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ABSTRACT

An expression for the total metallic energy is constructed as the sum of an average s-electron energy and of a d-energy term that has a minimum near the equilibrium lattice spacing. The model predicts reasonable cohesive energies for copper and silver. The calculation of the elastic constants reveals that, in the case of gold, the contribution from d-electrons to the total energy can not be represented by a sum of pairwise forces between the ions. The sensitivity of the results to the choice of the prefixed atomic d-orbitals is tested.

АННОТАЦИЯ

Полная энергия для благородного металла пишется как сумма двух член: средняя энергия s-электронов и d-энергия, имеющая минимум близко к равновесному кристаллическому объему. Энергии связи получаются разумно для Cu и Ag. Вычисление упругих постоянных указывает, что в случае Au вклад из d-электронов в полную энергию не может быть преставлен как сумма паровых сил между ионами. Чувствительность результатов на изменение использованных атомных d-функций исследуется.

KIVONAT

A nemesfémek teljes energiáját az átlagos s-elektron-energia és egy d-energia összegeként értelmezzük; ez utóbbi minimummal rendelkezik az észlelt rácsállandó közelében. A modell elfogadható kötési energiát szolgáltat réz és ezüst esetén. A rugalmas állandók számitásából kitünik, hogy arany esetében a d-energia nem értelmezhető az ionok közötti párjellegü erők öszszegeként. Megvizsgáljuk az eredmények érzékenységét különböző rögzitett atomi pályák felhasználása esetén.

The total metallic energy of noble metals have frequently been described by parametric expressions consisting of two terms: a nearly free s-electron energy and a repulsive pairwise interaction from the d-electrons[1]. Though the cohesive energy and the elastic constants could more or less be reproduced in this way, nonphysical values of the model parameters /like imaginary core radius/ show that the part played by the d-electrons in the binding is more complex than mere repulsion. In fact, the result of a detailed calculation[2] of the volume dependent total energy of copper has shown that the nature of the d-type energy contribution basically differs from a simple monotonic repulsion, since both the value of, and the pressure contribution from, the d term proved to be slightly negative at the equilibrium atomic radius, becoming repulsive only for smaller lattice spacings.

In this paper a new analytical expression is proposed to describe the d-electron contribution to the <u>volume dependent</u> energy of noble metals that reproduces this complex behaviour. Besides, a theoretical estimate of the band structure energy of the s-electrons is given, in order to check its effect on both the elastic and the volume dependent properties.

The total metallic energy is written[2] as

$$E = E_s + E_d \qquad\qquad /1/$$

where E_s is the average s-electron energy and E_d is a

d-type contribution. An expression with the required properties[2,3] for the d-energy can be constructed using the overlap integral S

$$E_d = -aw + bw^2 ; \qquad w = \frac{S(R_{nn})}{R_{nn}} \qquad /2/$$

where R_{nn} is the nearest neighbour distance in the lattice and the "effective" overlap integral is defined through the radial d-function R_d by

$$S(R_{nn}) = \int_0^\infty R_d(r) R_d(|\underline{r} - \underline{R}_{nn}|) r^2 dr$$

Since the overlap energy integral in a tight binding scheme is essentially proportional to S/R_{nn}, w varies with the lattice spacing roughly like the width of the d band. The energy of an s-electron as the function of the atomic radius R_a can be written as

$$E_S = E_0(R_a) + E_1(R_a) + E_M(R_a) + E_{BS}(R_a; r_c) \qquad /3/$$

where the first term contains the kinetic, exchange and correlation energy of the homogeneous electron liquid,

$$E_0 = \frac{2.21}{R_a^2} \lambda_0 - \frac{0.916}{R_a} + E_{cor}(R_a) \qquad /4/$$

E_M is the Madelung energy $-\frac{1.8}{R_a}$ /in rydbergs/ and E_{BS} is the "band structure" energy arising from the scattering of the s-electrons in the periodic lattice. The factor λ_0 accounts[2] for the stretching of the

free s-band; it is the common "orthogonalization hole"
factor

$$\lambda_c = \left(1 - (r_c/R_a)^3\right)^{-1} \qquad /5/$$

with the ionic radius r_c determined[2] from the inner atomic
s-functions.

The term E_1 accounts for the fact that the average
potential energy $(s|V|s)$ of the s-electrons differs from
that of a homogeneous charge density in the pure Coulomb
field of a unit charge. For simple metals, where the ion-
electron potential becomes coulombic outside a certain core
radius $r_i < R_a$ one has $E_1 \sim 1/R_a^3$. In the case of
noble metals, however, due to the incomplete screening by
d-electrons, the potential differs from $-e^2/r$ even in the
outer regions of the atomic sphere, thus

$$E_1 = (s|V|s) + \frac{3}{2}\frac{e^2}{R_a} = \left(s\left|-\frac{11e^2}{r}\right|s\right) + E_{sd} + \frac{3}{2}\frac{e^2}{R_a} \qquad /6/$$

where $|s)$ is the actual s-electron state /e.g. an OPW state/,
E_{sd} is the sum of the Coulomb and exchange interactions
of the s-electron with the 10 d-electrons. If one neglects
E_{BS} and calculates the Madelung energy in the spherical
approximation, the formulae /3/ - /6/ become equivalent to
the expression for the s-energy used in Ref. 2.

The first two terms on the right-hand side of /6/ can be
brought to a form that can be compared to $(s|V|s)$ for a
simple metal, by introducing the effective charge Z_{eff}
felt, on the average, by the s-electron inside the atomic
sphere,

$$(s|V|s) \equiv \left(s\left|-\frac{11e^2}{r}\right|s\right) + E_{sd} = \left(s\left|-\frac{Z_{eff}e^2}{r}\right|s\right) \qquad /7/$$

Further, assuming the s-density constant outside r_c , and zero inside, one gets /in ry units/

$$(s|V|s) = Z_{eff} \lambda_0 \left(-\frac{3}{R_a} + \frac{3r_c^2}{R_a^3}\right) \qquad /8/$$

which is the well known expression for the bottom of the s-band for an s-p metal. The presence of d-electrons makes Z_{eff} depend on R_a , which has physical consequences even though Z_{eff} is nearly stationary at the observed atomic volumes. /The form /8/ with a nearly stationary Z_{eff} was also found[2] by using actual OPW s-functions ./ That Z_{eff} must have a maximum where the d orbitals begin to overlap appreciably is easily understood. For large R_a, Z_{eff} tends to unity, while for smaller lattice spacings the screening by d-electrons becomes more complete due to the OPW-shaped s-functions and the readjustment of the d-density on compression.

In calculating Z_{eff} renormalized atomic d-functions were used[4]. One notices that the model has only two adjustable parameters a and b, and all the other parameters $\left(r_c, R_d(r)\right)$ needed in the calculation are independently determined atomic data.

The atomic and metallic input data and the derived Z_{eff} are shown in table 1. The parameters a and b were determined by fitting to the observed values of the atomic radius and bulk modulus. The resulting d-energies for Cu and Ag displaying the characteristic minimum near the equilibrium volume are seen in fig. 1. From the results for

the cohesive energy and the pressure derivative of the
bulk modulus, shown in table 1., one finds acceptable
agreement with experiment for copper and silver. As
for gold, the much larger disagreement for the energy indi-
cates the breakdown of the assumption of weakly overlapping
atomic-like d-functions. /Gold has, in fact, a much broader
d-band than copper and silver./

To illustrate the sensitivity of the results to varying
the input atomic parameters /d-functions, r_c / table 1.
shows two sets of numbers obtained by using different
analytical atomic d-functions. We notice that the largest
change occurs, through the variation of Z_{eff}, in the value
of E_s, while E_d, P_d and B_d proved to be rather insensitive.
The difference in the E_c values belonging to different
sets of HF orbitals shows the absolute limit of accuracy
by using prefixed atomic orbitals.

The role of the different contributions to the total energy
from s- and d-electron interactions is analysed in table 2.
in the case of Cu. One sees, first, that the most important
contribution to the <u>energy</u> comes from $E_c + E_1 + E_M$.
Second, both the s and d energy constituents are close
to a stationary value at $R_c = 2.66$ that is shown by the
small pressure values /in units of the equilibrium bulk
modulus/. Hence one realizes again[5, 2] that accounting only
for the s-energy would already lead to quite a good estimate
for the equilibrium volume and cohesive energy, while E_d
becomes essential in determining B. The term E_{Bs} was

estimated by using an empty core potential[6] with the charge Z_{eff}. To calculate the elastic constants C, C' the variations of $\dot{E}_s$ and E_d with shear deformations are needed. As to E_s , the contributions to the shear moduli from the electrostatic and structural terms are calculated as for an alkali metal. Although the usual assumption concerning the transformation properties of E_d is that it can be written as a sum of pairwise central interactions between the ions, its substantial role in determining C_{ik} /table 3./ suggests that any deviation from this behaviour affects the final result considerably. With this in mind should one look at table 3. which shows the results with the assumption that E_d is the sum of pair potentials. We notice first, that the contributions from E_{BS} are rather small. Further, one sees that the results generally improve with taking into account the R_α dependence of Z_{eff} /the agreement for Cu is the best when we use the d-energy found in ref. 2./ The disagreement is striking in the case of gold, both for C and C' . That this discrepancy is probably not caused by the particular choice of the d-energy is shown by the last row in table 3. In fact, by assuming besides the volume dependent energy terms only pairwise interactions, $c_{12} - c_{44}$ should be equal[7] to $B_V - 2P_V$, where the index V refers to the purely volume dependent terms in the energy; this holds independently of the form of the pair forces. Comparing the calculated values of $C_{12} - C_{44}$ with the observed deviation from the Cauchy relation for Cu, Ag, Au one can say, first, that the theoretical values are close to each other in all three cases. Second, the observed $c_{12} - c_{44}$ for gold is

much too large compared to the calculated value, showing
that here the actual d-electron energy contributes signi-
ficantly to the deviation from the Cauchy relation. The
results for Ag and Cu are less conclusive in this respect.
One can see, incidentally, that the rearrangement of the
d-charge on compression affects the calculated values of
$c_{12}-c_{44}$ rather seriously, because of the variation of Z_{eff}.
Non-zero values in column E_{BS} appear since this term
contains other than pairwise interactions[7] as well.

In conclusion, the energy expressions /1/, /2/, /3/ involving
a d-energy that is near to a minimum in equilibrium, seem
to be appropriate to describe the volume dependence of
the total energy for Cu and Ag. In calculating the second
derivatives of the energy, the readjustment of d-electrons
leading to the variation of the effective charge Z_{eff} is
essential. Describing the role of the d-electrons in the
binding by means of pair forces is certainly wrong for gold,
while it can not be ruled out for Ag and particularly for
Cu.

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Figure Caption

fig. 1.   The variation of the d-energy E_d with the atomic
radius, as given by equ. 2.

Table Captions

Table 1. Metallic and atomic input data for the noble metals
and the calculated cohesive energies E_c and pressure
derivatives of the bulk modulus $\frac{dB}{dP}$. For Ag cal-
culations were performed with two different sets of
atomic d-functions. The experimental values are in
brackets.

Table 2. Different energy contributions to the total energy
E , pressure P and bulk modulus B for copper. The
numbers in brackets are the results of Ref. 2.

Table 3. Different energy contributions to the elastic
moduli C, C' and $c_{12}-c_{44}$ for copper and final
results for Ag and Au. The numbers in brackets
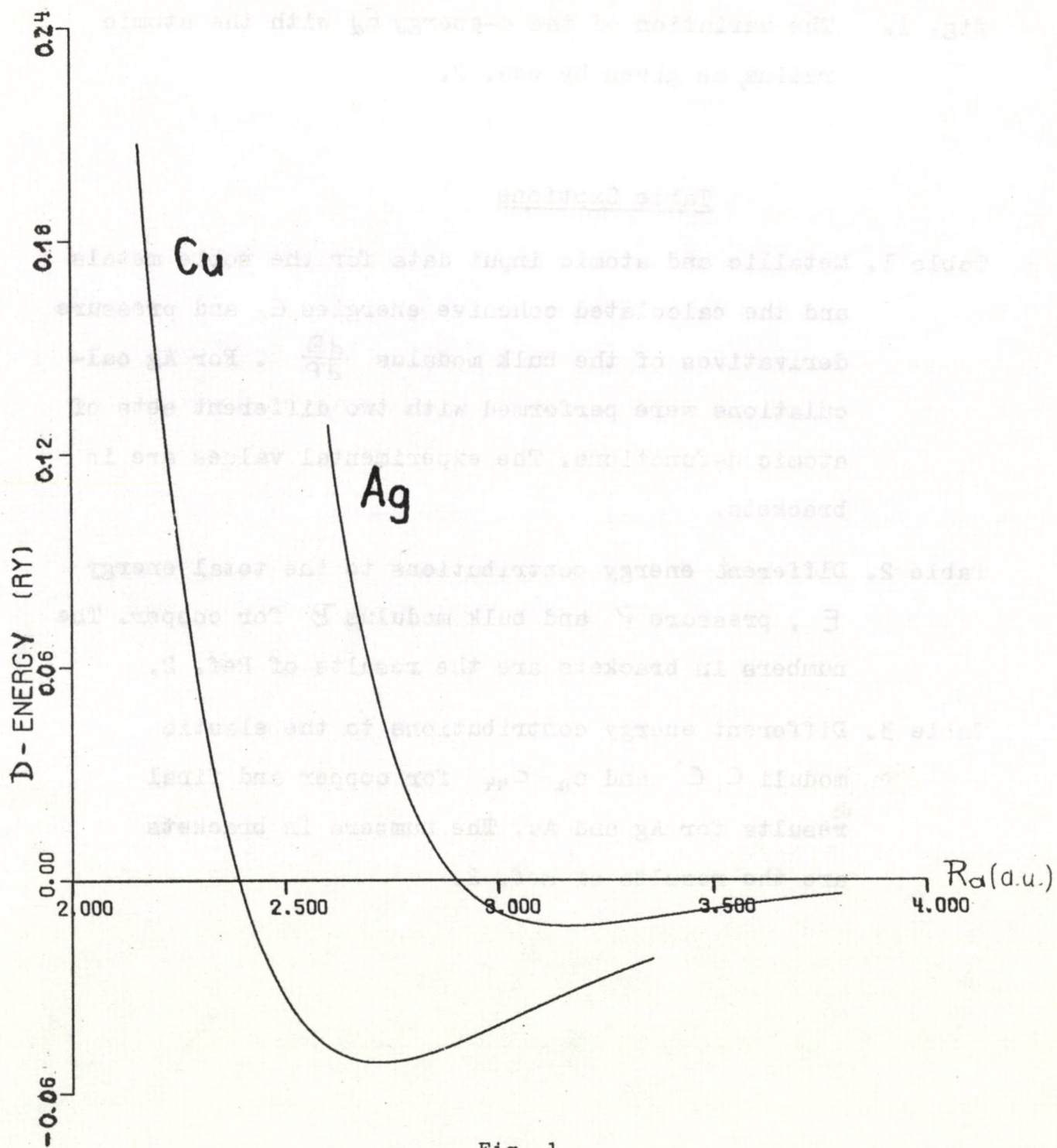are the results of Ref. 2.

Cu

Ag

D - ENERGY (RY)

0.24 0.18 0.12 0.06 0.00 -0.06

2.000   2.500   3.000   3.500   4.000

R_a (a.u.)

Fig. 1

table 1.

	Metallic input data	Atomic input data r_c/a.u./	R_d	$Z_{eff}(R_a^{ar})$	E_c/ry/	$\frac{dB}{dP}$
Cu	R_a=2.66 a.u. B =1420 kbar	1.27^a	Ref.^{a}	1.178	0.279 /0.257/	5.48 /5.59^e/ /7.7^f/
Ag	R_a=3.00 a.u. B =1065 kbar	1.60^b	Ref.^{b}	1.250	0.238 /0.218/	7.03 /6.18^e/
			Ref.^{d}	1.201	0.187 /0.218/	8.12 /6.18^e/
Au	R_a=3.00 a.u. B =1727 kbar	1.70^c	Pef.^{d}	1.231	0.108 /0.278/	7.13 /6.43^e/

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table 2.

	$E_0 + E_1 + E_M$	E_{BS}	E_d
E /ry/	a/ -0.778 b/ -0.778 $/-0.728/$	-0.017 -0.017	-0.065 -0.051 $/-0.035/$
P/B	a/ 0.005 b/ -0.003 $/0.035/$	-0.036 -0.037	0.031 0.040 $/-0.035/$
B /kbar/	a/ 453 b/ 566 $/790/$	-168 -166	1135 1020 $/630/$

a/ $Z_{eff} = Z_{eff}(R_a^{equ}) = 1.178$

b/ $Z_{eff} = Z_{eff}(R_a)$

table 3.

		E_0+E_1	E_M	E_{BS}	E_d	total/exp/	Ag total/exp/	Au total/exp/
				Cu				
C/kbar/	a/	0	260	−26	796	1030	780	1250
	b/	0	260	−26	695 /535/	929 /818/ /795/	692 /453/	1097 /423/
C'/kbar/	a/	0	29	8	376	413	288	531
	b/	0	29	8	319 /293/	356 /256/ /322/	238 /155/	429 /145/
$c_{12}-c_{44}-2P$ /kbar/	a/	159	0	−44	0	115	93	123
	b/	295 /411/	0	−41	0	254 /431/ /411/	214 /509/	343 /1207/

a/ $z_{eff} = z_{eff}(R_a^{equ})$ =const.
b/ $z_{eff} = z_{eff}(R_a)$

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