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ONE PARAMETER MODEL POTENTIAL FOR NOBLE METALS*

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ABSTRACT

A phenomenological one parameter model potential which includes s-d hybridization and core-core exchange contributions is proposed for noble metals. A number of interesting properties like liquid metal resistivities, band gaps, thermoelectric powers and ion-ion interaction potentials are calculated for Cu, Ag and Au. The results obtained are in better agreement with experiment than the ones predicted by the other model potentials in the literature.

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1. INTRODUCTION

The pseudopotential method has been successfully applied to the study of electronic properties of simple metals. The difficulties arise when this method is used in noble and transition metals because of the hybridization of d-states with the free electron like conduction band and of considerable sizes of ionic cores. The situation is further complicated by the fact that all the hitherto known noble metal model potentials contain two or more unknown parameters. Since there do exist uncertainties in the determination of some of the parameters, it is difficult to make completely unambiguous statements about the basic worth of any given model potential. Both from a practical and aesthetic point of view it is worth searching for a one parameter model potential applicable to the case of noble metals. In this paper we propose such a potential for the noble metals Cu, Ag and Au. Some of the transport properties are calculated and compared with experiment.

2. MODEL PSEUDOPOTENTIAL

In our search for a suitable model potential we are guided by the following physical arguments:

(i) It must contain a repulsive term arising from the exchange overlap (core-core) repulsion;

(ii) it must contain an attractive term to take into account s-d hybridization; and

(iii) it must be purely coulombic outside some fixed radius.

The following bare ion model potential for election - ion interaction satisfies all the requirements listed above:

$$w^b(r)=\begin{cases} \dfrac{Ze^2(R_m^2 - R_w r)}{R_w^2 (R_w - R_m)} & 0 < r < R_m \\ -\dfrac{2Ze^2}{R_w} & R_m < r < R_w \\ -\dfrac{Ze^2}{r} & R_w < r \end{cases} \qquad (1)$$

which says that the potential is repulsive from $r = 0$ to $r = \hat{R}_m = R_m^2/R_w$ (core redius), attractive and constant in the region $r = R_m$ to $r = R_w$ ($= (\frac{3\Omega}{4\pi})^{1/3}$, the Wigner - Saitz radius) and purely coulombic beyond. In the first region the denominator of the potential plays an important role in that with the increase of the core size the difference $R_w - R_m$ decreases leading to a correspondingly strong repulsive potential. In the intermediate region the potential is, of course, negative but, what is perhaps more important, it is more negative than, for example, the potential of Kulshrestha et al. [1]. This part gives an improved account of the s-d hybridization which has been introduced phenomenologically. The Fourier transform of (1) is given by

$$W^b(q) = \frac{4\pi}{\Omega q^3}\left[(AR_m^2 + B - AR_wR_m)\{\text{Sin } qR_m - qR_m \text{ Cos } qR_m\} - B\{\text{Sin } qR_w - qR_w \text{ Cos } qR_w\}\right.$$

$$\left. - \frac{AR_w}{q}\{qR_m \text{ Sin } qR_m + 2(\text{Cos } qR_m - 1)\} - Ze^2 qR_w \text{ Cos } qR_w\right] \qquad (2)$$

$$A = \frac{Ze^2}{R_w^2 (R_w - R_m)}$$

and $$B = \frac{2Ze^2}{R_w}$$

We may now proceed to compute the form factors, bandgaps, liquid metal resistivities, thermoelectric powers and the effective ion-ion interactions for the noble metals, based upon this pseudopotential. The procedure has been outlined, for example, in [2]. However, three simple exercises must first be carried out. These relate to the evaluation of the liquid metal densities and the parameter R_m and a check of the validity of the Born approximation.

i) Liquid metal density

The liquid metal densities of Cu, Ag and Au were first used by Moriarty [3]. In our calculation Ω has been determined by noting the position of the third maximum in the experimental structure factor curve of each of the metals Cu, Ag and Au [4]. The resulting values of Ω are tabulated in Table I.

ii) The parameter R_m

In the case of Cu we evaluate the form factor at ξ = (III) and equate it to the value determined by Burdick [5] by a fit to the optical data. For Ag and Au, we adopt a slightly different procedure. Here the starting point is the phase shift analysis of Micah and Young [6] who have also determined the value of w(III) for Ag and Au. The value of w(III) calculated from Eq.(2) is now equated to it and the parameter R_m thus determined. The resulting values are given in Table I.

The form factors for both liquid and solid phases for Cu, Ag, and Au are presented in Figs.1(a,b,c) respectively. We immediately note that the values of $q_o/2k_F$ for all the three metals are less than unity and around 0.6 in agreement with the proposal of Cohen and Heine [7].

iii) Validity of the Born approximation

As pointed out, for example, in [2] it is essential that $a(q)\,|\,w(q)\,|^2 << E_F^2$ for the born approximation to hold; upon which rests the derivation of the Ziman's resistivity formula. A plot of this quantity as a function of q is shown in Fig.2. It is clear that this condition is well satisfied by the potential (2) so that use of the Ziman's formula is legitimate.

The predicted values of liquid metal resistivity ρ_L and the thermoelectric power $\mathcal{E}$ are reported in Table II alongwith the experimental numbers [8,9] for comparison. The agreement between the experimental and theoretical ρ_L is exceptionally good for all the three metals under

investigation. It is interesting to compare it with the results obtained from the Borchi and DeGennaro potential which was adjudged to be the best from the set of pseudopotentials considered in [2] . In the present case the agreement between theory and experiment is even better.

Referring to the thermoelectric power ξ the values predicted by the potential (2), unfortunately, are not in agreement with the experiment, except for the fact that the negative signs are correctly reproduced. However, it is gratifying to note that the disagreement in the case of the present potential is far less violent than in the potentials of [2] . Naturally the effect of non-locality discussed there is expected to be equally important here also.

We next consider the results on the band gaps. The agreement is excellent for all the three metals. Again the superiority of the present pseudopotential over those of [2] comes out clearly when comparison is made with the predictions of the latter.

Finally we turn to the calculation of the ion-ion interaction based on the potential (1), applying the procedure outlined in the paper of Moriarty [10]. We have depicted asymptotic forms of the calculated ion-ion potentials in Fig. 3. It is seen that the minimum of Au is deeper than that of Cu which in turn is deeper than that of Ag . This is in agreement with the experimental fact that the binding energy E_o satisfies the inequalities $|E_o(Au)| > |E_o(Cu)| > |E_o(Ag)|$ This, for example, is not the case with the ion-ion potentials of Moriarty [10] and Sharma [11]. It is also instructive to compare our results with those of Mahanty and Taylor [12] who have

calculated the ion-ion potentials for Cu, Ag and Au using entirely different considerations, such as an extended inert gas model for the calculation of Van der Waals contribution to the ion-ion interaction and Born-Huang approximation [13] in the calculation of repulsion and exchange energy. They find that V_{min} = 0.0016 Ryd; 0.0009 Ryd; 0.0018 Ryd for Cu, Ag and Au respectively. This is to be compared with the values of V_{min} = 0.0020 Ryd; 0.0012 Ryd; 0.0027 Ryd for Cu, Ag and Au respectively obtained with our potential. Keeping in view the fact that the author of [12] have not included the screened coulomb repulsion of the ions in their calculations, the agreement is fairly good.

In summary, we see that the pseudopotential (1) holds a number of advantages over the other model pseudopotentials known in the literature.

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TABLE - I

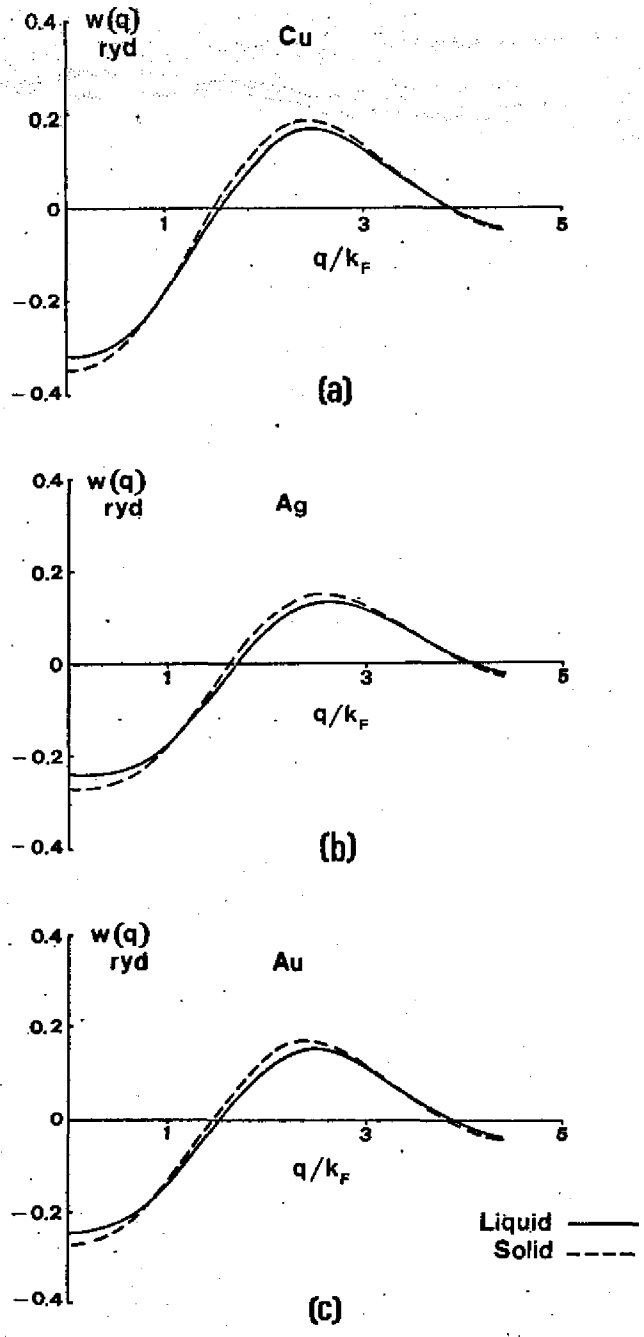
Given are the values of liquid density, parameter R_m and E_F (in a.u.) for Cu, Ag and Au.

Element	$\Omega_{liq.}$	R_m	E_F
Cu	89.54	1.84	0.4782
Ag	140.00	1.90	0.3815
Au	135.00	2.14	0.3963

TABLE - II

Predicted values of Bandgaps, liquid metal resistivities and coefficients of thermoelectric power of Cu, Ag and Au and the corresponding experimental values. Hubbard Sham [2] f(q) has been used in obtaining the theoretical values. ρ_L and ξ for Cu, Ag and Au have been evaluated at temperatures of 1150°C, 1000°C and 1150°C respectively.

		Present	Exp.[8, 9]
Cu	Bandgap(ryd)	0.352	0.350
	ρ_L(μ ohm cm)	20.80	21.10
	ξ	- 6.80	-3.50
Ag	Bandgap(ryd)	0.258	0.280
	ρ_L(μ ohm cm)	17.40	17.20
	ξ	-5.60	-1.90
Au	Bandgap(ryd)	0.320	0.300
	ρ_L(μ ohm cm)	31.05	32.00
	ξ	-6.80	-0.60



Form factors for Cu, Ag and Au for both liquid and solid metallic densities.

FIG 1

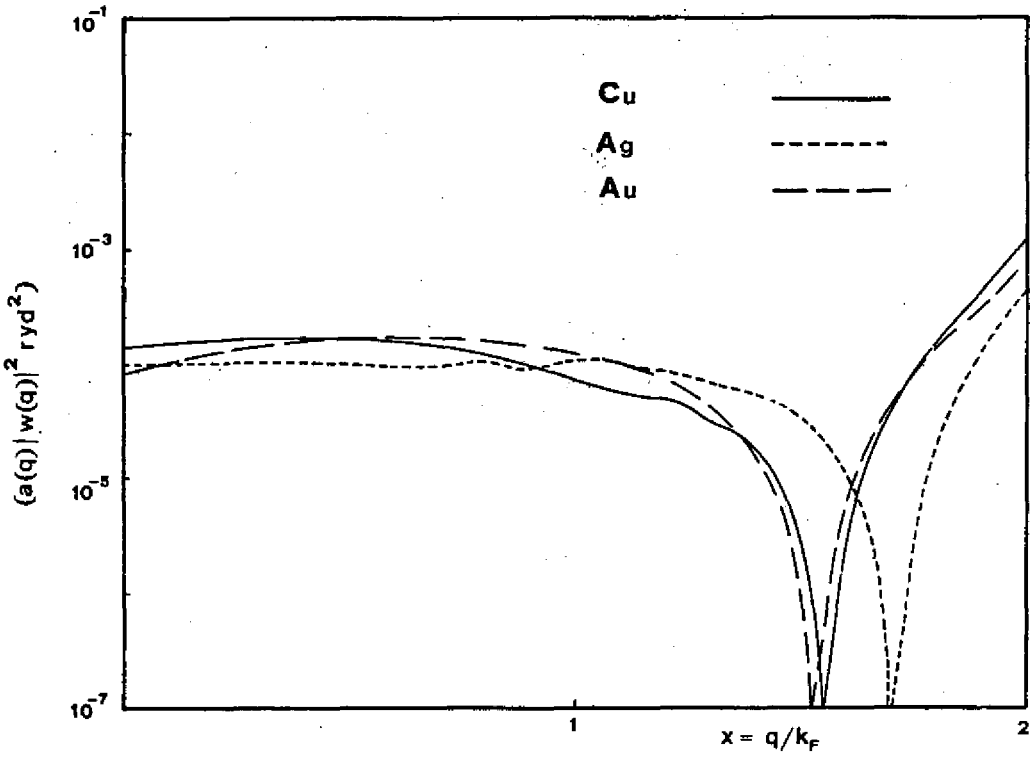


FIG 2

Plot of the function $a(q)|w(q)|^2$

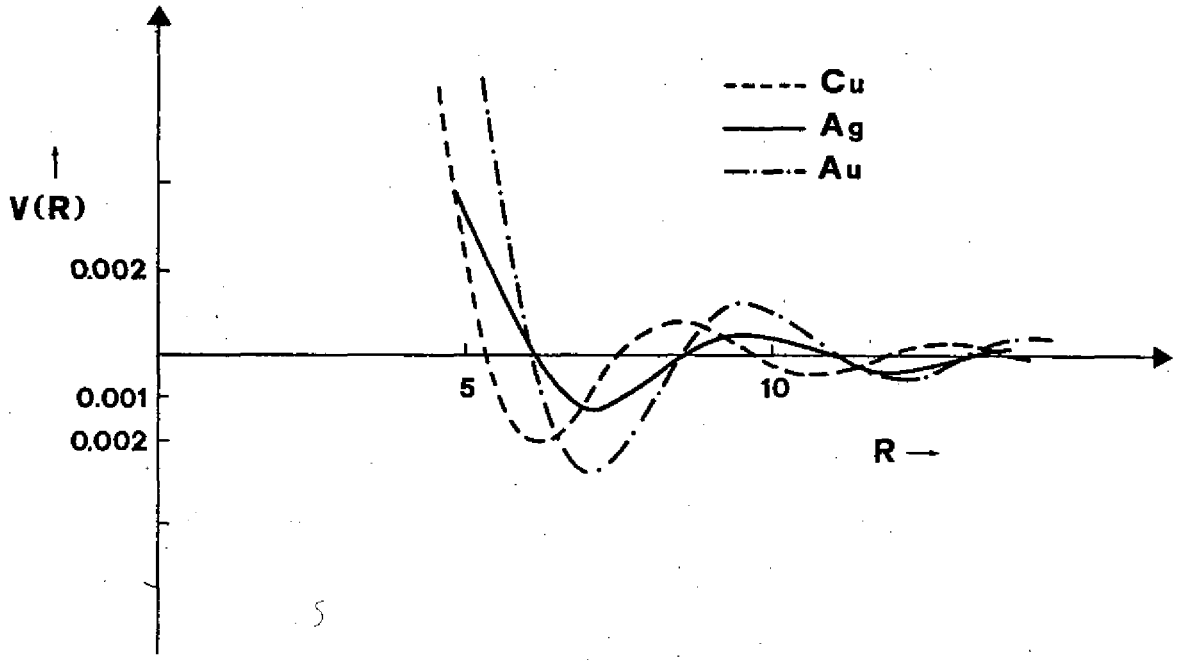


FIG 3

Asymptotic forms of the predicted ion-ion potentials for Cu, Ag and Cu.

FIGURE CAPTIONS

Fig. 1. Form factors for Cu, Ag and Au for both liquid and solid metallic densities.

Fig. 2. Plot of the function $a(q)|w(q)|^2$.

Fig. 3. Asymptotic forms of the predicted ion-ion potentials for Cu, Ag and Cu.

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