.

a low conductivity to a highly conducting state. In the case of fluid hydrogen at these high temperatures, pressures close to 2 Mbar are required to effect the transition.[4] The alkali metal elements rubidium and caesium—themselves recognized to be metallic under ambient pressure and temperature—continuously transform to an elemental state of very low conductivity by expansion at these high temperatures[8] (under a pressure of ca. 100 bar).

We note that all three fluids attain a limiting value for the electrical conductivity in the region of $2000\,\Omega^{-1}\,\text{cm}^{-1}$. Importantly, these measured conductivities are comparable to those calculated based on the assumption—reported by Ioffe and Regel,[9] and Mott[10]—that high-temperature fluids only metallize, and remain metallic, when the mean free path (Λ) of the valence (conduction) electrons becomes comparable to, or exceeds, the mean distance (d) between the particles supplying the electrons. The data shown in Figure 2 clearly demonstrate that all three high-temperature fluids are metallic according to the criterion $\Lambda \geq d$.

The periodicity in the physical and chemical properties of the elements derives from the periodicity in the electronic structure of the constituent atoms.[2] We can use this principle to highlight another important behavioural pattern common to fluid hydrogen, rubidium and caesium. A salient feature in Figure 2 is the substantial differences in elemental densities signalling the nonmetal-to-metal transition. The fluid elements are ultimately formed by the condensation of atoms possessing a common electronic structure—a single electron in the valence ns shell. A characteristic atomic property for these elements is, for example, the radius of the principal maximum in the charge density of the ns valence orbital (a^*).[11] Incorporating this into a scaling parameter of the form $N^{1/3}a^*$, where N denotes the valence (atomic) electron density, leads to the behaviour shown in Figure 3. The clear change in the slopes at the Mott-Ioffe-Regel value of $\sigma \approx 2000\,\Omega^{-1}\,\text{cm}^{-1}$ leads one to conclude that all three of these high-temperature fluids become metallic at a constant value of the scaling parameter $N^{1/3}a^* \approx 0.38$. Under the appropriate experimental conditions used in Figure 3 ($N^{1/3}a^* \geq 0.38$), the fluid elements hydrogen, rubidium and caesium can clearly be classified as metallic, with hydrogen now assuming the position of the lightest alkali metal of Group 1 in the periodic table.[2]

Interestingly, Mott predicted such a relationship ($N^{1/3}a^*$ = constant) in 1961,[5, 10] in his original discussion of the metal-to-nonmetal transition in hydrogen-like systems. In earlier contributions, Goldhammer[12] and Herzfeld[13] highlighted the fundamental importance of atomic properties in dictating the metallic or nonmetallic status of elements within the periodic classification. This approach is based upon a density-induced dielectric catastrophe,[7] whereby the static dielectric constant (ε) of an element diverges at the critical density (N_c) of the nonmetal-metal transition. The Goldhammer-Herzfeld criterion for metallization is thus for $N \rightarrow Nc = 3/(4\pi\alpha_0)$, $\varepsilon \rightarrow \infty$, where α_0 is the static polarizability of an isolated atom.

The relatively small value of α_0 for atomic hydrogen (0.67 Å³) necessitates the very high elemental densities required for the transition to metallic hydrogen (Fig. 2). In contrast the large polarizabilities for atomic rubidium (47.3 Å³) and caesium (59.7 Å³) ensure that the heavier members of Group 1 metallize at elemental densities commensurate with ambient conditions of this planet. The predicted metallization densities are thus $0.595\,\text{mol}\,\text{cm}^{-3}$ ($3.59 \times 10^{23}\,\text{cm}^{-3}$) for hydrogen, $8.38 \times 10^{-3}\,\text{mol}\,\text{cm}^{-3}$ ($5.05 \times 10^{21}\,\text{cm}^{-3}$) for rubidium and $6.66 \times 10^{-3}\,\text{mol}\,\text{cm}^{-3}$ ($4.01 \times 10^{21}\,\text{cm}^{-3}$) for caesium. These estimates (represented by arrows for each element in Fig. 2) are in remarkably good agreement with the experimental metallization densities, spanning almost three orders of magnitude, and encompassing the lightest to the heaviest naturally occurring alkali metal element.

It is now recognized[7, 14, 15] that, for a lattice of hydrogen-like atoms, the critical density for a dielectric catastrophe is also given by $N^{1/3}a^* \approx 0.38$; this establishes a direct link with Mott's theory and the experimental metallization densities of the alkali metal elements hydrogen, rubidium and caesium (Fig. 3).

The periodic law requires that the physical and chemical properties of the elements are a function of the electronic configurations of their atoms, and that they vary in a periodic manner with increasing atomic number.[2, 7] Here we have illustrated that the critical condition for the nonmetal-metal transition in the Group 1 elements hydrogen, rubidium and caesium is also a manifestation of the underlying periodicity in electronic structure of the constituent atoms.[13]

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[1] D. Mendeleef, *Principles of Chemistry*, 5th ed., Vol. 1, Longmans Green, London, **1891**, p. 23.
[2] P. W. Atkins, *The Periodic Kingdom* (Weidenfeld and Nicolson), London, **1995**.
[3] E. Wigner, H. B. Huntington, *J. Chem. Phys.* **1935**, *3*, 764.
[4] S. T. Weir, A. C. Mitchell, W. J. Nellis, *Phys. Rev. Lett.* **1996**, *76*, 1860.
[5] N. F. Mott, *Philos. Mag.* **1961**, *6*, 287.
[6] A. H. Cottrell, *Introduction of the Modern Theory of Metals*, The Institute of Metals, London, **1988**.
[7] P. P. Edwards, M. J. Sienko, *Int. Rev. Phys. Chem.* **1983**, *3*, 83.
[8] F. Hensel, H. Uchtmann, *Annu. Rev. Phys. Chem.* **1989**, *40:61*, 83.
[9] A. F. Ioffe, A. R. Regel, *Prog. Semiconductors* **1960**, *4*, 239.
[10] N. F. Mott, *Metal–Insulator Transitions*, Taylor and Francis, London, **1990**.
[11] J. T. Waber, D. T. Cromer, *J. Chem. Phys.* **1965**, *42*, 4116.
[12] D. A. Goldammer, *Dispersion und Absorption des Lichtes*, Teubner, Leipzig, **1913**.
[13] K. F. Herzfeld, *Phys. Rev.* **1927**, *29*, 701.
[14] K. F. Berggren, *J. Chem. Phys.* **1974**, *60*, 3399.
[15] P. P. Edwards, T. V. Ramakrishnan, C.N.R. Rao, *J. Phys. Chem.* **1995**, *99*, 5228.