Condensed states of excited cesium atoms

É. A. Manykin, M. I. Ozhovan, and P. P. Poluéktov

Kurchatov Institute Russian Science Center

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The basic properties of condensates of excited cesium atoms are determined for excitation levels $n = 10$–20. Estimates are derived for the equilibrium density, the binding energy, the surface tension, the resistivity, the transmission boundary, the bulk modulus, the sound velocity, and the melting point.

INTRODUCTION

Condensed excited states have been introduced in order to describe dense systems of excited atoms. The behavior of such systems changes qualitatively at the densities at which the wave functions of the valence electrons begin to overlap significantly. Individual states of the excited atoms are not suitable for determining the properties of dense systems, because of the pronounced perturbations. A condensed state of the excited atoms for which the valence electrons are collectivized and form a Fermi liquid around the atomic cores might serve as a basis here. A state of this sort has been proposed previously for describing highly excited semiconductors. Specifically, this is the well-known electron–hole state which arises as the result of a condensation of excitons, which are elementary excitations in semiconductors.[1] The concept of a condensed excited state makes it possible to include in the discussion a system of highly excited impurities in semiconductors and insulators. Some basic ideas regarding a condensate of excited atoms are set forth in some of our previous papers.[2–4]

In a study of a photodielectric effect involving excited impurities (Ga) in germanium, Bocharnikov *et al.*[5] observed a faster than linear increase in the dielectric constant with increasing concentration of the excited particles. This increase was a consequence of an interaction of excited centers. Condensed states of excited gallium impurities were probably being observed in that study. It is pertinent to note that the Fermi liquid of this system consists of holes. (It was recently shown that a transition to a superconducting state can occur at very high temperatures in similar systems.[6]) A detailed study of the optical breakdown of glasses led Glebov and Efimov[7] to suggest that the actual mechanism for the intrinsic optical breakdown of glasses is the abrupt onset of a spectrum of electron states corresponding to a collectivization of valence electrons and a "metallization" of the glass when the light reaches a certain critical intensity. Glebov and Efimov found qualitative support for the idea that an excited condensate forms in experiments on the optical breakdown of irradiated glasses. The condensate apparently forms at the center of the caustic, and the effects which are subsequently observed stem from an intense absorption of electromagnetic radiation by this condensate. Petrov and Kashkarov[8] observed a large number of defects in the surface layers of some irradiated semiconductors (Si and Ge) which were definitely not of thermal origin. We explained those experiments in Ref. 9, where we derived an equation of state of an excited condensate of impurities in a semiconductor (or insulator), and where we pointed out the mechanism for the onset of destructive stress. Zmuidzinas[10] presented some arguments for an anomalous increase in the lifetime of the excited condensate and for a possible superconducting transition, working from a two-band model of an insulator in a magnetic field.

Aman *et al.*[11] and Svensson *et al.*[12] recently carried out several interesting studies of dense systems of excited cesium atoms. Using time-of-flight mass spectrometry, Aman *et al.*[11] observed clusters of excited cesium atoms; the number of atoms in a cluster was on the order of 10^4. Svensson *et al.*[12] studied the current-voltage characteristic of a vacuum gap under the conditions favoring the formation of a condensate of excited Cs atoms. They observed a linear resistance. They estimated the resistivity of the condensate to lie between 10^{-3} and 10^{-2} $\Omega\cdot$m. Although the latter experiments do not provide unambiguous quantitative values of the properties of a condensate of excited Cs atoms, some estimates (albeit qualitative and preliminary) are necessary here.

Our purpose in the present study was to determine the basic characteristics of a condensate of excited cesium atoms.

HIGHLY EXCITED STATES OF CESIUM

The potential acting on an outer electron in a highly excited atom or molecule falls off as r^{-1} at sufficiently large distances. "Sufficiently large" distances are much greater than the size of the atomic or molecular core. A highly excited electron spends most of its time far from the core ($r \propto n^2$), where the wave functions can be described fairly accurately by Coulomb functions. These assumptions underlie a theory of a quantum defect which makes it possible to describe states of highly excited atoms and molecules on the basis of the hydrogen atom. The energy of the atoms can be written as $I_{n,l} = (-1/2)(n-\delta_l)^2$, where δ_l is the quantum defect, which for a given l is either a constant or a slowly varying function of the energy. (The quantum defect is related to the scattering phase shift for low-energy electrons: $\delta_l = \varphi_l/\pi$). The defect is large ($\delta_l \geqslant 1$) for states for which l is smaller than the maximum angular momentum of the core electrons. The quantum defect may be thought of as a measure of the short-range perturbation of the core in a hydrogen-like system. It is customary to use an effective quantum number $n^* = n - \delta_l$. For cesium atoms, the quantum defect for the S states is 4.05 (Ref. 13). Highly excited S states of cesium are thus described by a hydrogen-like model with an effective quantum number $n^* \approx n - 4$.

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TABLE I. Equilibrium properties of a condensate of excited Cs atoms.

Excitation level n	Core radius R_n, a.u.	Interatomic distance L_a, Å	Equilibrium density ρ, cm^{-3}	Binding energy B, K
6S ground state	3	6	$9{,}1\cdot 10^{21}$	9590
10	54	67	$6{,}5\cdot 10^{18}$	2600
11	76	91	$2{,}5\cdot 10^{18}$	1990
12	102	120	$1{,}1\cdot 10^{18}$	1590
13	132	153	$5{,}3\cdot 10^{17}$	1310
14	165	189	$2{,}8\cdot 10^{17}$	1120
15	203	231	$1{,}6\cdot 10^{17}$	960
16	244	275	$9.2\cdot 10^{16}$	840
17	289	324	$5{,}6\cdot 10^{16}$	740
18	339	378	$3{,}5\cdot 10^{16}$	660
19	392	435	$2{,}3\cdot 10^{16}$	600
20	449	497	$1{,}6\cdot 10^{16}$	540

forms from them are conveniently described through the use of the concept of a pseudopotential.[14] The wave function of the outer electron in the excited atom is orthogonal with respect to all lower-lying states. In other words, the wave function executes pronounced oscillations in the core region, where these states are localized. The kinetic energy of the outer electron is therefore large in this region. This large kinetic energy balances the potential energy, so an effective repulsive pit appears in the core region when atoms are described by pseudopotentials and pseudowave functions which become the same as the actual wave functions in the outer region.

The pseudopotential most convenient for numerical estimates is the Ashcroft pseudopotential, which uses a cancellation. Specifically, it sets the potential in the core region equal to zero (the empty core model).[14] The pit radius R_n of the pseudopotential is found from the agreement of energy terms. For this purpose we use a variational procedure with a single-parameter exponential function in the outer region, where the potential acting on an electron is the Coulomb potential. Table I lists the parameters of the Ashcroft pseudopotential R_n of excited S states of Cs atoms for various values of the main quantum number n. For comparison, we also show the corresponding parameters for ordinary (i.e., unexcited) cesium in all the tables below.

ENERGY FUNCTIONAL OF THE CONDENSATE

Let us assume that at absolute zero the condensed phase is made up of excited atoms, all of which are in the same n–S state. As in the case of an ordinary metal, we can classify the energy states of the electron as either outer (valence) or inner. The valence electrons form a collective Fermi liquid, in which the ion system is immersed. For the inner states of an excited atom, the overlap of wave functions is extremely slight, and these states effectively remain highly localized near the atomic centers. The interaction of the valence electrons with the ion system is specified by a pseudopotential v_a, which is a superposition of the pseudopotentials of the individual ions:

$$v_a=\sum_j v_n(\mathbf{r}-\mathbf{R}_j). \tag{1}$$

The summation here is over the direct-lattice vectors $\mathbf{R}_j$, and $v_n(\mathbf{r}-\mathbf{R}_j)$ is the pseudopotential of an individual excited atom. According to the cancellation theorem,[14] we can use the empty-core model for v_n:

$$v_n(\mathbf{r})=\begin{cases}0, & r<R_n\\ -1/r, & r\geqslant R_n\end{cases}. \tag{2}$$

To estimate the properties of the condensate of excited atoms, we use density functional theory,[15] in which the energy of the system of electrons, E, is a single-valued functional of the electron density $\rho(\mathbf{r})$:

$$E=T[\rho]+\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{xc}[\rho]+\int d\mathbf{r}\rho(\mathbf{r})v_a(\mathbf{r}). \tag{3}$$

Here $T[\rho]$ is the kinetic-energy functional of the system of noninteracting electrons, and $E_{xc}[\rho]$ is the exchange-correlation energy functional. The second term in (3) is the Hartree energy, and the last describes the electron–ion interaction.

To refine the exchange-correlation energy functional, we introduce an exchange-correlation hole with a charge density $\rho_{xc}(\mathbf{r},\mathbf{r}')$, with which the electrons of the system interact. The charge density of the hole can be expressed with the help of the binary correlation function $g_\rho(\mathbf{r},\mathbf{r}';\lambda)$, where λ is an interaction constant:

$$\rho_{xc}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')\int_0^1[g_\rho(\mathbf{r},\mathbf{r}',\lambda)-1]d\lambda. \tag{4}$$

The exchange-correlation energy functional is defined as the energy of the interaction of the electrons of the system with the charges of the exchange-correlation hole:

$$E_{xc}[\rho]=\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

The problem of calculating $E_{xc}[\rho]$ reduces to one of choosing a binary correlation function, integrated over the interaction constant,

$$G(\mathbf{r},\mathbf{r}')=\int_0^1[g_\rho(\mathbf{r},\mathbf{r}';\lambda)-1]d\lambda,$$

which incorporates both Pauli (exchange) and Coulomb correlations in the motion of the electrons.

Although we do not know the general form of the correlation function $G(\mathbf{r},\mathbf{r}')$ for arbitrary density distributions $\rho(\mathbf{r})$, there are certain exact relations which always hold. The following limits always hold:

$$\lim_{r_{12}\to\infty} G(\mathbf{r},\mathbf{r}')=0, \quad \lim_{r_{12}\to 0} G(\mathbf{r},\mathbf{r}')=-1, \tag{6}$$

where $r_{12} = |\mathbf{r} - \mathbf{r}'|$. In addition, there is a sum rule in force, which states that the total charge of the hole at each point in space is equal to one:

$$\int d\mathbf{r}'\rho(\mathbf{r}')G(\mathbf{r},\mathbf{r}')= -1. \tag{7}$$

If we let $\rho(\mathbf{r})$ approach a constant value, i.e., in the case of a uniform distribution of electrons with a density ρ^h, then the function $G(\mathbf{r},\mathbf{r}')$ becomes the correlation function of a uniform electron gas:

$$\lim_{\rho(\mathbf{r})\to\rho^h} G(\mathbf{r},\mathbf{r}')=G^h(\mathbf{r},\mathbf{r}'). \tag{8}$$

The distribution function can be broken up into two parts: $G(\mathbf{r},\mathbf{r}') = G_x(\mathbf{r},\mathbf{r}') + G_c(\mathbf{r},\mathbf{r}')$, where $G_x(\mathbf{r},\mathbf{r}')$ incorporates the exchange correlations, and $G_c(\mathbf{r},\mathbf{r}')$ incorporates the Coulomb correlations. The following exact equations hold for the exchange-correlation function:

$$\lim_{r_{12}\to\infty} G_x(\mathbf{r},\mathbf{r}')=0, \quad \lim_{r_{12}\to 0} G_x(\mathbf{r},\mathbf{r}')=-{}^1/_2, \tag{9}$$

$$\int d\mathbf{r}'\rho(\mathbf{r}')G_x(\mathbf{r},\mathbf{r}')=-1, \tag{10}$$

$$\lim_{\rho(\mathbf{r})\to\rho^h} G_x(\mathbf{r},\mathbf{r}')=G_x^h(\mathbf{r},\mathbf{r}'). \tag{11}$$

The exchange-correlation function of a uniform electron gas is $[k_F = (3\pi^2\rho^h)^{1/3}]$

$$G_x^h(\mathbf{r},\mathbf{r}')=-\frac{9}{2}\left[\frac{\sin(k_Fr_{12})-k_Fr_{12}\cos(k_Fr_{12})}{k_Fr_{12}}\right]. \tag{12}$$

The following exact equations hold for the Coulomb-correlation function:

$$\lim_{r_{12}\to\infty} G_c(\mathbf{r},\mathbf{r}')=0, \quad \lim_{r_{12}\to 0} G_c(\mathbf{r},\mathbf{r}')= -{}^1/_2, \tag{13}$$

$$\int d\mathbf{r}'\rho(\mathbf{r}')G_c(\mathbf{r},\mathbf{r}')=0, \tag{14}$$

$$\lim_{\rho(r)\to\rho^h} G_c(\mathbf{r},\mathbf{r}')=G_c^h(\mathbf{r},\mathbf{r}'). \tag{15}$$

The Coulomb-correlation function of a uniform electron gas can be written[16]

$$G_c^h(\mathbf{r},\mathbf{r}')=-{}^1/_2\exp(-\alpha r_{12})\cos(\beta r_{12}), \tag{16}$$

where $\alpha = 3^{1/2}\beta$, $\beta = (-\pi\rho^h/8\varepsilon_c)^{1/2}$, ε_c is the correlation energy per electron in the uniform electron gas.

The kinetic-energy functional of a system of noninteracting electrons can be written in terms of a density matrix:

$$T[\rho]=-\frac{1}{2}\int d\mathbf{r}\nabla_r{}^2\Gamma(\mathbf{r},\mathbf{r}')_{\mathbf{r}=\mathbf{r}'}.$$

The following expression[17] holds in the Hartree–Fock approximation:

$$T[\rho]=\int d\mathbf{r}\left[-\frac{1}{2}\rho(\mathbf{r})\Delta_rA(\mathbf{r},\mathbf{r}')_{\mathbf{r}=\mathbf{r}'} + \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}-\frac{\Delta\rho(\mathbf{r})}{4}-\frac{1}{2}\nabla_rA(\mathbf{r},\mathbf{r}')_{\mathbf{r}=\mathbf{r}'}\nabla_r\rho(\mathbf{r})\right], \tag{17}$$

where

$$A(\mathbf{r},\mathbf{r}')=[-2G_x(\mathbf{r},\mathbf{r}')]^{1/2}.$$

The most accurate approximation for calculating the exchange-correlation functional and the kinetic functional is the approximation of a nonlocal density.[17,18] In this approximation, the correlation function is parametrically chosen in the same form as for a uniform electron gas. At each point in space, the parameters which determine this function are chosen in accordance with sum rules (10) and (14). An effective Fermi wave vector $k(\mathbf{r})$ is introduced in the function $G_x(\mathbf{r},\mathbf{r}')$, and a parameter $\beta(\mathbf{r})$ is introduced in the function $G_c(\mathbf{r},\mathbf{r}')$. The values are calculated at each point from the conditions

$$\int d\mathbf{r}'\rho(\mathbf{r}')G_x{}^h(\mathbf{r},\mathbf{r}';k(\mathbf{r}))=-1, \tag{18}$$

$$\int d\mathbf{r}'\rho(\mathbf{r}')G_c{}^h(\mathbf{r},\mathbf{r}';\beta(\mathbf{r}))=0. \tag{19}$$

If the binary correlation function has been determined for a given electron density distribution, then the exchange-correlation energy can be calculated from our basic equation (5) with the help of (4). According to (17), the kinetic-energy functional is given by

$$T[\rho]=\int d\mathbf{r}\left\{\frac{3}{10}[3\pi^2\rho''(\mathbf{r})]^{2/3}\rho(\mathbf{r})+\frac{|\nabla\rho(\mathbf{r})|^2}{8\rho}-\frac{\Delta\rho(\mathbf{r})}{4}\right\}. \tag{20}$$

Here $\rho'(\mathbf{r}) = k^3(\mathbf{r})/3\pi^2$.

The nonlocal-density approximation makes it possible to deal correctly with abrupt changes in the electron density $\rho(\mathbf{r})$. However, the local density approximation (LDA) or "local-density model," which is considerably simpler, is most often used in calculations.[15] Formally, this approximation involves choosing the expression for the charge density of an exchange-correlation hole in the form

$$\rho_{xc}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})G^h(\mathbf{r},\mathbf{r}';\ \rho(\mathbf{r})). \tag{21}$$

In other words, the constant density ρ^h in the correlation function of the uniform electron gas is replaced by the real density $\rho(\mathbf{r})$, which depends on a spatial coordinate. The energy functional simplifies considerably in this case.[4] The exchange-correlation energy is given by the integral

$$E_{xc}[\rho]=\int d\mathbf{r}\varepsilon_{xc}(\rho)\rho(\mathbf{r}), \tag{22}$$

where

$$\varepsilon_{xc}(\rho)=-\frac{3}{4\pi}(3\pi^2)^{1/3}\rho^{1/3}(r)-0{,}44\left(\frac{4\pi}{3}\right)^{1/3}\rho^{1/3}(r). \tag{23}$$

For the kinetic energy we have the expression

$$T[\rho]=\int d\mathbf{r}t(\rho)\rho(\mathbf{r}), \tag{24}$$

where

$$t(\rho)=\frac{3}{10}(3\pi^2)^{2/3}\rho^{2/3}(\mathbf{r})+\frac{|\nabla\rho(\mathbf{r})|^2}{8\rho^2(\mathbf{r})}-\frac{\Delta\rho(\mathbf{r})}{4\rho(\mathbf{r})}. \tag{25}$$

Numerical calculations[4] show that the LDA model is valid if the radii of the pseudopotentials are not too large. The approximation of a nonlocal density has to be used only

TABLE II. Estimated properties of a condensate of excited Cs atoms.

Excitation level, n	Surf. tension σ, erg/cm^2	Resistivity ρ_e, $\Omega\cdot$m	Transmission boundary, λ, μm
6S ground state	85,0	$2\cdot10^{-7}$	0,36
10	1,0	$3\cdot10^{-4}$	13
11	0,4	$5\cdot10^{-4}$	21
12	0,2	$7\cdot10^{-4}$	32
13	0,1	$1\cdot10^{-3}$	46
14	0,06	$1\cdot10^{-3}$	63
15	0,03	$2\cdot10^{-3}$	85
16	0,02	$3\cdot10^{-3}$	110
17	0,01	$3\cdot10^{-3}$	141
18	0,008	$4\cdot10^{-3}$	178
19	0,006	$5\cdot10^{-3}$	219
20	0,004	$7\cdot10^{-3}$	267

if the radius of the heart in the empty-core model reaches values on the order of 10^3.

PARAMETERS OF A CONDENSATE OF EXCITED CESIUM

To estimate the parameters of a condensate of excited Cs atoms, we use the spherical-cell method, which works well for *sp* bands.[19] We also use the local-density approximation. According to Ref. 4, the LDA model works well up to excitation levels $n\sim30$. Since there are no corrections for intercell interactions in the approximation of the spherical cells, the integrals in the expressions for the energy functional can be taken within a single cell. As a trial distribution of the electrons within a cell, we use a single-parameter Gaussian profile which minimizes the energy of the system:

$$\rho(\mathbf{r})=\rho_0\exp[(r-R_{WS})^2/D^2],$$

where $R_{\rm WS}=(R_n+D)$ is the radius of the cell, and R_n is the radius of the Ashcroft pseudopotential of the corresponding n state of the excited atom. A distribution width $D\approx1.8R_n^{0.4}$ turns out to be the optimum width here.[3]

The binding energy (or adhesion energy) B is defined as the difference between the energy per atom in the condensate and the binding energy of an electron in the unperturbed excited atom.

Table I shows numerical values of the interatomic distances L_a, of the equilibrium density ρ, and of the binding energy B.

Table II shows estimates of the surface tension σ, the resistivity ρ_e, and the transmission boundary (the maximum light wavelength which is transmitted) λ of the condensate. The surface tension was found from the formula $\sigma\approx4B/\pi L_a^2$. The resistivity was found from $\rho_e\approx mv/pe^2l_e$, where v is the average electron velocity, and l_e is the mean free path. Here we are adopting $l_e\approx L_a/2$. The transparency boundary is determined from an estimate of the electron plasma frequency of the condensate.

The phase state of the condensate at various temperatures is of much interest. To determine the melting point of the condensate we use the Lindemann melting condition, according to which melting sets in when the mean square amplitude of the vibrations of the ions reaches an appreciable level in comparison with the interatomic distances.[20] If we use the Debye model for the phonons, we can show that the Lindemann parameter is related to the melting point T_m and to the sound velocity v_s by the simple relation $\gamma=1.6\ k_BT_m/M_iv_s^2$, where k_B is the Boltzmann constant, and M_i is the mass of the ion. For lattices of most types we would have $\gamma\approx1/16$ (Ref. 20). Assuming that the parameter γ for the condensate is the same as that for ordinary metallic cesium, we find the melting point of the condensate $T_m^{\rm CES}-T_m^{\rm Cs}(v_s^{\rm CES}/v_s^{\rm Cs})^2$, where CES stands for condensed excited states. The sound velocity is determined by the volume of a unit cell, Ω; by the bulk modulus $b=\Omega d^2E/d\Omega^2$, where E is the condensate energy; and by the mass of the ion: $v_s=(b\Omega/M_i)^{1/2}$. Table III shows estimates of the melting

TABLE III. Mechanical properties of a condensate of excited Cs atoms.

Excitation level n	Bulk modulus b, dyn/cm^2	Sound velocity v_s, cm/s	Melting point $T_m^{\rm CES}$, K
6S ground state	$2\cdot10^{10}$	$0{,}97\cdot10^5$	302 *
10	$2\cdot10^7$	$1{,}1\cdot10^5$	387
11	$8\cdot10^6$	$1{,}1\cdot10^5$	387
12	$4\cdot10^6$	$1{,}2\cdot10^5$	461
13	$2\cdot10^6$	$1{,}2\cdot10^5$	461
14	$1\cdot10^6$	$1{,}3\cdot10^5$	541
15	$6\cdot10^5$	$1{,}3\cdot10^5$	541
16	$4\cdot10^5$	$1{,}4\cdot10^5$	627
17	$2\cdot10^5$	$1{,}4\cdot10^5$	627
18	$2\cdot10^5$	$1{,}4\cdot10^5$	627
19	$1\cdot10^5$	$1{,}5\cdot10^5$	720
20	$8\cdot10^4$	$1{,}5\cdot10^5$	720

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*The value of $T_m^{\rm Cs}$ is given for the ground state point of the condensate for various excitation levels. Shown for comparison here are values of the bulk modulus and the sound velocity.

Interestingly, the sound velocity does not decrease with increasing excitation level, although the elastic modulus of the condensate decreases rapidly. This decrease is offset by a rapid increase in the volume of the unit cell. Figuratively speaking, the propagation of sound is opposed by the low elasticity of the system but promoted by the long "strides—the interatomic distances. Since the sound velocity in the condenstate does not decrease, the melting point of the condensate does not become lower. This extremely unusual property of the condensate is even more surprising in view of the rapid decrease in the binding energy. It is found that the condensate remains in a solid state even at temperatures comparable to the binding energy. It should be kept in mind, however, that the condensate is easily deformed and compressed, as can be seen from the small values of the bulk modulus.

METASTABLE NATURE OF THE CONDENSATE

Condensed excited states at high excitation levels are long-lived metastable states.[21] Their lifetime can apparently be unlimited. The reasons are the spatial separation of the initial and final states of the valence electrons and the formation of a broad potential barrier between them. The barrier arises because of specific quantum-mechanical effects in the highly nonuniform Fermi liquid. These effects can be summarized by saying that the interaction of electrons with an exchange-correlation hole is predominant in the region in which the electron density is relatively high.[4]

A classical analog of this interaction is the interaction of a charged particle with its image at the boundaries of spherical Wigner–Seitz cells. The valence electrons are blocked near the cell boundaries; they can penetrate into the internal regions, where the lower-lying states are localized, only by tunneling through the broad potential barrier. However, the exchange-correlation interaction leads to the appearance of a potential barrier only when parameters reach certain values. For example, it was shown in Ref. 22 that, in a model with a rigid neutralizing background (i.e., in a model which is qualitatively different from the Overhauser model, in which the background is absolutely deformable), the exchange-correlation interaction leads to an instability of a uniform electron distribution and to the formation of charge density waves only when the parameter $r_s = (3/4\pi\rho)^{1/3}$ reaches the value $r_s = 17a_0$ for two-dimensional systems or $r_s = 26a_0$ for three-dimensional systems (a_0 is the first Bohr radius). Potential barriers appear in the system of ions at excitation levels $n^* > 3$ (Ref. 4). Figure 1 shows the effective intracell one-particle potential of the valence electrons in a condensate of excited Cs atoms with $n = 10$: $W = v_i + v_H + v_{xc}$, where v_i is the potential of the cesium ion, v_H is the Hartree potential, and $v_{xc} = -1.93\rho^{1/3}$ is the effective local exchange-correlation potential. According to (3), the latter potential incorporates not only exchange but also correlation. It thus differs from the Slater exchange potential by a numerical factor.

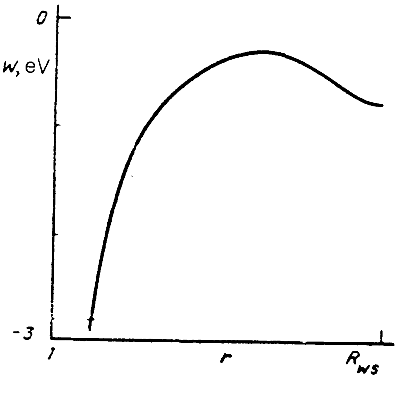

FIG. 1. Effective potential of the valence electrons, W (eV), inside a unit cell for a condensate of excited Cs atoms ($n = 10$). This cell radius is $R_{\rm WS} = 63$; the value of the potential at the cell boundary is $W_{\rm WS} = -0.757$; the maximum value is $W_{\max} = 0.299$; and the Fermi level is $E_F = -0.517$.

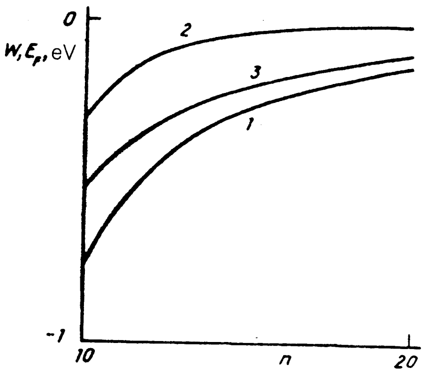

FIG. 2. Effective potential of the valence electrons in a condensate, $W_{\rm WS}$ (1) and $W_{\max}$ (2), and position of the Fermi level, E_F (3), versus the excitation level n of the Cs atoms.

Figure 2 shows values of the effective potentials at the boundary of Wigner–Seitz cells, $W_{\rm WS}$ (an analog of the bottom of the valence band of the condensate), along with the maximum values $W_{\max}$, which characterize the height of the potential barrier. The position of the Fermi level E_F of the valence electrons is also shown here. To determine the position of E_F, we make use of the circumstance that the valence band at the condensate is narrow in energy space. In other words, we make use of the small parameter max-$[|(\varepsilon_i - \varepsilon_j)/\varepsilon_i|] < 1$, where ε_i are the eigenvalues of the Kohn–Shem equation. From density functional theory we have

$$\sum \varepsilon_i = E + E_H - E_{xc} - \int d\mathbf{r} v_{xc}\rho(\mathbf{r}).$$

Making use of the narrowness of the bands, $\Sigma\varepsilon_i \approx NE_F$, we thus find $E_F \approx (E + E_H + \frac{1}{3}E_{xc})/N$ where N is the number of electrons. As can be seen in Fig. 2, the Fermi level is below $W_{\max}$ for condensed states of excited Cs atoms with $10 < n < 20$.

CONCLUSION

Condensed excited states arise when there are a large number of excited atoms, because of the strong interaction between these atoms. The thermodynamic functions of systems of atoms excited to the same state, in a mixture with unexcited atoms, were first discussed by Mal'nev and Pekar.[23] Although the results which they derived are valid, strictly speaking, only at small deviations from the ideal case, they reached the conclusion that the system is unstable and that it decays into two phases. The experiments which have been carried out to date do not yield satisfactory estimates of the properties of the condensate (which possibly forms). It is thus not possible to calculate anything more accurate than fairly crude model-based estimates. Cesium appears to be a suitable material for experiments, especially since it is simple to obtain a large number of excited atoms in this case. The estimates above will make possible a directed effort to search for a condensate and to determine its properties.

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