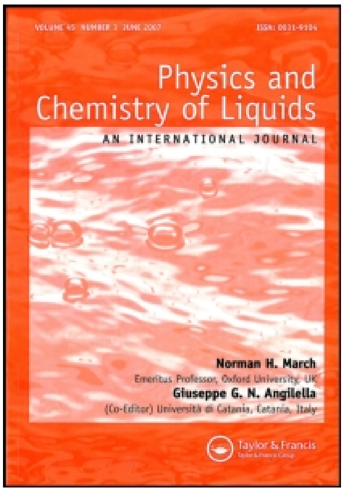

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Force Fields in Liquid and Solid Cu Metal: Relation Between Quantum Chemical and Density Functional Treatments

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FORCE FIELDS IN LIQUID AND SOLID Cu METAL: RELATION BETWEEN QUANTUM CHEMICAL AND DENSITY FUNCTIONAL TREATMENTS

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Two types of force field are compared and contrasted for condensed Cu in metallic phases. The first is a conventional liquid metal pair potential, accessible through inversion of the measured liquid structure factor $S(q)$. The form of this, for $T = 1423$ K, and number density $\rho = 0.075\ 54\ \text{Å}^{-3}$ is known from the very recent work of Rajagopalan and Srinivasa Rao and from the earlier study of Arai and Yokoyama. This potential is suitable to discuss structural rearrangements only at the specific atom volume $\Omega = \rho^{-1}$ referred to above.

The second type of force field is appropriate for crystalline Cu lattices with different local coordination numbers. As a concrete example, the work of Carlsson *et al.* on face-centered-cubic Cu metal is analyzed in terms of the ${}^1\Sigma_g$ and ${}^3\Sigma_u$ potential energy curves of the free-space Cu dimer. The relation to Cu clusters is briefly referred to.

Keywords: Local coordination numbers; structure factor inversion; copper dimer

1. INTRODUCTION

The purpose of the work is to compare and contrast what are basically two very different types of force field as applied specifically to describe condensed phases of metallic Cu. We shall start with liquid metal Cu.

Following the proposal of Johnson and March [1] to invert the liquid structure factor $S(q)$ to extract a pair potential $\Phi(r)$ for a given liquid metal, the work of Reatto *et al.* [2] has brought the proposal to full fruition for liquid Na near its freezing point. Perrot and March [3]

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have subsequently given a density functional theory of the pair potential $\Phi(r)$ for liquid Na for the same thermodynamic state, which exhibits all the major characteristics of the 'diffraction' potential of Reatto *et al.* [2].

Very recently, work of Rajagopalan and Srinivasa Rao [4] has appeared, in which the diffraction data on $S(q)$ reported by Waseda and Ueno [5] has been inverted to determine a pair potential $\Phi(r)$ for liquid Cu at 1423 K. The comparison of their inversion $\Phi(r)$ with the earlier pair potential by Arai and Yokoyama [6] is shown in Figure 6 of ref. [4]. The agreement is excellent. However, we must stress here that this pair potential only applies at the atomic volume Ω corresponding to the thermodynamic state of the liquid metal Cu at which the structure factor $S(q)$ was measured. We shall return to this point briefly, after turning to discuss the crystalline face-centred-cubic phase of metallic Cu.

2. PAIR POTENTIALS FOR FACE-CENTRED CUBIC Cu LATTICE

Carlsson *et al.* [7] have reported an *ab initio* pair potential for face-centred cubic Cu. Their method consisted in calculating the cohesive energy $E_c(r_1)$ as a function of the nearest neighbor distance r_1 at some 15 atomic volumes, out to a volume at which E_c had decreased to less than 0.015 *eV*. The form $E_c(r_1)=a\exp(-br_1-cr_1^2)$ was adopted for r_1 greater than those explicitly used. They then give a procedure by which $E_c(r_1)$, for a given lattice (in the present case fcc) could be inverted to yield a pair potential $\Phi(r)$. Their potential is redrawn in Figure 1, where it is compared with the liquid potential [4] discussed above. The other pair potentials in Figure 1 are the potential of Englert, Tompa and Bullough [8] (ETB) and that of Johnson and Wilson [9] (labelled Φ_J) and the potential of ref. [4] (shown by dots). As Carlsson *et al.* [7] emphasize their potential has significantly greater depth than the other potentials primarily because of definition. Specifically, for the potential of ref. [4], the cohesive energy is a sum of a volume-dependent-term, denoted by E_Ω below and a pair potential sum:

$$E_c = E_\Omega + \sum_{i<j} \Phi(r_{ij}, \Omega). \tag{1}$$

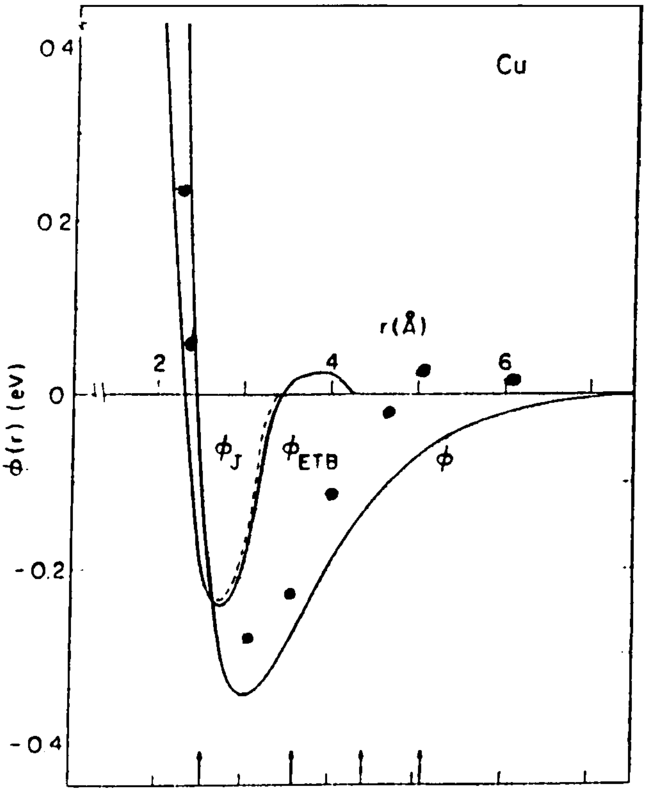

FIGURE 1 Shows four different pair potentials $\varphi(r)$ for condensed phases of metallic Cu. Lowest curve at large r is potential of Carlsson *et al.* [7]. Black dots refer to potential obtained from inversion of liquid structure factor $S(q)$ in ref. [4]. φ_{ETB} denotes potential of ref. [8], while φ_J is pair potential recorded in ref. [9]. (see also Fig. 2 below over reduced range of r).

Nevertheless, the liquid metal potential (dots) in Figure 1 (corresponding to $\Omega^{-1} = 0.07554$ Å^{-3}) has some similarity to the potential given by Carlsson *et al.* [7] for fcc Cu. (see also Figure 2 over smaller range of r).

Our purpose below is to examine whether the cohesive energy $E_c(r_1)$ for fcc Cu can be useful analyzed in a very different, quantum-chemical, fashion.

We note first that for K (also considered in bcc lattice by Carlsson *et al.*) Rubio and March [10] have shown that their density functional curves for various lattices with different coordination numbers z can

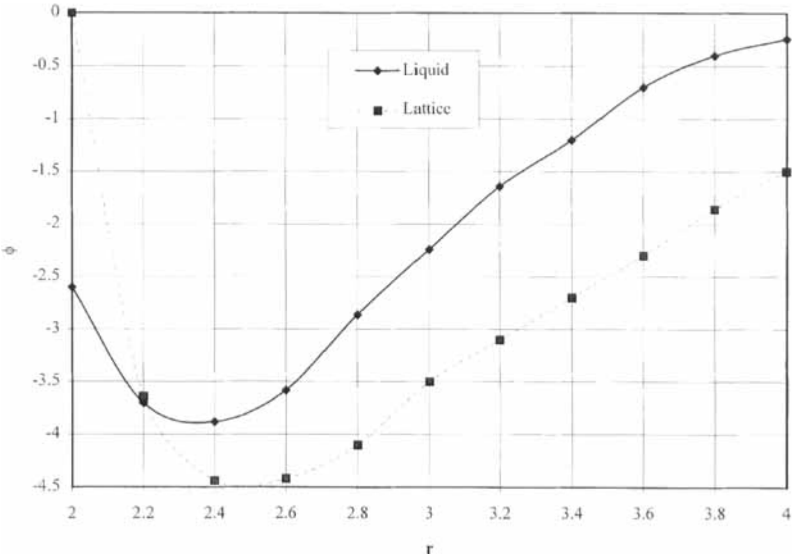

FIGURE 2 Liquid pair potential for Cu at 1423 K and number density $\rho = 0.075\ 54$ Å^{-3}. (Upper curve at large r: redrawn from Rajagopalan and Srinivasa Rao [4]). Lower curve shows, for comparison pair potential extracted from theoretical calculations of cohesive energy of face-centred cubic Cu over a wide range of near-neighbour distance r_1. (Modified from Carlsson *et al.* [7].) See also Figure 1, over wider range of r ref. [7].

indeed be represented to useful accuracy in terms of free-space dimer potential energy curves. More specifically, using dimer $^1\Sigma_g$ and $^3\Sigma_u$ potential energy curves for K_2 in free space, Rubio and March [10] show that the cohesive energy $E_c(r_1)$ of the s-p metal K is well described as a function of coordination number z by the form [11]

$$E_c(r_1) = (1/2)zR(r_1) - f(z)g(r_1), \tag{2}$$

which emerges from the use of the Heisenberg Hamiltonian with near-neighbor interactions. The function $f(z)$ is slowly varying with z, being 4 for fcc ($z = 12$) and bcc ($z = 8$) and 3 for simple cubic (sc: $z = 6$). Rubio and March have proposed the approximation $f(z) \sim 2.9$ for the diamond lattice (see also below) with $z = 4$. Here, $R(r_1)$ is the triplet $^3\Sigma_u$ potential energy curve of the free-space dimer, while $g(r_1)$ is the 'exchange' contribution which is half of the difference between the triplet $^3\Sigma u$ and the singlet $^1\Sigma g$ potential energy curves.

2.1. Quantum-Chemical Form (2) Applied to Cu Metal

We return at this point to the *d*-electron metal Cu. It is relevant to note that Cha *et al.* [12] have performed photoelectron spectroscopy of Cu_n-clusters, with n from 1 to 18 atoms. They compare their data on Cu_n^- clusters with the calculated level structure of Na_n clusters [13]. The role of interaction of s and p electrons with the $3d$ electrons in Cu has to be considered, to account for the quite different behavior of the two types of clusters. The Cu clusters with up to 18 atoms exhibit gaps of 0.2 – 1.5 eV between the individual atomic shells and as Cha *et al.* [12] stress they should therefore behave as semiconductors. Nevertheless, these workers conclude that the electrons in the outermost orbital corresponding to the 4S atomic states are truly delocalized in the Cu_n^- clusters.

With this as background, we return to the cohesive energy curve $E_c(r_1)$ obtained by Carlsson *et al.* [7] for fcc Cu. We have used in eqn. (2) the Cu_2 potential energy curves $^1\Sigma_g$ and $^3\Sigma_u$ plotted by Morse [14]. It then rapidly becomes apparent that the second term on the right-hand side of eqn. (2) is larger than the first. This immediately tells us that the energy differences between fcc and body-centered cubic structures will be very small for Cu metal, while lower coordination structures are unlikely to be favored over a range of near-neighbor distance which one might hope to explore experimentally.

$Ec(r_1)$ constructed from the quantum-chemical approximation, based on the Heisenberg Hamiltonian [11] is plotted in Figure 3. The quantum-chemical approach is not fully quantitative in its prediction of the equilibrium lattice constant see ref. [7] for density functional curve as it is largely dominated by the minimum in the ground-state $^1\Sigma_g$ potential energy curve of the dimer. However, we can construct using eqn. (2) the $E_c(r_1)$ for a lower coordination lattice, and therefore, for comparison we have added in Figure 3 the results for bcc ($z = 8$), simple cubic ($z = 6$), for which the quantity $f(z)$ in eqn. (2) is equal to 3 and for the diamond ($f(z) = 2.9$) lattices.

Finally, we return to the connection between the curves of Figure 3 and the liquid pair potential shown in Figure 1. This latter pair potential must only be used to compare points of the same atomic volume Ω on $E_c(r)$ plots for different lattice coordination numbers-not for equal r.

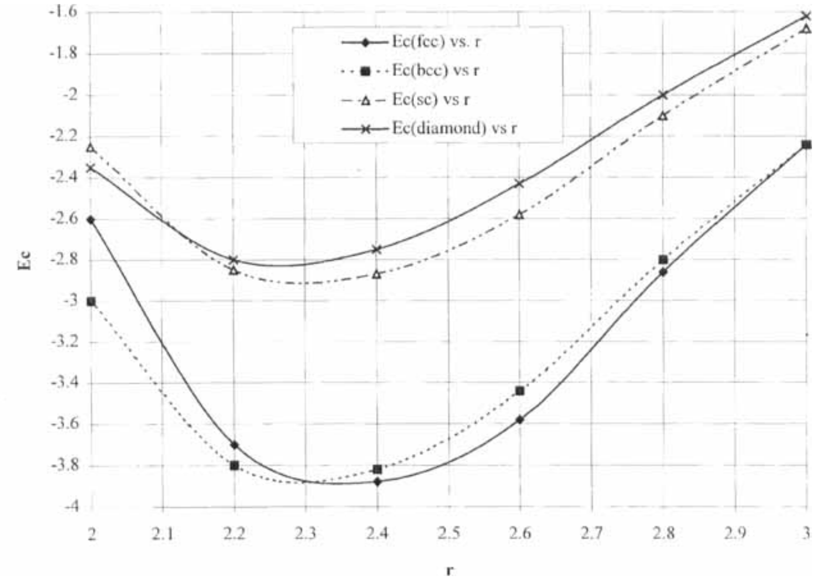

FIGURE 3 Use of quantum-chemical model as a function of coordination number z to compare cohesive energies E_c of fcc ($z = 12$), bcc ($z = 8$), simple cubic ($z = 6$) and diamond ($z = 4$) lattices for Cu. Note that the correct equilibrium near-neighbour distance r for fcc Cu is somewhat greater than that predicted by the quantum-chemical model. Energies of fcc and bcc lattices are close together because $f(z) = 4$ for both $z = 12$ and 8, and term involving $f(z)$ in eqn. (2) dominates E_c over a substantial range of r.

3. SUMMARY AND FUTURE DIRECTIONS

Motivated by the recent work on the inversion of the structure factor $S(q)$ of liquid Cu, at 1423 K and atomic volume $\Omega = 132.4\,\text{Å}^3$, to obtain a pair potential $\phi(r, \Omega)$ to use in eqn. (1), we have first brought this potential into contact with that obtained by Carlsson *et al.* [7], Figures 1 and 2 show the two potentials, compared also with earlier work on solid Cu. As discussed by Carlsson *et al.* [7], there are no oscillations in their $\phi(r)$ derived from the cohesive energy $E_c(r)$ of fcc Cu as a function of near-neighbor distance r. As anticipated, this is to be contrasted with the (relatively mild) oscillatory behavior [4, 5] of the 'diffraction' potential $\phi(r, \Omega)$ of eqn. (1).

Secondly, we have explored further the utility of the quantum-chemical model represented by eqn. (2) for solid Cu phases. Figure 3 the quantum-chemical result for fcc ($z = 12$), Cu, obtained from the

Cu dimer potential energy curves given by Morse [14]. There is fair agreement with the density functional curve of ref. [7], though the equilibrium lattice constant is a little too short from the chemical approach. This agreement has prompted us to predict cohesive energy curves $E_c(r_1)$ for other structures and the results are also recorded in Figure 3. Over a substantial range of r, the term $f(z)g(r)$ in eqn. (2) dominates $E_c(r)$ and high coordination structures are therefore favoured by the chemical model.

Returning to potentials of the 'diffraction' form as in eqn. (1), one can only predict energy differences between different lattice structures at constant atomic volume Ω in the absence of accurate knowledge of E_Ω. Thus, the liquid metal potential shown in Figure 1 can give only the locus of constant volume curves as one moves between the different (now lattice) structures in Figure 3. Clearly, when good structural data becomes available for states of liquid Cu, say along the liquid-vapour coexistence curves towards the critical point, it will be of considerable interest to construct the loci referred to above, thereby connecting the cohesive energy curves for different lattices as depicted in Figure 3. Finally, the chemical model of eqn. (2) seems worthy of much wider study, in view of encouraging results for heavier alkalis for K, Rb and Cs [10], and now for a variety of phases of Cu.

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