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#### DISCUSSION

Morimoto, T.: I would like to ask you about the problem concerning the stability of divacancy. I remember that you mentioned in the paper given by Corless and March that the calculation made by Seeger and Bross made mistake and you found the interaction probability, contrary to their calculation, could be repulsive. However, I suppose that the exchange interaction among the localized electrons in the vicinity of point defects is important. How is this interaction treated in the present paper?

March, N. H.: Our treatment differed from Seeger and Bross in that we gave a full Hartree treatment of the binding energy  $\Delta E$ , whereas they used the change in the eigenvalue sum as a measure of  $\Delta E$ . Using our eigenvalue for a divacancy in Cu, we also found attraction, but when this was corrected in the usual Hartree manner we obtained repulsion.

You are quite right in supposing that the results are altered by including exchange. In fact, unreasonable predictions are found, and while the final answer must await a correct many-body treatment in the density range appropriate to real metals, it seems clear that because of screening a Hartree-Fock method is bad physically, as correlation effects are largely compensating exchange.

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# On the Electronic Structure of Metallic Alloys with Application to Size Effects, Chemical Interactions and Compressibility

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The study of the electronic structure of impurities in metals shows the existence of oscillations in the electronic density and electric potential around each impurity. This model is applied to some properties of alloys: chemical energies of interactions, size effects and compressibilities. It is predicted that these properties depend mainly on the valency of the pure matrix. Experimental results are discussed, for monovalent metals (noble and alkali metals), divalent metals (Mg, Zn, Cd) and trivalent aluminium. They are in agreement with the theory.

transitional metals begins to be well under- paper, this model is applied to some properties stood: it has been shown particularly that of dilute alloys v.i.z. chemical energy of there exists long range oscillations of electronic interaction between impurities, size effects and

The electronic structure of impurities in non density around each impurity site.<sup>1),2)</sup> In this

compressibilities. Alloys of different valency and period are studied and a short discussion of vacancy is given.

## 1. Electronic Structure of Impurities

The first description of an impurity was given by the Thomas-Fermi method: the screening potential is then  $ze^{-\lambda r}/r$  in which z is the difference in valency. A more detailed study of the screening has been made<sup>1</sup>: it gives in addition to the Thomas-Fermi screening, oscillations in the electronic density and electric potential behaving at large distances as  $\alpha \cos(2k_F r + \varphi)/r^3$ , being roughly proportional to  $z (k_F$  is the Fermi wave vector).

Fig. 1 shows the changes in electronic density  $\Delta \rho(r)$  as a function of r, calculated

from the model of a selfconsistent Hartree screening potential and for small  $z^{s_0}$ .

Fig. 2 gives the electronic potential V(r). The asymptotic value at large distances is plotted as deduced from:

$$\Delta \rho(r) \simeq -z \frac{k_F}{(2\pi k_F + 1)^2} \frac{\cos 2k_F r}{r^3}.$$

The positions of first neighbour atoms are indicated for monovalent (Ag) divalent (Mg) and trivalent (Al) matrices. One concludes that the sign of  $\Delta\rho(r)$  and V(r) at the next neighbouring sites depends uniquely on the valence of the matrix. Particularly, there is a change in sign in V(r) between monovalent, divalent and trivalent matrices. Similar conclusions are valid for electric fields and field



gradients. For monovalent metals, the value of V(r) is not very different from the Thomas-Fermi value: this explains some success in using this method (but it may be noticed that the sign of the curvature is wrong). The results can be extended to Bloch electrons and to any type of defect without drastic changes. In this paper the asymptotic formula will be used (it can be seen on Fig. 2 that it is a good approximation even on first neighbour sites):

$$V(r) \simeq \alpha \frac{\pi}{k_F (2\pi k_F + 1)^2} \frac{\cos 2k_F r}{r^3}$$

and the phase  $\varphi$  is assumed to be zero (this is valid for not too large perturbations). This potential is applied in two cases:

a) valence effect:  $\alpha = z$ 

b) period effect (*e.g.* K in Rb):  $\alpha$  is calculated with orthogonalized plane waves for Bloch waves and pseudopotentials<sup>4)</sup>.



- - - Thomas-Fermi.

#### 2. Some Physical Properties of Alloys

The *chemical energy* of interaction between two impurities of small charge  $z_1$  and  $z_2$  is:  $W(r) = z_1 z_2/(2\pi)^3 \int e^{i\mathbf{K} \cdot \mathbf{r}} d^3 \mathbf{K} / K^2 \varepsilon(\mathbf{K})$ , where  $\varepsilon(\mathbf{K})$  is the static dielectric constant for wave number  $\mathbf{K}$ . Using the simplified potential function above, the energy for any type of defect is  $W(r) \simeq [\alpha_1 \alpha_2 \pi / k_F (2\pi k_F + 1)^2] \cos 2k_F r / r^3$ .

The size effects and the change in compressibility due to impurities are calculated in the following model: if  $z_0$  is the valency of the matrix, the force exerted on an ion at distance r from the impurity is  $F(r) = -z_0 \partial V / \partial r$ . The calculation is done as for a uniform isotropic medium with the compressibility of the pure metal. Considering only the next neighbours at distance  $r_0$  from the impurity, the forces  $F(r_0)$  are replaced by a uniform pressure p exerted on the sphere of radius  $r_0$ : p = $nF(r_0)/4\pi r_0^2$  (*n* being the number of next neighbours). Then the relative change of the crystalline parameter a per unit concentration x is:  $\delta a/ax = \gamma nr_0 F(r_0)/9\Omega$ ,  $\Omega$  being the atomic volume. One deduces also the relative change in compressibility per unit concentration:

$$\frac{\delta \chi}{\chi x} = \frac{\chi n r_0^2}{9\Omega} \cdot \frac{dF(r_0)}{dr_0}$$

This model overestimates slightly the elastic energy and underestimates  $\delta a$  and  $\delta \chi$  by a factor of the order of unity.

#### 3. Numerical Comparison with Experiment

As it has been said above, the effects depend mainly on the *valency* of the matrix. The comparison for different case follows:

### a) Monovalent Metals

For noble metals the interaction W must be repulsive and have the value  $z^2 \ 0.03 \text{ eV}$ .

Experiments give<sup>5)</sup>:

*Cu* Zn 0.048 eV *Ag* Cd 0.065 eV *Cu* Ga 0.103 eV *Ag* In 0.125 eV

The relative size effects divided by the difference in valency z of the impurities are, for isoelectronic sequency

	Exp. <sup>6)</sup>	Th.
ба	in Cu $\sim 0.04$	0.02
azx	in Ag $\sim 0.04$	0.02

The compressibility changes are:

	Exp.	Th.
δχ	in Cu $\sim 0.6$	0.2
$\chi z x$	in Ag $\sim 0.45$	0.2

The experimental data are somewhat scattered for size effects and widely scattered for compressibilities.

Size effects in alloys of noble metals with other noble metals may be explained in the same way, if one assumes a change in sign in the pseudopotentials of Cu and Ag Au.

Size effects in alloys of alkali metals are given below:

	$Cs \mathrm{K}$	KCs	<i>Rb</i> Cs	Cs Rb
Exp.	-0.14	0.13	0.07	-0.075
Th.	-0.06	0.075	0.04	-0.04

b) Divalent Metals

Divalent metals are hexagonal: Mg has a nearly close packed hexagonal structure, Zn and Cd deviate appreciably from close packing. These metals must then show appreciable anisotropy.

The interaction may be attractive as shown in Fig. 2 and have the value  $\sim -z^2$  0.015 eV: measurements<sup>5)</sup> give the right sign for Cd and Zn alloys. Numerical comparison is satisfactory (Zn Ga -0.025 eV, Cd In -0.02 eV). Deviation from close packed structure may possibly give formation of linear zones. Experimentally, the size effects have the same sign for a and c parameters in Mg, opposite signs in Zn; this is understandable as Mg is close packed hexagonal. In the case of Zn alloys the relative change in volume  $\delta v/v =$  $2\delta a/a + \delta c/c$  has the good order of magnitude, but in such an anisotropic material, it is easier to compress along the c axis than perpendicular to it; this might explain the opposite changes in c and a.

#### c) Trivalent Metals

In this case, as shown on Fig. 2, the interaction between impurities is attractive  $W \sim$  $-z^2 0.01 \,\mathrm{eV}$ . Measurements yield roughly this value for Cu Ag and Zn in Al. The formation of Guinier Preston zones in Al Zn, Al Ag and Al Cu alloys is thus explained on the basis of chemical interactions (the case of Al Cu giving rise to plane zones is due to difference in size effects for isoelectronic alloys give:

		Exp. <sup>6)</sup>	Th.
ба	Mg	0.06	0.035
ax	Si	-0.05	-0.035

It should be noticed that the sign of the effect is opposite to the case of noble alloys. This model gives thus the right sign and a good order of magnitude. The situation is less clear for impurities which belong to different periods. In conclusion, it can be said that this model explains qualitatively and semiquantitatively, the interaction between impurities and the changes in the parameters and compressibilities in diulte alloys. Particularly, it gives the right sign, which depends only on the valency of the pure metal and changes from monovalent to multivalent metals. This sign change is due to the oscillatory part of the electronic density and electric potential around each impurity.

The same model can be used for vacancies, although interaction between vacancies is poorly described because vacancies are strong perturbations. But, interactions of vacancies with impurities in noble metals (attraction of energy -z 0.03 eV), in aluminium (attraction of energy -0.03 eV for Zn) and divalent Zn (anisotropy and change in sign from Ag to In impurities) are understood in sign and order of magnitude. The situation is similar for size effects (contraction in noble metals and alkali metals as is experimentally observed).

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#### DISCUSSION

**Thomson, R.**: Yoshida and Kino at Hiroshima have obtained evidence that in Al, magnesium impurities are attracted to vacancies, while silicon impurities are repelled, which is just as you predict.

**March, N. H.**: Your predictions on interaction energies depend on the use of a potential determined by a first-order method. The work of Murray and myself indicates that second-order corrections change the displaced charge and the potential very appreciably for an excess valence>1.

**Blandin, A.**: I agree that the calculations reported here were done only in the perturbation approach (small z). But, for strong perturbations, I do not think that a second order perturbation calculation is sufficient. In fact, if the perturbation is strong enough to give phase-shifts in the scattering of the order of or greater than  $\pi/2$ , then perturbation method is very slowly convergent and even may be divergent. In such a case, it is better to take a rough potential which obeys the Friedel rule.