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Valence charge in a solid at 0 K viewed as a pressure-ionization effect

B. K. Godwal
Neutron Physics Division, Bhabha Atomic Research Centre, India

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Modified Saha ionization theory has recently been used to obtain the dominant pressure and thermal ionization effects in the "intermediate" region (0.5—10 TPa) of the equation of state. The present work is aimed at providing the justification for the use of this theory in the presence of interactions. The valence charges at 0 K at normal density as determined using this theory are in very good agreement with their normal valence charges for a number of elements. The equation of state as computed from it is also in good agreement with the Thomas-Fermi-Dirac equation of state. Finally the theory is shown to simulate the valence transition under pressure in Eu and Yb.

I. INTRODUCTION

The pressure-volume (PV) data in the so-called "experimental" region are obtained using static or dynamic shock compression experiments. Theoretical attempts[1,2] have also been made using energy-band methods to interpret these data. The potential parameters (which depend on the atomic configuration) which enter these calculations continue to assume their normal pressure values. This is because the pressure and thermal ionization effects in this region do not lead to core ionization.[3]

In the "intermediate" pressure region (viz., 0.5—10 TPa) some experimental PV shock Hugoniot data have been recently generated.[3] In developing a suitable theoretical description for this region, the ionization of core electrons leads to complications in the energy-band model (it changes the potential). The transfer of electrons into the conduction band increases the ionic charge, thus decreasing the effective core size.[4] In our[3] approach to the intermediate region from the experimental side, the valence charge on the atom at 0 K is viewed as a pressure-ionization effect. The screened Coulomb modified form of Saha's equation[5,6] is used to obtain the pressure and thermal ionization of the condensed matter which becomes important in the intermediate region (see Table I). As is well known, the ordinary Saha ionization theory[7] assumes that the thermodynamic system is a mixture of ideal gases with no interaction between them, so it is not surprising that this theory is not valid at high densities. In the present paper we show that the modifications made in Saha's theory by Rouse[5] simulate the high-density effects. We also find that in the high-density, high-temperature region, the equation of state[5,6] obtained from it merges with the well-accepted Thomas-Fermi-Dirac (TFD) equation of state,[8] and for the normal solid-state densities it predicts the correct valence charge for metallic solids.

Further, Bundy and Dunn[9] have recently measured the electrical resistance of Eu above 400 kbar and temperatures down to 2.3 K. Based on their phase diagram, these authors find that there is one phase below 150 kbar and a different phase above. In this regard Johansson and Rosengren,[10,11] on the basis of their generalized phase diagram for the lanthanides, point out that Eu and Yb, because of the tendency of the $4f$ shell to be half filled, are divalent in the normal solid state, whereas the others are trivalent. But upon compression, both these elements should go over to trivalent metallic states. In the present work, we first predict the normal valence states for Eu and Yb using modified Saha ionization theory, and then use it to show the existence of in-

TABLE I. Pressure and thermal ionization in the intermediate region for Al and Mo. Z^* denotes the valence charge for a given density and temperature along the experimental shock PV curve (Hugoniot).

Element	$\frac{V}{V_0}$	T (eV)	Z^*	Remark
Al	0.32	7.7	3.02	Thermal ionization
Mo	0.331	0.0	6.10	Pressure ionization

termediate valence states and the final trivalent state under high pressure.

II. MODIFIED SAHA IONIZATION THEORY

The successful use of the Saha ionization theory at high density solely depends on the formulation of a model for monatomic matter that takes into account the high-density effects like lowering of the ionization potentials, partition function cutoff, and the pressure-ionization effects. These are brought about by Rouse[5] in Saha ionization theory via CSCP (complete screened Coulomb potential) interaction, which is given by

$$V(r)=\begin{cases} V_i(r)=-Ze^2\left[\dfrac{1}{r}-\dfrac{1}{D+A}\right]\,, & r\le A\\[2ex] V_0(r)=-Ze^2\dfrac{D}{D+A}\,\dfrac{\exp[(A-r)/D]}{r}\,, & r\ge A\end{cases}\tag{1}$$

where D is the screening radius and $A(=D/2)$ is the mean minimum radius of the ion atmosphere. The screening radius as shown by Pines and Nozières[12] is given by the relation $\frac{4}{3}\pi D^3 N_a=1$, where N_a is the number of atoms/cm^3.

The modified Saha equation is[5,6]

$$\frac{C_i}{C_{i+1}}=N_e\frac{h^3}{2(2\Pi m_e kT)^{3/2}}\frac{U_i}{U_{i+1}}\times\phi_i\exp(\chi_i/kT)\ .\tag{2}$$

Here i is the charge of the ion, N_e is the number of free electrons/cm^3, N_i is the number/cm^3 of ion i, N_a is the total number of atoms/cm^3, N is the total number of free particles/cm^3, C is the concentration of free electrons, C_i is the concentration of ion i,U_i is the CSCP electronic partition function of ion i, χ_i is the CSCP difference in ground-state energies between ions i and $i+1$, and ϕ_i is the CSCP relative occupation probability for the outer orbitals of ion i. U_i, χ_i, and ϕ_i are determined from the solutions of the radial Schrödinger wave equation with CSCP interaction.[5]

Following are the detailed expressions for χ_i, ϕ_i, and U_i as given by Rouse.[5] The variation of χ_i as a function of screening radius is

$$\chi_i=I_i[1+(C_2a_0/Z_i'D)^2+C_3(a_0/Z_i'D)^3]^{-1}\ ,\tag{3}$$

where I_i is the ionization potential of the isolated ion i,[13] $C_2=0.71248$, $C_3=6.4364$, a_0 is the Bohr radius, and Z_i' is the net core charge of ion i. [In Eq. (3), C_2 and C_3 are not ion concentrations.] The relative occupation probability $\phi_i(D)$ is

$$\phi_i(D)=\exp[-(\delta a_0 n^2/Z_i'D)^m]\ ,\tag{4}$$

where $m=1$ for $Z_i'D\ge\delta a_0 n^2$ and $m=3$ for $Z_i'D<\delta a_0 n^2$, and δ is the parameter added for ions with two or more bound electrons that is proportional to the maximum of the charge probability densities in the closed-shell configurations of He, Ne, Ar, and Kr as given by Slater.[14]

The two hydrogenic electronic partition functions used are referred to as $U_i^{(1)}$ and $U_i^{(2)}$ given by

$$U_i^{(1)}=w_i+w_{i+1}(Z_i'D)^{3/2}[4.441\times10^{11}\exp(-0.9\chi_i/kT)]+1.089\times10^{11}\exp(-\chi_i/kT)\ ,\tag{5}$$

where w_i is the ground-state degeneracy for ion i,[13] and $U_i^{(2)}$ is given by

$$U_i^{(2)}=w_i+2w_{i+1}\sum_{n=2}^{n^*}n^2\phi_n\exp(-E_n/kT)+w_{i+1}(Z_i'D)^{3/2}(1.089\times10^{11})\exp(-\chi_i/kT)\ ,\tag{6}$$

where n^* is defined as the maximum bound state and is given by

$$n^{*2}=0.59Z_iD/a_0\ .$$

If $n^*>10$, then $U_i^{(1)}$ is used, and if $n^*\le 10$, $U_i^{(2)}$ is used where

$$E_n=\chi_i[1-(1/n^2)]\ .$$

It is observed from these solutions that U_i has a cutoff and χ_i is lowered at high densities as compared to the isolated ion case. Further, the quantity that does decrease in the CSCP solutions as $D\rightarrow0$ is the normalization integral. This suggests that the probability of finding a bound eigenstate relative to the corresponding Coulomb state can be defined by the ratio of the CSCP normalization (pressure ioni-

TABLE II. Valence-charge prediction for various elements in the periodic table. — — are the values less than 10^{-10}. The concentrations of higher ionic species which are negligibly small are also not shown.

Element	Z	Concentration of ionic species (ρ/ρ_0=1.0, T=0.0)		D (Å)	A (Å)	$Z^*=\sum_{i=1}^{Z} iC_i / \sum_{i=1}^{Z} C_i$	Valence charge
Li	3	C	5.0107×10^{-1}	1.731	0.866		
		$C1$	4.968×10^{-1}				
		$C2$	2.143×10^{-3}			1.0	1
		$C3$	5.523×10^{-10}				
Be	4	C	6.872×10^{-1}				
		$C1$		1.245	0.622		
		$C2$	3.412×10^{-1}			2.005	2
		$C3$	1.804×10^{-3}				
Al	13	C	7.50×10^{-1}	1.582	0.791		
		$C1$					
		$C2$					
		$C3$	2.499×10^{-1}			3.00	3
		$C4$	8.750×10^{-5}				
Fe	26	C	7.5×10^{-1}				
		$C1$		1.412	0.706		
		$C2$	4.332×10^{-9}			3.00	2,3
		$C3$	2.4999×10^{-1}				
		$C4$	6.404×10^{-8}				
Zr	40	C	7.996×10^{-1}				
		$C1$					
		$C2$	3.0496×10^{-7}	1.773	0.886	3.99	4
		$C3$	2.258×10^{-3}				
		$C4$	1.798×10^{-1}				
		$C5$	3.599×10^{-4}				
Nb	41	C	8.331×10^{-1}				
		$C1$					
		$C2$					
		$C3$	1.734×10^{-7}	1.636	0.818	4.98	5,3
		$C4$	1.415×10^{-1}				
		$C5$	1.654×10^{-1}				
		$C6$	5.388×10^{-5}				
Mo	42	C	8.581×10^{-1}				
		$C1$					
		$C5$		1.550	0.775	6.0	6
		$C6$	1.430×10^{-1}				
		$C7$	1.52×10^{-7}				
Eu	63	C	6.6666×10^{-1}				
		$C1$		2.254	1.127	2.0	2
		$C2$	3.3333×10^{-1}				
Yb	70	C	6.6666×10^{-1}				
		$C1$					
		$C2$	3.3333×10^{-1}	2.158	1.072	2.0	2

zation) to the Coulomb normalization. As noted by Rouse[5] the screened Coulomb results for the effective maximum bound state with the radius of the mean atomic volume as the effective screening radius are in excellent agreement with the observed drop in the line intensities of solar hydrogen in both photosphere and chromosphere. This justifies the definition of relative occupation probability.

III. VALENCE-CHARGE DETERMINATION

The modified Saha equation together with

$$C=\sum_{i=1}^{Z} iC_i \tag{7}$$

and

$$C+\sum_{i=0}^{Z} C_i=1 \tag{8}$$

was solved by iteration using ionization potentials and ground-state degeneracies.[13,15] The output quantities are the free-electron density N_e and the various C_i's. From the latter, the effective charge is defined to be

$$Z^*=\sum_{i=1}^{Z} iC_i \Big/ \sum_{i=1}^{Z} C_i \tag{9}$$

for $C_0 \approx 0.0$. This also determines the core charge which can be used to fix the core radius.[16]

The above theory was applied to various elements in the periodic table. The concentrations of various ionic species present in the plasma at $\rho/\rho_0=1$ and at zero temperature[17] are displayed in Table II. It is seen that the ionization spectrum is very sharp. For example, for Al and Mo the most dominant ionic species present in the solid-state plasma are Al^{3+} and Mo^{6+}. Changing the Maxwell-Boltzman partition function for free electrons to the Fermi-Dirac function (U_e) had a negligible effect on the Saha solutions. This is because N_e and U_e occur as a ratio. At the normal density, negligible lowering of ionization potentials was observed due to electrostatic fields in high-density plasma. The valence-charge results were found to be very sensitive to the pressure-ionization term. Without it the valence charges at normal density and 0 K for Al and Mo are, respectively, 1.8 and 2.5. The valence charges determined using Eq. (9) are also given in Table II. Also given are the values of A and D which enter the CSCP interaction potential [see Eq. (1)]. The excellent agreement with the normal valence charges for these elements can be seen. This was also found true for a number of other elements.

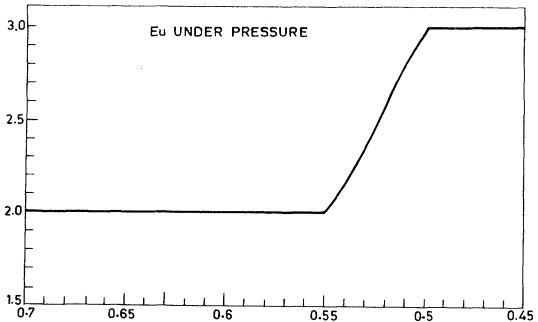

FIG. 1. Valence-charge variation with compression for Eu.

IV. VALENCE TRANSITION IN Eu AND Yb

It is seen from Table II that this theory predicts correctly the normal valence charges for Eu and Yb at 0 K. The valence-charge variation was further investigated using this theory under compression. It is seen from Fig. 1 that Eu remains divalent up to the compression of 0.55. It then takes nonintegral valencies and finally goes to the trivalent state at $V/V_0=0.5$. On further compression it remains in its trivalent state as seen from Fig. 1. We attribute this to the pressure ionization of $4f$ electrons. Thus it is seen that this theory works not only at normal pressure but under high pressure also. In the pseudopotential energy-band method of Rosengren and Johansson[11] the cohesive energy of a divalent solid (like Eu and Yb) gets increased by promoting a $4f$ electron to the conduction band; under compression the band gap is reduced so that the promotion becomes energetically favorable. As is seen from Fig. 1 the valence transition in Eu occurs at $V/V_0=0.55$, which is different from the value of $V/V_0 \approx 0.62$ as observed by Rosengren and Johansson.[11] This difference is perhaps due to the fact that our model neglects the details of atomic structure for specific atoms. The present model was also applied to Yb. We found that Yb starts showing nonintegral valencies at a compression of $V/V_0=0.75$ and attains the trivalent state at $V/V_0=0.7$. This is again in accordance with the observations of Rosengren and Johansson.[18]

V. CONCLUSION

We thus believe that Saha's theory as modified by Rouse[5] is applicable for calculating pressure and thermal ionization in condensed matter as it takes into account the high-density effects like lowering of the ionization potentials, partition function cutoff, and the broadening of the energy levels of an ion into bands. These effects are brought about by Rouse[5,19] via the CSCP interaction. The proof of this is in fact the prediction of correct valence charges for a number of metals and the valence transitions under pressure for Eu and Yb.

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[13] The first few ionization potentials used by us in these calculations are taken from C. E. Moore, NSRDS-Natl. Bur. Stand. (U.S.) Report No. 34, 1970 (unpublished). The net core charges Z_i' were calculated using these. The higher ionization potentials and ground-state degeneracies were computed in accordance with Refs. 6 and 15. For Eu and Yb, see Refs. 10 and 11.

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[17] Actually, the calculations were done for a finite nonzero value of temperature, which was then decreased ($T \rightarrow 0$) until the solutions became independent of it.

[18] These authors predict that the valence transition in Yb should occur earlier (i.e., smaller pressures) than in Eu (see Refs. 10 and 11).

[19] C. A. Rouse (Ref. 5) has also shown that equation of state computed from his screened Coulomb solutions for Fe yielded results in reasonable agreement with TFD equation of state (EOS) at high densities where TFDEOS is accepted.