*ЖЭТФ, 1997, том 111, вып. 5, стр. 1601–1610*

# RYDBERG MATTER — A LONG-LIVED EXCITED STATE OF MATTER

*L. Holmlid*[1], *E. A. Manykin*[2]

[1] *Reaction Dynamics Group, Physical Chemistry University of Göteborg*
*S-412 96 Göteborg, Sweden*
[2] *Superconductivity & Solid State Physics Institute*
*Russian Research Center «Kurchatov Institute»*
*123182, Moscow, Russia*

Submitted 11 June 1996

The theory of condensed excited matter, the so-called Rydberg matter (RM), is examined briefly. Explicit results are given for several physical quantities, notably, the work function and the resistivity, for which experimental results exist. The most important aspects of the experiments, which are fully described elsewhere, are discussed. Large densities of Rydberg species are formed in the experiments with cesium vapor in contact with carbon (graphite) surfaces. The resistivity of the RM formed is found to be $10^{-2}$–$10^{-3}\Omega\cdot$m under varying conditions, while theory gives the order of $10^{-3}\Omega\cdot$m. The work function is experimentally found to be less than 0.7 eV, perhaps even less than 0.5 eV. Two different methods were used to extract this quantity from thermionic diode data. These work function values are much lower than reported for any known material, especially at the high temperatures used, and they thus give strong support of the description of RM as a very dilute metal. Theory gives values ranging from 0.6 down to 0.2 eV, depending on the principal quantum number, which is estimated to be $n = 12$–$14$ from the lifetime calculations and from the known pressure. Supporting evidence is found from spectroscopic studies of RM, from jellium calculations, and from recent confirming experiments. From the good agreement between theory and experiment we conclude that RM exists.

## 1. INTRODUCTION

The theoretical treatment of a phase consisting of highly excited atoms of the so-called Rydberg type (hydrogenic atoms with one excited electron) indicates that a metal with a density as low as a gas can exist. Recent experimental results on the resistivity and work function indicate that such metals do exist, in the form of Rydberg matter (RM). We will here consider the new theoretical and experimental arguments for the existence of RM.

The theoretical reason for introducing RM is that local excitations cannot satisfactorily explain the behavior of electronically highly excited systems. Instead, the interactions between the excitations in the system must be taken into account. Such a collective or condensed state of matter, which is formed from excited atoms or other excited species was proposed in a series of theoretical studies [1–4]. When atoms are excited to high electronic states of the Rydberg type, their size increases rapidly. Since the excited electrons spend almost all their time far from the core ions in the atoms, the wave functions of highly excited atoms overlap strongly when such atoms are brought together. At large densities and not too high temperatures, excited atoms can form a solid-like condensed phase with the ions in a regular lattice, which we call a Rydberg crystal, as shown in Fig. 1. At higher temperatures, a liquid state of excited matter, which is another form of RM should exist.

One prerequisite for valid experimental tests of the existence of RM is that RM can be

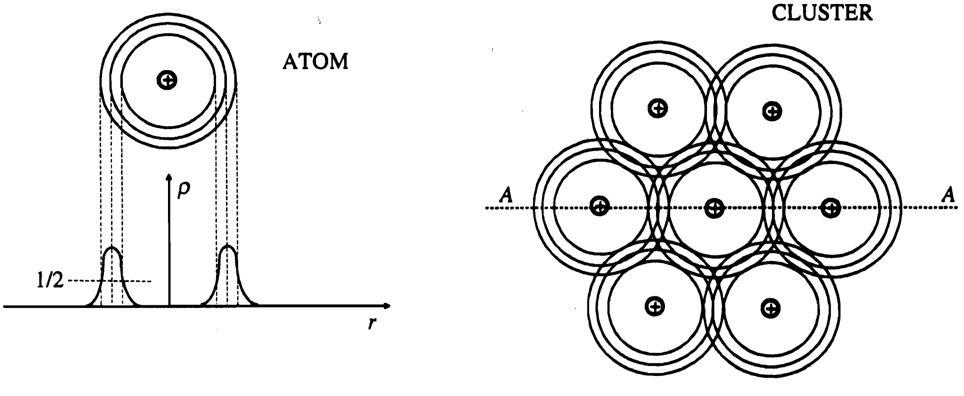

**Fig. 1.** The electron density $\rho$ in a Rydberg atom as a function of distance (top panel) and a cluster of RM. The central positive core ions are indicated by plus signs. The interatomic distance in RM with atoms in state 13 S is 15 nm according to theory [7]

formed in macroscopic quantities, which in turn requires that large densities of Rydberg species can be obtained. The use of new methods of forming Rydberg species has now lead to this achievement, and in our experiments, a volume of 30 mm$^2$ of RM of cesium atoms can be formed routinely in a flow system which continuously renews RM. We will show that the accumulated experimental evidence now shows good agreement with theoretical predictions, and that this by itself proves the existence of RM. However, it may be even more convincing if unique results can be provided by experiments, i. e., results which cannot be attributed to any known material. This is found, we believe, in the case of the work function of RM. Of course, low work functions of surfaces have been studied for a long time. In many technical applications of electron physics low work functions of electrodes are required, and the combination of low work function and metallic properties is extremely important in many situations. Examples are provided by thermionic energy converters and MHD generators, where current densities up to the order of 100 A·cm$^{-2}$ should be obtained to make the devices work efficiently. The difficulties in formation or construction of such surfaces have for a long time been serious obstacles for the technical development. Thus, several approaches have been tested, but with very limited success. The alkali metals have the lowest work functions among the elements, at approximately 1.8 eV for Cs, and a layer of Cs on metallic surfaces can have an even lower work function, at 1.5 eV for nearly a monolayer. The standard theory for work functions of metals [5] states that the average electron density, or the corresponding positive ion density in the material, should be decreased if very low work functions are found. This explains, at least partly, why the low density monolayers of alkali metals deposited on other metals have lower work function than the pure alkali metals themselves. Following this idea, various experiments have been done to decrease the work function by diluting the alkali-metal atoms with other nonmetal atoms, and very low work functions, down to 1.2 eV, have also been obtained for various oxides and alkali metal-oxygen coadsorbed phases on metal surfaces [6]. Of course, the resistivity increases for such materials, but at high temperatures and for thin layers this drawback is not of great importance. The goal to reach even lower work functions is thus clear: to further increase the distance between the alkali atoms. This is where the theory of RM is important also from an applied point of view, since it states that a low density, and thus low work function, metallic material can be constructed. The prerequisite is that Rydberg states should be formed in large densities and be condensed on a surface which can remove the condensation energy.

## 2. THEORY OF RYDBERG MATTER

In Rydberg matter the excited valence electrons are shared between many atoms in the material and form a degenerate Fermi liquid. Due to delocalization, the kinetic energy of the electrons decreases considerably when the condensed phase is formed. As a result, the binding energies of the excited atoms become high enough to keep the atoms in place. The potential energy for the valence electrons in Fig. 2 shows that the probability of these electrons coming close to the core ions is very small.

The different properties of RM are well described by pseudopotential theory and density functional theory similar to the theory of simple metals [4]. The Rydberg matter is therefore

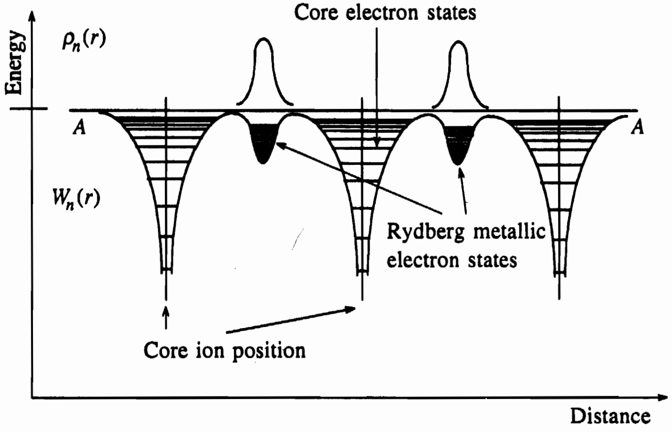

**Fig. 2.** Potential energy diagram for the electrons in RM, along the line A-A in Fig. 1. The electron density $\rho$ is indicated

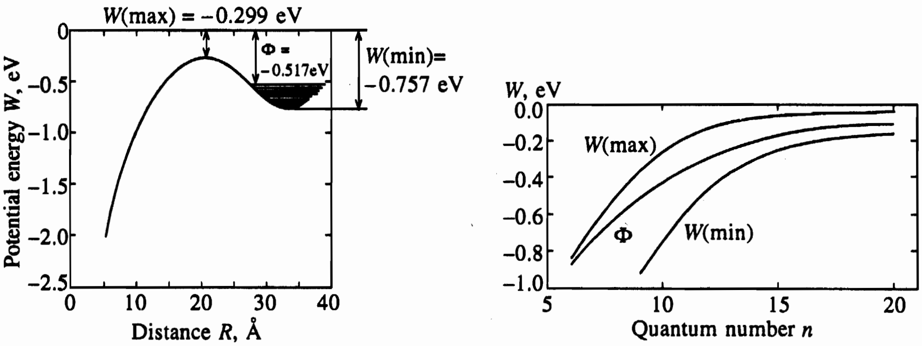

**Fig. 3.** One-electron potential energy for the excited electrons in RM with $n = 10$. The energy parameters indicated are also shown separately as functions of $n$. The work function $\Phi$ is the absolute value of the Fermi energy $E_F$

assumed to consist of identical Rydberg atoms. A substantial role should be played by effects due to the inhomogeneity of the electron density. This is a new aspect, which is characteristic of far-from-equilibrium matter like RM, while this effect is very small for ordinary condensed matter. The theory of RM shows that the exchange and correlation effect leads to self-trapping of the electrons where the electron density differs substantially from zero [4]. Figure 3 shows the result of a numerical calculation within the framework of the Wigner-Seitz cell potential for RM with the excitation level $n = 10$ (Refs. [4, 7]), as well as the relevant energy parameters as a function of $n$. The question of applying the density functional theory to the RM problem is discussed in detail in Ref. [4]. It is shown there, that the problems of describing excited states by density-functional methods can be overcome by combining this theory with the pseudopotential concept.

The lifetime of the Rydberg crystal is, of course, of great importance. The decay of RM is caused by electron transitions to low-lying unfilled energy levels. The Rydberg matter is therefore inherently unstable and has a finite lifetime. At first glance, the lifetime of RM seems to be shorter than that of the isolated atoms, which is attributable to the strong Coulomb interaction of the electrons. As the excitation level increases, however, the lifetime of RM is expected to increase rapidly due to the spatial separation of the initial and final states of the electrons, as in free Rydberg atoms, and due to specific effects on the local field in the strongly nonuniform electron liquid of RM. The higher the level of excitation, the more strongly the electrons are drawn to the boundaries of the unit cells, while the final states for the decay transitions remain localized at the core ions. Recombination therefore cannot occur into all low-lying states corresponding to isolated atoms. The interaction between the electrons leads to the formation of an effective potential barrier to the penetration of valence electrons into the region close to the core ions. Thus, RM can be a long-lived excited state of matter. The high excitation energy in the condensed matter also makes possible decay processes involving several electrons, for example, the Auger processes. The lifetimes including such processes are calculated in Ref. [8] and are still found to be of the order of several seconds or longer for some excitation levels.

## 3. CALCULATED QUANTITIES

Various parameters characterizing the Rydberg crystal state can be calculated by the methods mentioned above [4]. Some examples are presented in Table. The Rydberg crystal is a good electrical conductor [8], and its work function is thus a well-defined quantity of great interest. Due to the low electron density, the Rydberg crystal is transparent to visible light. It becomes opaque to electromagnetic radiation only at frequencies lower than its own plasma frequency or at wavelengths longer than some transparency boundary wavelength, which is far out in the IR for the excitation levels in Table.

One basic problem with this type of calculation is that the excitation level, i.e., the principal quantum number for the combining atoms, must be assumed. This parameter is not known directly from the experiments. However, the vapor pressure before condensation in the experiments in Refs. [9, 10] is of the order of 1 mbar. Assuming that the diameters of the Rydberg atoms are the same as the interatomic distances in a gas of this pressure, one finds $n$ approximately equal to 16. It is likely that some contraction is taking place as a result of the condensation, and it is thus reasonable to perform the calculations for $n$ = 12–14. The calculated values for the density at $n = 13$ in Table correspond to a pressure of 60 mbar or

**Parameters of the cesium RM crystal**

| State of atoms | Density $\rho$, cm$^{-3}$ | Binding energy $B$, eV/atom | Melting point $T_m$, K | Work function $\Phi$, eV | Transparency boundary $\lambda$, $\mu$m | Lifetime $\tau$, s |
|---|---|---|---|---|---|---|
| 12 S | $1.1 \cdot 10^{18}$ | 0.14 | 460 | 0.23 | 32 | 25 |
| 13 S | $5.3 \cdot 10^{17}$ | 0.11 | 460 | 0.2 | 46 | 5 |
| 14 S | $2.8 \cdot 10^{17}$ | 0.1 | 540 | 0.18 | 63 | 80 h |

an equivalent $n$ value of 9. Thus, $n$ = 12–14 appears to be a good choice of excitation level, lacking more detailed information from the experiments. A more detailed discussion is found in Ref. [8].

## 4. RESULTS AND DISCUSSION

The experimental results have been obtained using new techniques to create large densities of highly excited Rydberg species. Alkali atom Rydberg species are generally the simplest to form because of the low ionization energy of alkali atoms. The new techniques employ diffusion of alkali ions from the bulk of nonmetallic materials. For example, in the case of graphite surfaces it was shown that the emission of Cs$^+$ ions gives rise to a near-resonant process that forms Rydberg species from the emitted ions and thermal electrons [10–12]. By increasing the pressure of Cs vapor in contact with such surfaces and by ensuring that diffusion in the material takes place, large densities of Rydberg species of Cs and K have been formed. Small particles (clusters) [13] and macroscopic amounts of RM [9, 10] can be formed by using Cs vapor. Also, alkali-doped metal-oxide surfaces (e. g., promoted catalyst surfaces) have been shown to give large densities of Rydberg species of K [14–16]. The behavior observed for RM formed by such methods is qualitatively the same as the predicted behavior: it is, for example, transparent to visible light, and it emits much less light than an ordinary plasma when it carries a large current. That the observed matter is very energetic is easy to observe through explosions of the matter under simultaneous emission of visible light or charged particles, both for small particles of RM [17] and for large layers of RM on surfaces [18]. In one experiment clusters of RM were collected on a liquid-nitrogen-cooled surface [17]. They were de-excited by ion impact, which gave small microflashes (small white explosions) with an energy content approximately as expected from RM theory. Collection times longer than a few minutes gave no increase in the number of flashes during de- excitation, and the intrinsic lifetime of RM at that temperature was estimated to be a few minutes. This lifetime is of the same order of magnitude as that given in Table, with values ranging between 5 s and 80 h. The main recombination channels for the kind of RM, which consists of highly excited Cs atoms, have been recently investigated. A detailed description of this study is found in Ref. [8]. The decay proceeds, as a rule, by the Auger recombination mechanism.

Of special importance are the values of the resistivity, which were determined for RM of cesium at a temperature of approximately 800 K. These measurements were made in a flow system which renews the RM continuously between two partially graphite-covered electrodes in a vacuum chamber. This chamber is a thermionic diode, which is characterized as a thermionic energy converter. The complete apparatus has recently been described elsewhere [19]. The electron current flows from the cold to the hot electrode. The interelectrode space can be observed visually during the measurements; this space is not glowing. (When a plasma is formed between the electrodes, this region is glowing and the maximum possible conducted current is much lower.) The experiment is designed in such a way that possible artifacts, like leakage paths on isolators, can be rejected directly from the experimental results. Further, the hot electrode is heated by the impinging electrons, which shows that the current passes through the interelectrode space. A resistivity of $10^{-3}$–$10^{-2}\Omega\cdot$m is found from the linear resistive behavior of the current-voltage characteristics [9]. The range in values is due to the varying conditions for a large number of experiments done at different electrode temperatures and cesium pressures. The resistive behavior is found only with graphite layers on the electrodes. Calculations give the resistivity of RM for the levels $n = 12$–$14$ of the order of $10^{-3}\Omega\cdot$m. The agreement between theory and experiment is therefore very good.

The surface work function of RM was determined in similar experiments in the same kind of apparatus [19], which forms RM from Cs vapor in contact with a pair of electrodes, partially covered with graphite. It is worth noting that the colder electrode of the two plane parallel electrodes supports the RM, and that the electron current which is observed is emitted from the cold surface to the hot surface (the reverse current is usually much smaller). The maximum current density is very large, up to 500 A$\cdot$cm$^{-2}$ at an applied voltage of 30 V. As stated in the introduction, the extremely low values of work function found in the experiments are conclusive evidence that RM exists. We must therefore examine the measurement methods in detail.

Two different methods were used to extract the work function from the current-voltage behavior observed: 1) the maximum current density method, and 2) analysis of the diode characteristics of the plasma-RM setup. From the Richardson formula for the electron emission current density, we clearly see, that a current density, $i_{max} = 500$ A$\cdot$cm$^{-2}$, corresponds to a work function of 0.82 eV at 800 K, which is the temperature of the cold emitting surface. This value of $i_{max}$ is the highest current density measured in the setup because of the experimental limitations like power supply availability and melting of the electrodes. The current density at this point still increases linearly with the applied current. We thus can state that the work function of RM in this experiment is $< 0.8$ eV. The measurement of the current density depends on the correct determination of the electron emitting area. Through a window of the apparatus we can observe the faint glow from the current-carrying part of the interelectrode space, and thus ascertain that there is no large current emission from adjacent parts of the apparatus. If the emitting area was 50% larger in reality, the work function would be 0.85 eV. In reality, the area used in the calculation is not emitting homogeneously, so the central part, which has a larger emission, also has a somewhat lower work function.

The diode analysis procedure is carried out in the following way. The typical current-voltage characteristics of the plasma diode is shown in Fig. 4*a*. In the first and second quadrants, the electron current from the hot electrode is measured as a positive current by definition. With increasing voltage to the right, i.e., with a more negative voltage on the cold electrode, the thermal current from the hot electrode will decrease, showing a Boltzmann tail. The steepest descent of this fall-off curve indicates the approximate output voltage, where the work function $\Phi_E$ of the hot electrode is equal to the sum of the so-called barrier index (which contains the work function $\Phi_C$ of the cold electrode and the plasma drop) and the output voltage $V'_{out}$:

$$\Phi_E = V_b + V'_{out}. \tag{1}$$

The fall-off curve must be limited by the density of the thermal emitted electron current from the hot electrode, as expressed by the Richardson equation

$$i_e = AT_E^2 \exp(-V_b/k_B T_E), \tag{2}$$

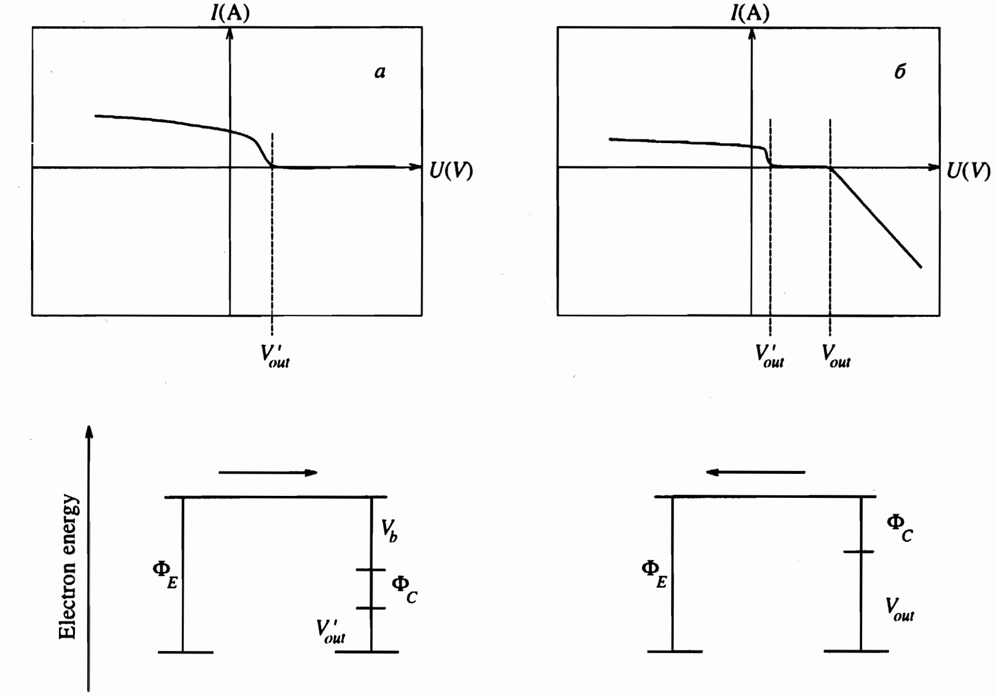

**Fig. 4.** Current — voltage (I-V) characteristics of the cesium-vapor-filled thermionic diode. The ordinary behavior, together with a description of the energetics for the electrons in the diode, is shown in (*a*). The signs used are conventional; the positive current visible in the second quadrant is emitted from the hot electrode. The special behavior caused by RM formation, with two break points in the curves and a very large electron current from the cold electrode in the fourth quadrant, is shown in (*b*). The energetics shown in (*b*) corresponds to the break point farthest to the right

which gives the barrier index $V_b$ from the measured current density and hot electrode temperature $T_E$. This can be understood more easily from the lower part of Fig. 4*a*, where the energy of the electrons is shown. This analysis is a standard procedure for the study of thermionic converter performance.

In the case of RM formation in the thermionic diode, there exist two break points or knees on the curve, as seen in Fig. 4*b*. The break point at the lowest voltage $V'_{out}$ (to the left in the figure) corresponds to the point at which the electron emission from the hot electrode is small, i. e., to a case similar to that analyzed with the help of Fig. 4*a*. The right-hand break point at $V_{out}$ indicates the onset of electron emission from the cold electrode, which increases approximately linearly with the applied voltage above this voltage point. Here another relation can be found from the lower part in Fig. 4*b*:

$$\Phi_E = \Phi_C + V_{out}. \tag{3}$$

Combining Eqs. (1) and (3), we obtain

$$V_b = (V_{out} - V'_{out}) + \Phi_C. \tag{4}$$

This relation indicates that the work function of the cold electrode covered with RM should be regarded a constant (axis cut-off) in a linear relationship between the barrier index and the

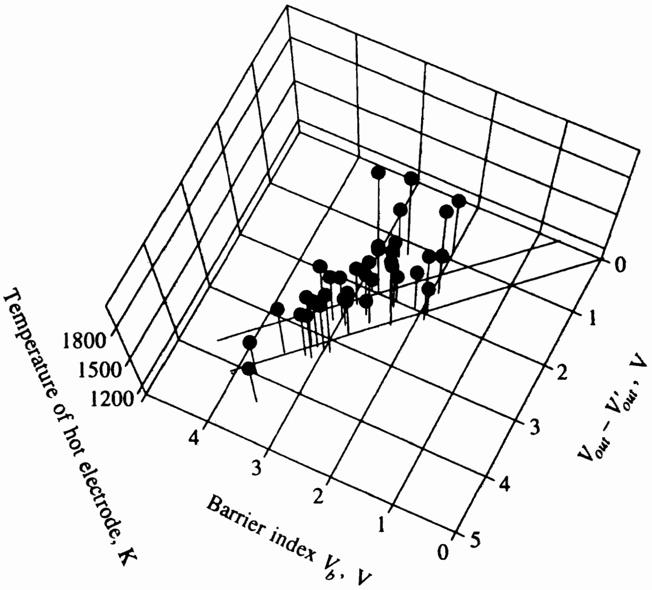

**Fig. 5.** A plot of the barrier index $V_b$ versus the voltage difference $(V_{out} - V'_{out})$ for the two break points in the I — V characteristics for the thermionic diode with RM formation. The two lines demonstrate the linear relationship between the two parameters at not too high temperatures of the hot electrode

voltage difference between the break points. The data from a large number of runs with different temperatures of the hot electrode is plotted in Fig. 5, with the barrier index and the break-point voltage difference on the $x$ and $y$ axes, respectively. As in Ref. [10], an approximate linear relationship is observed. In the figure, the temperature of the hot electrode is now plotted in the $z$ direction. We see that most of the results fall within a band with the work function $\Phi_C$ (barrier index value at zero difference voltage) between zero and 0.7 eV. The few data points at low difference voltage and high barrier index are found for higher temperatures of the hot electrode than the other data points, which might mean that the plasma voltage drop has a somewhat different character in those cases. It is important to realize that no data point with $V_b < (V_{out} - V'_{out})$ should exist. This condition is satisfied (excluding one data point), which strongly supports the analysis of the data. The work function of the RM was thus found to be less than 0.7 eV [10]. No known material has such a low work function, especially at such a high temperature. The calculated value of the work function for RM is extremely small, ranging from 0.6 eV down to 0.2 eV for a value of $n$ approaching 20, as shown in Table and Fig. 3. This value is just below the upper limit found experimentally. Similar diode experiments performed recently by a group in the Kurchatov Institute using graphite surfaces were shown to give extremely large current densities [20]. This confirms the results of our experiments.

Very low values of work function have also been found recently in simple jellium calculations [21, 22]. Such calculations are performed for a dilute alkali metal, replacing the inhomogeneous electron density in RM with a constant, smeared-out, electron density in the jellium approximation. In Ref. [22], the same densities of RM were used for the jellium calculations, as in the more accurate calculations in Refs. [1–4, 7, 8]. The work function from the jellium calculation follows the same trend with the excitation level (value of $n$) as the RM calculations. However, the work function values are even lower, which is expected since the volume over which the electrons can move is much larger in the jellium model, where there is no excluded volume around the ion cores. This is discussed in greater detail in Ref. [22]. It is encouraging that the two widely different theoretical models give similar values of the work function, and the results in Ref. [22] strongly support the correctness of the RM theoretical treatment. The real work function for RM is likely to be between 0.5 and 0.1 eV at $10 < n < 20$ (Ref. [22]).

A direct spectroscopic study of RM in the same apparatus as used for the other experiments discussed here [19] is quite instructive [22]. In this test, the spectra of the free Cs atoms were recorded under conditions of an ordinary plasma and also during conditions of RM formation with no glowing plasma. With RM, the current was generally higher and the voltage drop lower than for the plasma. It was barely possible to run comparison experiments where the current in the presence of RM was as low as that during plasma conditions. Under these conditions, the spectral lines were a factor of 10–20 weaker in RM mode than in the plasma mode. Since the emitting Cs atoms must exist outside the RM within the viewing angle of the optical fiber, the fraction of free Cs atoms in the diode interelectrode space becomes very low, i. e., probably lower than 0.05 of all atoms there. This clearly indicates that the other atoms there are not free, i. e., they are bound in the RM, which is a much better conductor than the plasma.

## 5. CONCLUSION

The good agreement between theory and experiment makes it possible for us to conclude confidently that RM exists. Even if the discussion here has mainly described RM of cesium, it is now clear that RM can also be formed from other atoms and molecules. The Rydberg matter of hydrocarbons as clusters [24] and of hydrogen as surface layers has been reported [18]. It is likely that RM appears naturally in many situations, e.g. RM seems to be the likely explanation for the phenomena known as ball lightning [25]. This explanation was proposed by Manykin et al. [3].

We thank Robert Svensson for performing the experiments discussed in this article.
This work was partially supported by the Russian Fund for Fundamental Research (Grant №95-02-06384-a).

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