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STRUCTURAL ENERGETICS OF NOBLE METALS

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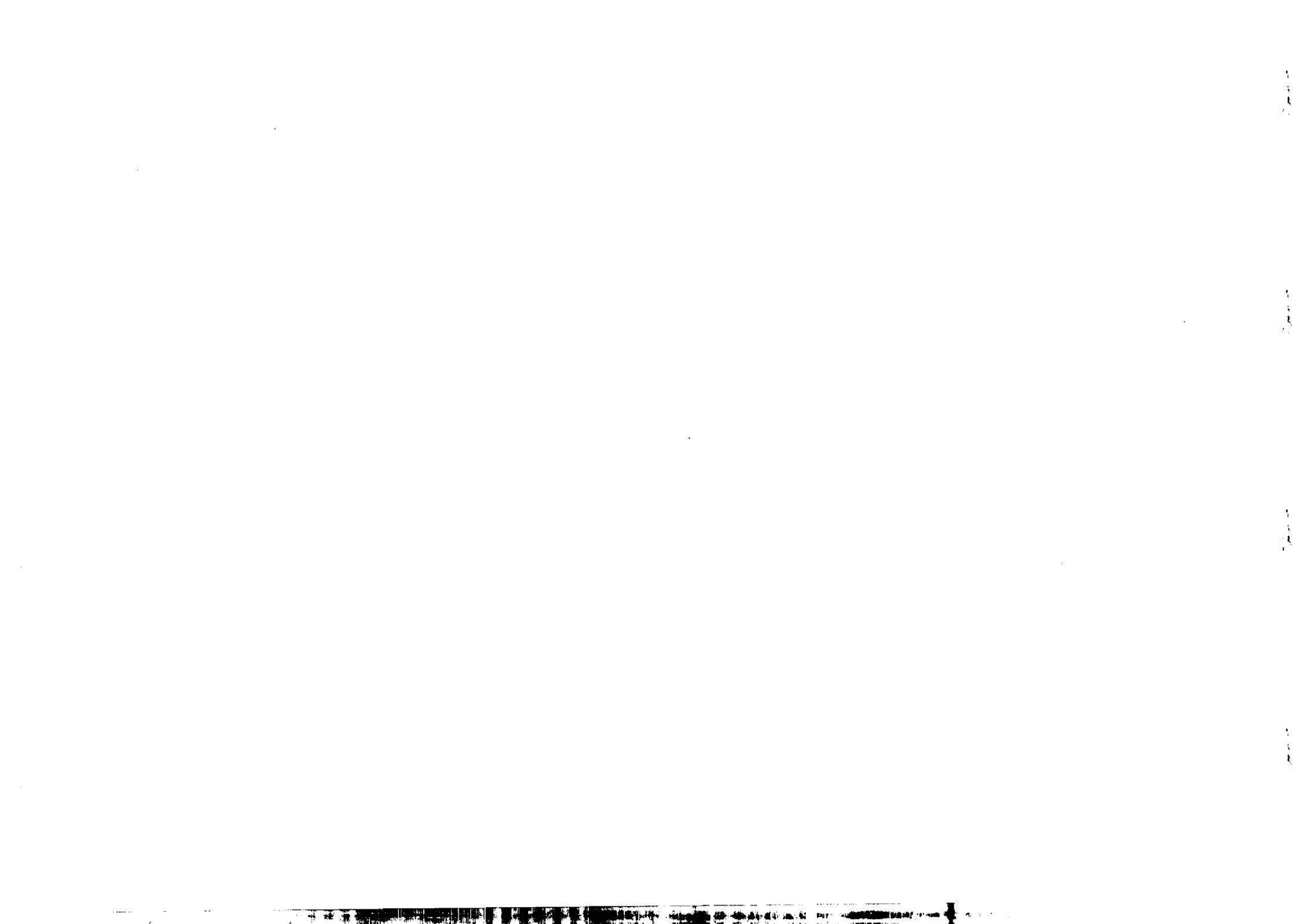


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STRUCTURAL ENERGETICS OF NOBLE METALS \*

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ABSTRACT

Structural energetics of the noble metals, namely Cu, Ag and Au are investigated by employing a single-parameter pseudopotential. The calculations show that the lowest energy for all of these metals corresponds to FCC - their observed crystal structure. The one-electron contribution to the free energy is found to dominate the structural prediction for these metals. The present investigation strongly emphasizes that the effects due to band hybridization and core-core exchange play a significant role on the structural stability of the noble metals.

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I. INTRODUCTION

Pseudopotential theory has been a formidable tool for studying crystal structure of metals and their alloys. And, it is reiterated here that the application of the pseudopotential theory is limited to simple metals and their alloys. This is because the interaction between a conduction electron and an ion in such a system can be described in terms of a weak pseudopotential. In particular, the systems in which none of the Brillouin zone planes of the non-zero structure factors for the relevant structures cut the Fermi sphere, are easily amenable to a perturbative treatment (Heine and Weaire 1970). But for systems like the noble metals the Fermi surfaces are already cut by the zone faces and additional complications appear due to the presence of the filled d bands just below the Fermi level. Incidentally, there is no major difficulty about using pseudopotentials for these metals as long as one confines oneself to states around the Fermi level and does not expect it to describe the whole band structure including d bands. Considering these simplified assumptions there are some efforts to determine the crystal structure of the noble metals. The pioneering approach due to Blandin (1966) and Blandin *et al.* (1966), however, could predict an HCP structure instead of the observed FCC structure. Recently, Stroud and Ashcroft (1971) also found the HCP structure having a lower energy than the FCC for pure Cu. These attempts imply that for the systems having d electrons in the close vicinity of the Fermi levels the application of the pseudopotential needs more careful assessment. It is important to note that although the d bands are filled and should not be of direct importance in determining the crystal structure, the s-d band hybridization effects may well be relevant. The derivation of a positive stacking fault energy for FCC Cu by Jacobs (1969) essentially emphasises that hybridization effects should be included in calculating energetics of the noble metals. Recently, using a resonant model potential theory that includes the repulsive potential due to the overlapping d states in the theory, Dagens (1977) could predict the correct crystal structure for all the three noble metals. These calculations in fact reconfirm the importance of the hybridization effects in modelling pseudopotentials for these metals. But the problem with the resonant model potentials or the hitherto known transition metal pseudopotentials (Animalu 1973) is that they contain two or more unknown parameters. Now since there do exist uncertainties in determining 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 single parameter model potential applicable to

the case of noble metals. Recently, Idrees *et al.* (1982) proposed a single-parameter noble metal pseudopotential that includes the s-d hybridization and core-core exchange contributions; this potential could reproduce some of the transport properties which are in better agreement with experiments. Consequently, it is tempting to employ this pseudopotential to calculate the structural energies of the noble metals.

The present paper is arranged as follows: in Sec.II the pseudopotential formalism appropriate for a static metal is briefly presented. In Sec.III the calculated results on the three noble metals are presented and discussed in detail. Finally, some concluding remarks are made in Sec.IV.

## II. BASIC FORMULATION

Consider a metal consisting of  $N$  ions of valency  $Z$  contained in a volume  $\Omega$ . The interaction between a conduction electron and a single ion is modelled by a bare pseudopotential  $v(r)$ ; for simplicity  $v$  is assumed to be a local function of  $r$ . The pseudopotential for an arbitrary static arrangement of ions is

$$V(\underline{r}) = \sum_i v(|\underline{r}-\underline{R}_i|) \quad (1)$$

where  $\underline{R}_i$  refers to the positions of the  $i^{\text{th}}$  ion in the lattice. To second order in the perturbing potential and considering only the configurational disorder the total structural energy is given by

$$\langle U_{\text{tot}} \rangle_c = \langle U_2 \rangle_c + \langle U_M \rangle_c \quad (2)$$

Here  $\langle U_2 \rangle_c$  is the effective band structure contribution associated with the redistribution of electrons caused by replacing the positive charge background by the ions and is given by

$$\langle U_2 \rangle_c = \frac{1}{\Omega} \sum_{\mathbf{q} \neq 0} \chi(\mathbf{q}) [v(\mathbf{q})]^2 |S(\mathbf{q})|^2 \delta_{\mathbf{q},\mathbf{q}'} \quad (3)$$

where  $\chi(\mathbf{q})$  is an interacting response function of the electron gas,  $\mathbf{g}$  is a reciprocal lattice vector of the underlying lattice and  $S(\mathbf{q})$  is the relevant structure factor. Similarly, the Madelung contribution is <sup>\*</sup>)

$$\langle U_M \rangle_c = \frac{1}{2\Omega} \sum_{\mathbf{q} \neq 0} \frac{8\pi Z}{q^2} [ |S(\mathbf{q})|^2 \delta_{\mathbf{q},\mathbf{q}'} - N ] \quad (4)$$

which arises from the direct ion-ion interaction; the latter is assumed to be purely Coulombic.

Now the effective band structure contribution given by Eq.(2) includes the effects of electron-electron interactions, double-counting, etc. and consequently following Evans *et al.* (1979) we write

$$\begin{aligned} \langle U_2 \rangle_c &= \frac{1}{2\Omega} \sum_{\mathbf{q} \neq 0} \chi_0(\mathbf{q}) [v_{sc}(\mathbf{q})]^2 |S(\mathbf{q})|^2 \delta_{\mathbf{q},\mathbf{q}'} \\ &\quad - \frac{1}{2\Omega} \sum_{\mathbf{q} \neq 0} \chi_0^2(\mathbf{q}) [v_{sc}(\mathbf{q})]^2 U_{ee}(\mathbf{q}) |S(\mathbf{q})|^2 \delta_{\mathbf{q},\mathbf{q}'} \end{aligned} \quad (5)$$

where  $\chi_0(\mathbf{q})$  is essentially the Lindhart function and  $v_{sc}(\mathbf{q})$  is the screened pseudopotential. In Eq.(5) the first term is the one-electron contribution arising from the band structure of screened (neutral) pseudo-atoms. The second term in (5) corrects for double counting of the electron-electron interaction which occurs in the first term.  $U_{ee}$  appearing in this term is simply given by

$$U_{ee}(\mathbf{q}) = \frac{8\pi}{q^2} [1 - f_{xc}(\mathbf{q})] \quad (6)$$

where  $f_{xc}(\mathbf{q})$  accounts for the exchange and correlation of the interacting electron gas (e.g. see Heine and Weaire 1970).

<sup>\*</sup>) Atomic units are used throughout taking  $\hbar = m = 1$  and  $e^2 = 2$  so that energies are measured in Rydbergs.

### III. RESULTS AND DISCUSSION

The present calculations use the single-parameter noble metal pseudopotential proposed by Idrees et al. (1982)

$$U(q) = \frac{8\pi Z}{q^3} \left[ (\alpha R_m + \beta - \alpha R_s R_m) (\sin q R_m - q R_m \cos q R_m) - \beta (\sin q R_s - q R_s \cos q R_s) - \frac{\alpha R_s}{q} \left\{ q R_m \sin q R_m + 2 (\cos q R_m - 1) \right\} - q R_s \cos q R_s \right]$$

$$\left[ \alpha = R_s^{-2} (R_s - R_m)^{-1}, \beta = 2 R_s^{-1} \right], \quad (7)$$

where  $R_m$  is the said parameter and  $R_s$  is the Wigner-Seitz radius given by  $R_s = (3\Omega_a/4\pi)^{1/3}$ ,  $\Omega_a$  being the atomic volume. The Sham-Hubbard form of exchange and correlation is also used in the calculations. The input parameters are obtained from Table I. The calculated results displayed in Table II show that the lowest energy for each metal corresponds to FCC structure - the observed structure for these metals. It is noted that the typical energy difference between crystal structures is of the order of  $10^{-3}$  Rydbergs per atom. For the HCP structure we use the ideal c/a ratio because it is inferred that the minimum of the total energy for this structure lies at or in the close vicinity of the ideal ratio (e.g. see Heine and Weaire 1970, p.280). Here it is relevant to note that the dominant Madelung term  $\langle U_m \rangle_c$  follows the sequence BCC-FCC-HCP in predicting crystal structure for these metals and this is consistent with the earlier calculations (e.g. Sholl 1967). It is the one-electron term  $\langle U_{1e} \rangle_c$  that favours the observed FCC structure for these metals and the structural sequence for Cu and Ag is FCC-HCP-BCC; for Au this is FCC-BCC-HCP. On the other hand, even though the double-counting correction term is the smallest in the total structural energy for each of these metals, structurally it is more sensitive than the largest Madelung contribution. This contribution follows the sequence HCP-FCC-BCC for Cu and Ag and the sequence FCC-HCP-BCC for Au.

From Table II it is noted that for Ag and Au the energy differences between crystal structures are quantitatively distinct; but for Cu there is a strong competition between the FCC and HCP structure and the FCC structure is only narrowly stabilized. Now looking at the electronic structure

for Cu (Heine and Weaire 1970) it is noted that hybridization does not affect very much the upper d bands, but states in the lowest band all round the Brillouin zone faces have their energies lowered. These points are to some extent specific to the FCC structure. For example, in the HCP structure all d bands hybridize about equally. This might be a presumable situation which brings the HCP energy closer to the FCC energy in Cu.

### IV. CONCLUSIONS

The present calculations predict the observed FCC structure for all the three noble metals. The effects due to band hybridization and core-core exchange are noted to play a dominant role on the structural stability of these alloys. Here we consider some critical remarks relevant to the present calculations:

1) It is noted that the d bands in Cu (Heine and Weaire 1970) lie in the middle of a broad free-electron-like band composed of states of predominantly s-p symmetry, so there is a hybridization of these bands, resulting in a rearrangement of the band structure. In accordance with the scattering theory the relevant potential is said to exhibit a narrow resonance (Heine 1967) at the energy of the d bands. This mixed situation necessitates a mixed theory that will include both resonance and hybridization. In the present calculations the potential considers hybridization alone; so it is also essential to consider resonant effects in the theory. This conclusion may, however, improve the structural prediction, but again it will introduce additional unknown parameters in the potential and this is not the aim of the present paper.

2) The atomic structures of the noble metals clearly indicate that, in accordance with the so-called cancellation theorem (e.g. see Cohen and Heine 1970, p.54) the relevant core states for these metals are fairly cancelled out; but the third states are totally uncanceled giving rise to strong non-local effects in the potential. Thus it is essential to include these effects in the theory for the noble metals.

3) For practical purposes one should consider lattice vibrations in the theory. Recently (Rahman and Rahman 1981) it has been noted that the energy differences between crystal structures for various structural contributions decrease as the lattice vibrations are included. This implies that the overall prediction will not change by including lattice vibrations.

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Table I

Input data used in the calculations. Here  $\Omega_a$  denotes the atomic volume,  $R_m$  the parameter with the potential and  $k_F$  the radius of the free electron Fermi sphere

Metal	$\Omega_a^\dagger$ (au)	$R_m^*$ (au)	$k_F^\dagger$ (au)
Cu	78.90	1.84	0.7163
Ag	113.30	1.90	0.6366
Au	113.20	2.14	0.6368

† Obtained from Cohen and Heine (1970), p.196.

\* Obtained from Idrees et al. (1982).

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Table II

The various structural terms per atom for Cu, Ag and Au calculated in the static lattice approximation. The calculations use a single-parameter noble metal pseudopotential due to Idrees *et al.* (1982) and the Sham-Hubbard exchange function. Here  $\langle U_{le} \rangle_c$  denotes the one electron contribution,  $\langle U_{x-bs} \rangle_c$  the double-counting correction term<sup>†</sup>,  $\langle U_m \rangle_c$  the Madelung contribution and  $\langle U_{st} \rangle_c$  the total structural energy. Units are Rydbergs.

Metal	$\langle U_{le} \rangle_c (\times 10^{-1})$	$\langle U_{x-bs} \rangle_c (\times 10^{-2})$	$\langle U_m \rangle_c$	$\langle U_{st} \rangle_c$	Prediction
Cu FCC	-0.396601	-0.298805	-0.673334	-0.715982	FCC
BCC	-0.380626	-0.262362	-0.673376	-0.714062	
HCP	-0.395027	-0.313666	-0.673289	-0.715929	
Ag FCC	-0.581476	-0.506557	-0.596850	-0.660063	FCC
BCC	-0.556739	-0.437102	-0.596887	-0.656932	
HCP	-0.565753	-0.517727	-0.596815	-0.658568	
Au FCC	-0.757974	-0.660620	-0.597049	-0.679452	FCC
BCC	-0.724416	-0.567849	-0.597086	-0.675206	
HCP	-0.697577	-0.634470	-0.597014	-0.673117	

† The effective band structure contribution is  $\langle U_2 \rangle_c = \langle U_{le} \rangle_c + \langle U_{x-bs} \rangle_c$ .

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