

MADDELUNG SURPRISES

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INTRODUCTION

charge transfer and screening effects in alloys highly important

- isomorphous CPA
- polymorphous CPA
- calculations for large supercells
- simple model: can contribute to better understanding

ISOMORPHOUS CPA

- screened impurity model (SIM)

$$q_i = q^A \text{ or } q^B, V_i = V^A \text{ or } V^B$$

$$V_i = -\frac{e^2 q_i}{R_1}, \quad E_i^{Mad} = -\beta \frac{e^2 q_i^2}{R_1}$$

- screened CPA ($\beta = 1$)

- neutral atomic spheres

good only for small charge transfer

POLYMORPHOUS CPA

B. Ujfalussy, J.S. Faulkner, N.Y. Moghadam, G.M. Stocks, and Y. Wang: Phys. Rev. B **61** 12005 (2000)

q_i and V_i assume individual values for each atom

- charge correlated model (CC)

q_i and V_i depend on the type of neighbors

Johnson and Pinski, PRB **48** 11533 (1993)

- CPA + local field

reaction of A and B atoms on variation of external potential

Bruno, Zingales, and Milici PRB **66** 245107 (2002)

LARGE SUPERCELLS

hundreds or even thousands of atoms

- locally self-consistent multiple scattering (LSMS)
- locally self-consistent Green functions (LSGF)

qV-linear relation:

$$a_i q_i + V_i = k_i,$$

where a_i and k_i are constants that depend only on the type of atom (A or B), but not on the concentration of the alloy

qV-relation

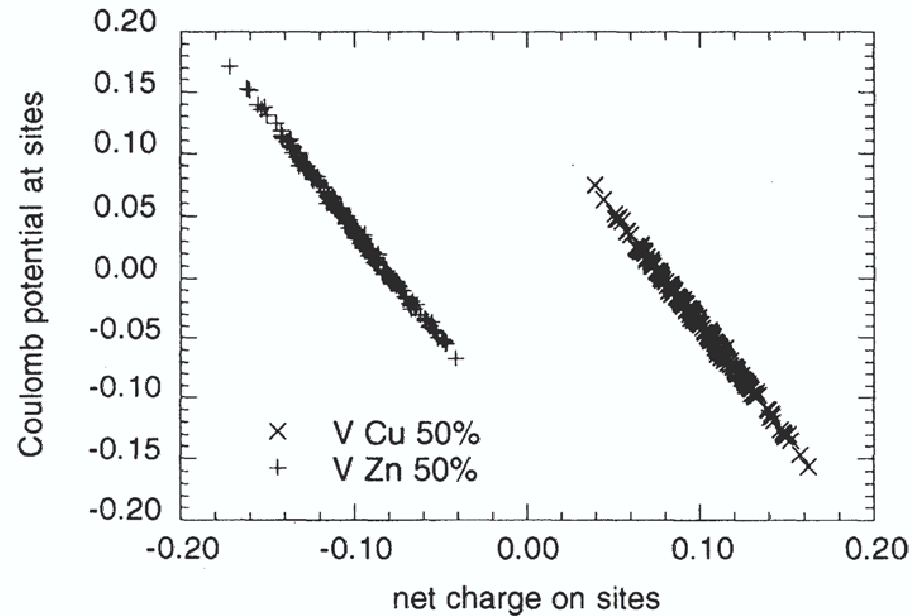


FIG. 1. The Coulomb potential V^i versus the charges q^i on the 432 sites in the cell for a 50% Cu-Zn alloy with the bcc crystal structure. The plus signs are the data points for sites that have a Zn atom on them and the crosses are for Cu. The potentials and charges are in dimensionless atomic units as described in the text.

Faulkner, Wang, and Stocks, PRB **52** (1995), 17106.

statistics of net charges

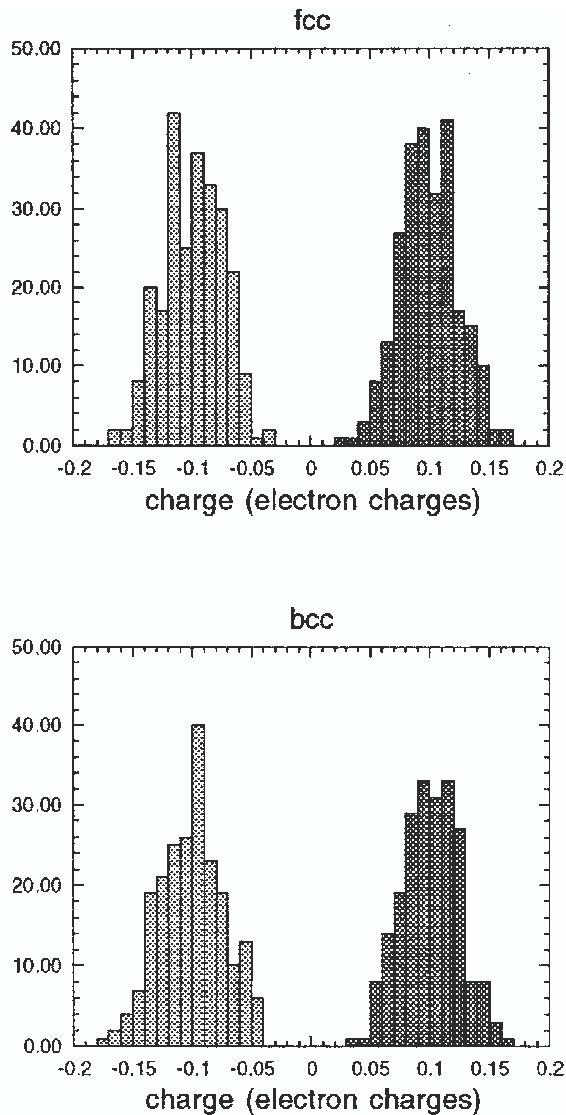


FIG. 1. A histogram distribution showing the charges on the sites of two 50% copper-zinc disordered alloys. The charges with positive sign correspond to copper atoms, which gain electronic charge in the alloy. The negative charges are associated with the zinc atoms. The upper panel is for models of fcc alloys with $a = 6.90$ a.u. calculated with supercells that contain 500 atoms, and the lower panel is for bcc alloys with $a = 5.50$ a.u. and 432 atoms.

Faulkner, Moghadadam, Wang, and Stocks, PRB **57** (1998), 7653.

MODEL

E. Bruno, L. Zingales, and Y. Wang: PRL **91** (2003), 166401.

$$E(\{q_i\}) = E^{\text{loc}}(\{q_i\}) + E^{\text{Mad}}(\{q_i\}) = \sum_i \frac{a_i}{2} (q_i - b_i)^2 + \frac{1}{2} \sum_{i,j} M_{ij} q_i q_j ,$$

b_i ... bare charge

q_i ... net charge

a_i ... strength of electron-electron interaction

M_{ij} ... Madelung matrix

$$M_{ij} = \begin{cases} e^2 / R_{ij} & \text{for } i \neq j \\ 0 & \text{for } i = j \end{cases}$$

SOLUTION

minimization of energy:

$$a_i(q_i - b_i) + \sum_j M_{ij}q_j = 0$$

$$q_i = \sum_j G_{ij}a_jb_j$$

$$G = H^{-1}, \quad H = A + M, \quad A_{ij} = a_i\delta_{i,j}, \quad H_{ij} = a_i\delta_{i,j} + M_{ij}.$$

matrix H ... Hessian of energy

matrix $G = (H - z)^{-1}$... resolvent of H at $z = 0$

similarity to a **one-particle single-band tight-binding model** of the electronic structure

Hessian H ... model Hamiltonian

Madelung matrix

real, symmetric: has real eigenvalues

depends only on R_{ij} : easy to diagonalize using lattice Fourier transform

$$M(\mathbf{k}) = \sum_i e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} M_{ij}, \quad M_{ij} = \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d^3\mathbf{k} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} M(\mathbf{k})$$

Ewald summation technique:

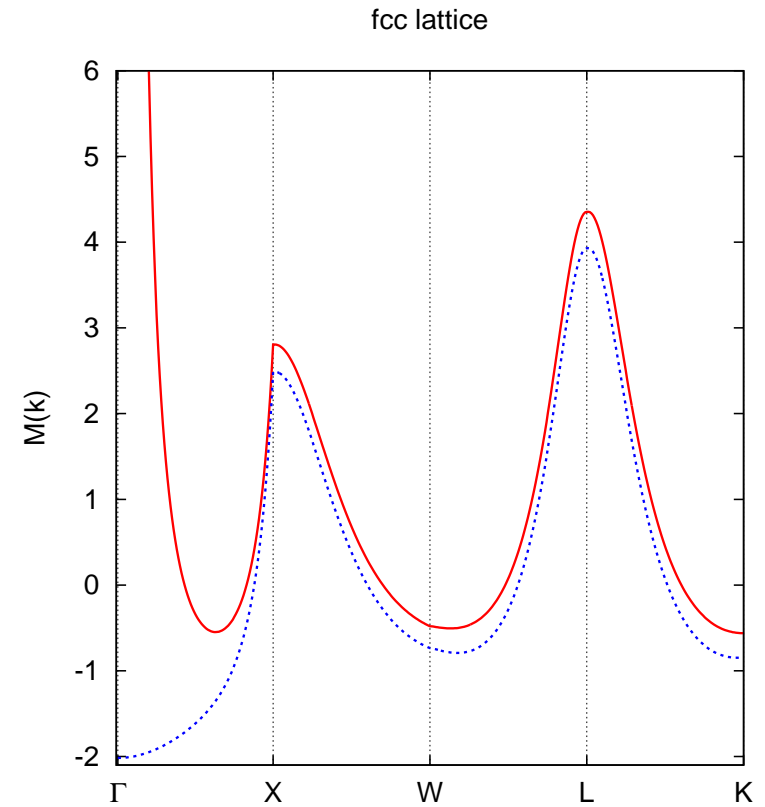
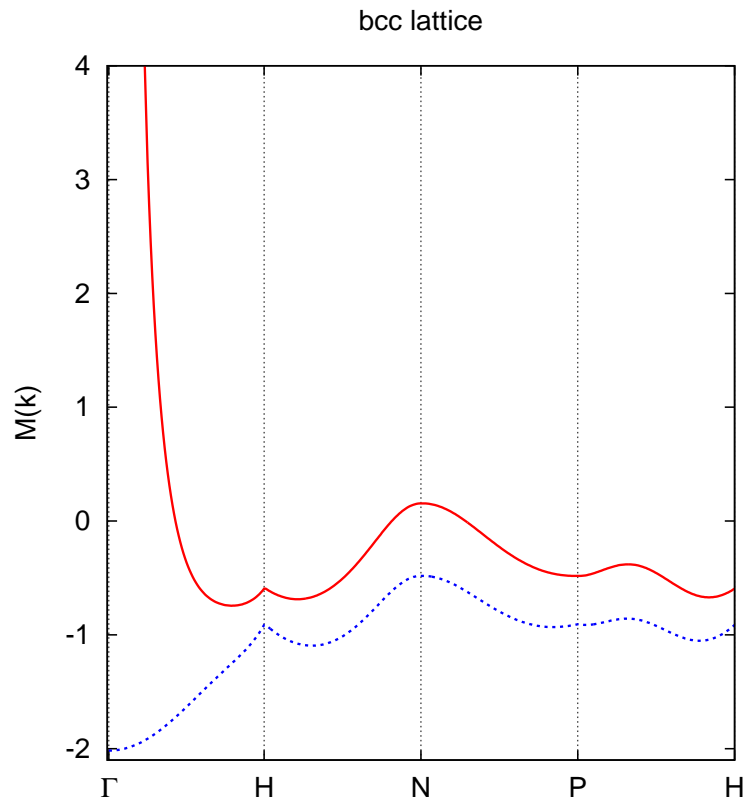
$$e^{-2} M(\mathbf{k}) = \sum_{\mathbf{R} \neq \mathbf{0}} \frac{\exp(i\mathbf{k}\mathbf{R})}{|\mathbf{R}|} = -\frac{1}{\rho\sqrt{\pi}} + \frac{4\pi}{\Omega_0} \sum_{\mathbf{K}} \frac{\exp\{-[\rho(\mathbf{k} + \mathbf{K})]^2\}}{|\mathbf{k} + \mathbf{K}|^2} + \sum_{\mathbf{R} \neq \mathbf{0}} \exp(i\mathbf{k}\mathbf{R}) \frac{\text{erfc}[|\mathbf{R}|/(2\rho)]}{|\mathbf{R}|},$$

$\rho = \Omega_0^{1/3} / (2\sqrt{\pi})$... optimal choice

comments

- asymptotics for $|\mathbf{k}| \rightarrow 0$: $M(\mathbf{k}) \approx \frac{4\pi}{\Omega_0} \frac{1}{|\mathbf{k}|^2}$, $M(\mathbf{k}) = \frac{4\pi}{\Omega_0} \frac{1}{|\mathbf{k}|^2} + m(\mathbf{k})$
- long-range electrostatic interaction $\rightarrow \sum_j G_{ij} = 0$... charge neutrality condition $\sum_i q_i = 0$ is fulfilled automatically, no Lagrange multiplier is needed
- random alloy $A_x B_y$ ($y = 1 - x$)
- in what follows **non-random case**: $a_i = a$ for all lattice sites i
- random case: $a_i = a^A$ or a^B can be solved using the CPA

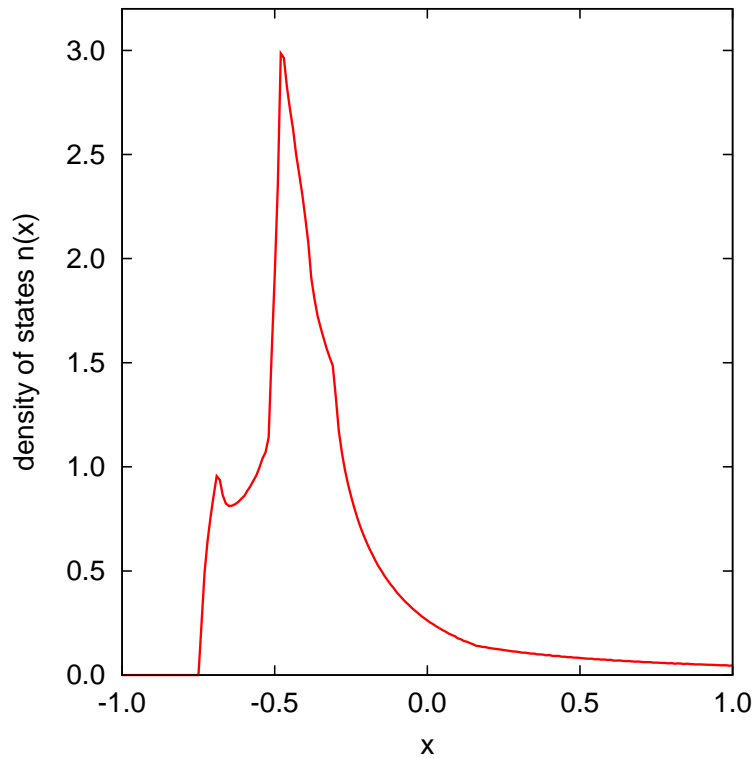
"Band structure" of the Madelung matrix



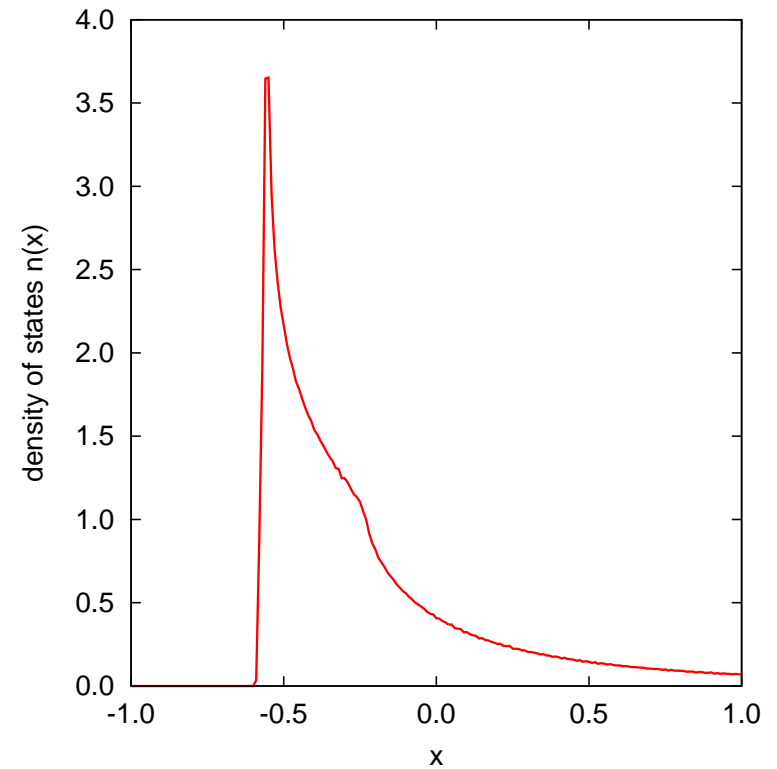
$$\Omega_0 = 1$$

"Density of states" of the Madelung matrix

bcc lattice



fcc lattice



tail for large x : $n(x) \propto x^{-5/2}$

SCREENING

change one or two charges q_i, q_j, \dots , all others let to relax so as to attain minimum of energy

$$E(q_i) = E_i + B_i q_i + \frac{1}{2} C_i q_i^2, \quad C_i = a_i^{\text{scr}} = \left[\frac{\partial^2 E(\{q_i\})}{\partial q_i^2} \right]_{\text{relaxed}} = 1/G_{ii}$$

$$M_{ij}^{\text{bare}} = e^2 / R_{ij} = \frac{\partial^2 E(\{q_i\})}{\partial q_i \partial q_j}$$

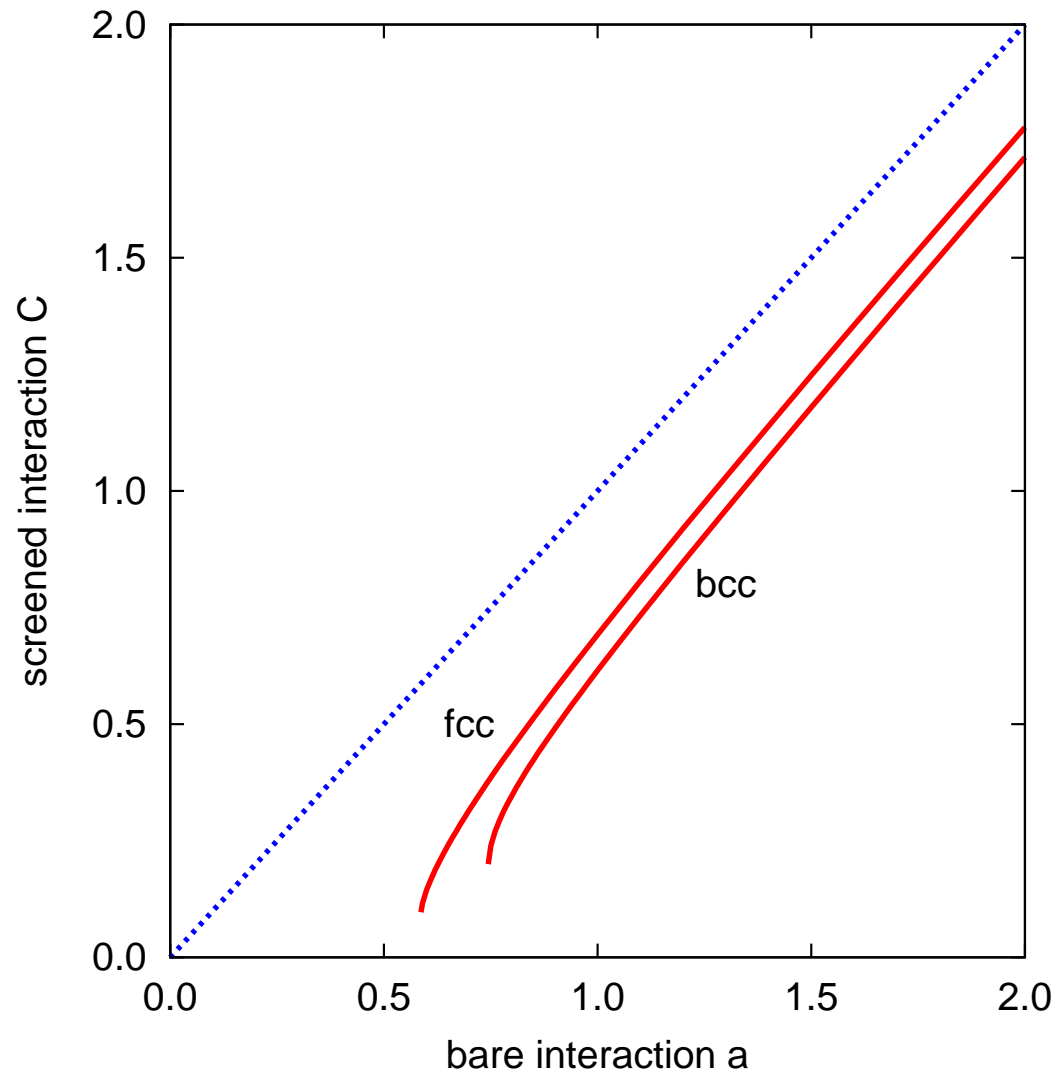
$$M_{ij}^{\text{scr}} = \left[\frac{\partial^2 E(\{q_i\})}{\partial q_i \partial q_j} \right]_{\text{relaxed}} = - \frac{G_{ij}}{G_{ii} G_{jj} - G_{ij} G_{ji}}$$

$$\delta q_i = \frac{G_{ij}}{G_{jj}} \delta q_j$$

Madelung contribution to Ising Hamiltonian parameters

$$V_{ij}^{\text{Mad}} = V_{ij}^{\text{AA}} + V_{ij}^{\text{BB}} - 2V_{ij}^{\text{AB}} = M_{ij}^{\text{scr}} (q^A - q^B)^2$$

Screened on-site interaction



PARAMETERS OF THE MODEL

can be extracted either from supercell calculations or from the local-field CPA calculations

a_i ... on-site electron-electron interactions

$$a_i = \frac{\partial^2 E(\{q_i\})}{\partial q_i^2} \quad \text{or} \quad a_i = E(n+1) + E(n-1) - 2E(n) \quad \dots \text{variable net charge}$$

compare with Hubbard U

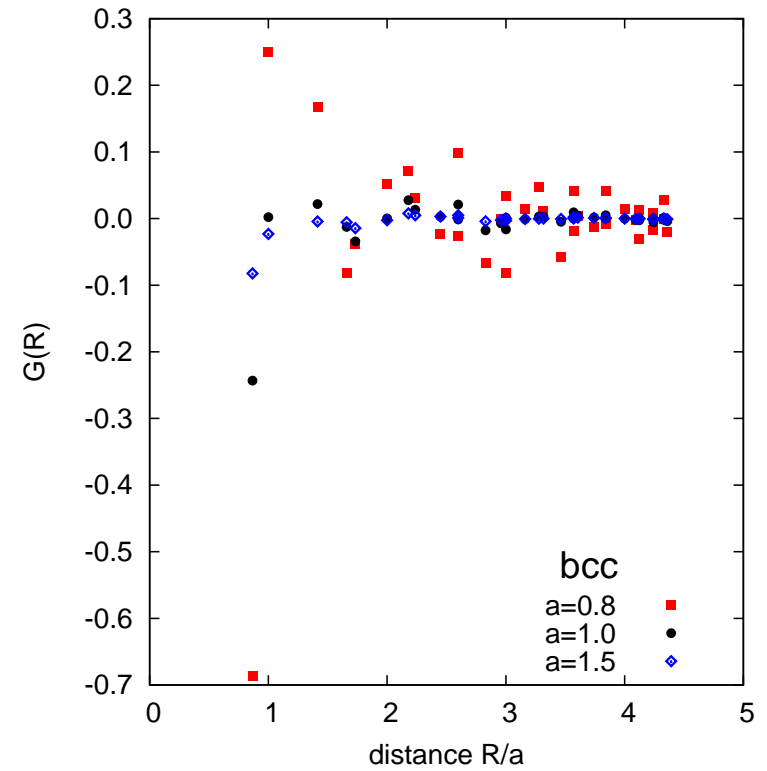
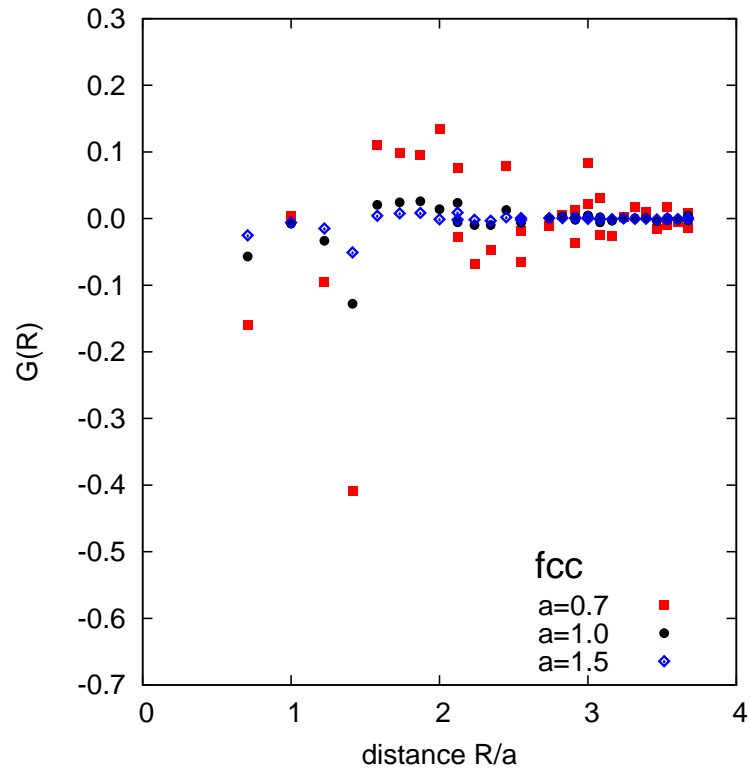
$$E_{\text{int}} = \frac{1}{2} U N_d (N_d - 1), \quad U = \frac{\partial^2 E_{\text{int}}}{\partial N_d^2}$$

$$U = E(d^{n+1} s^0) + E(d^{n-1} s^2) - 2E(d^n s^1)$$

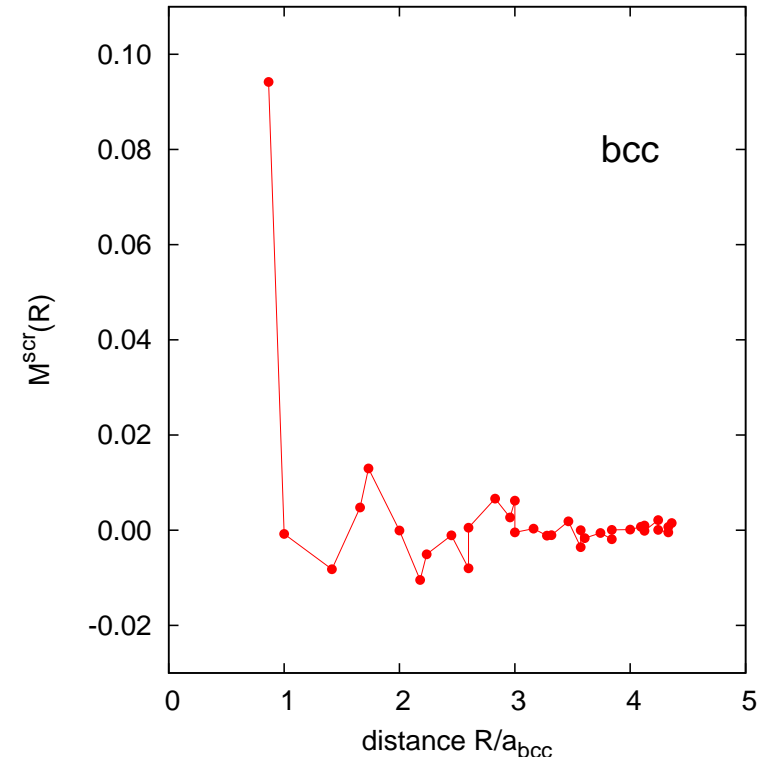
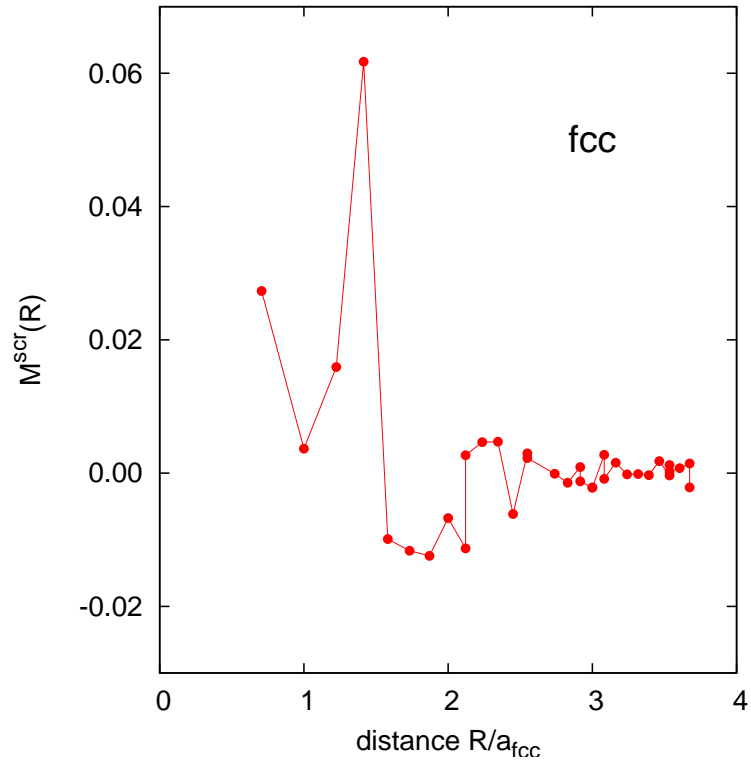
... constant net charge and thus efficient intraatomic screening

b_i ... bare net charges: $\bar{q}^Q = a G_{ii} b^Q = \frac{a}{C} b^Q, \quad (C < a)$

Off-diagonal matrix elements of the GF

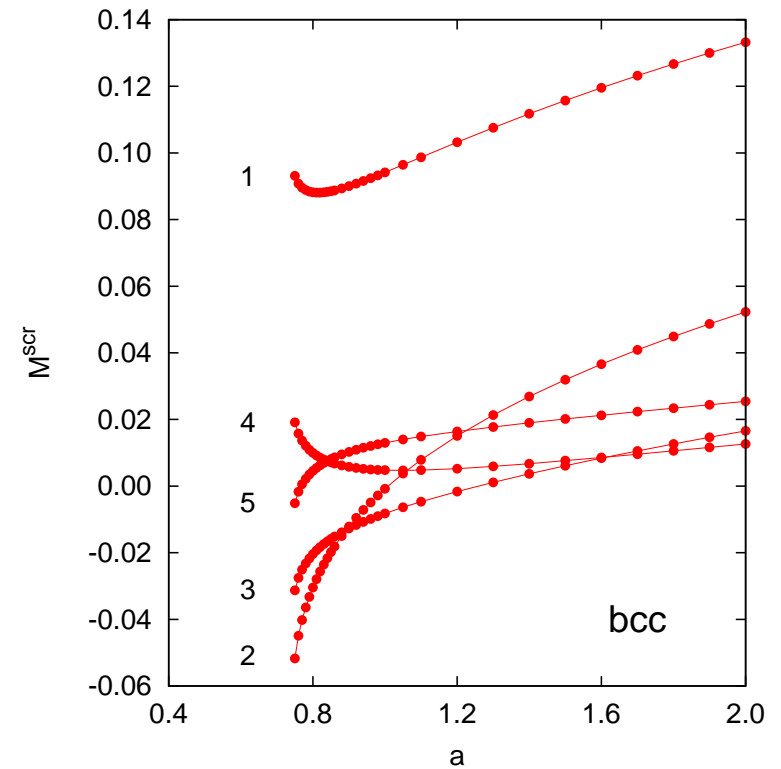
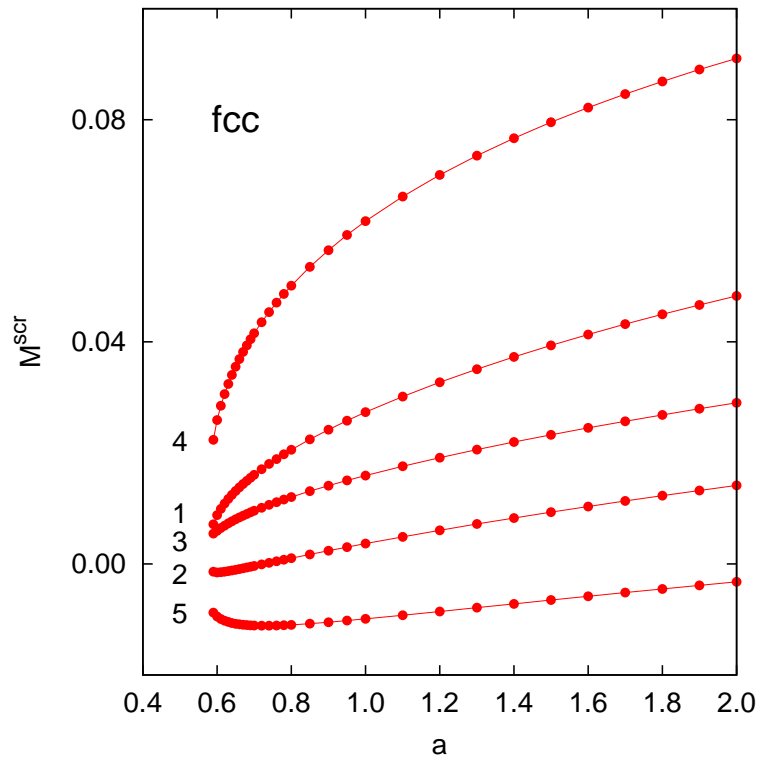


Screened electrostatic interaction



$$a = 1$$

Screened electrostatic interaction



$$\lim_{a \rightarrow \infty} M_{ij}^{\text{scr}} = M_{ij}^{\text{bare}} = \frac{e^2}{R_{ij}}$$

Probability distribution of local charges I

$$q_i^Q = \bar{q}^Q + a(b^A - b^B) \sum_j' G_{ij} \delta\eta_j$$

$\eta_i = 1$ if site i is occupied by atom Q , $\eta_i = 0$ otherwise

$$\delta\eta_i = \eta_i - \langle \eta_i \rangle$$

$S = \sum_j' G_{ij} \delta\eta_j$... random variable, **distribution function of S ?**

$\chi(t) = \int_{-\infty}^{\infty} d\xi e^{i\xi t} p(\xi)$... characteristic function

Theorem: *If X_1, X_2, \dots is a sequence of independent random variables whose characteristic functions are $\chi_1(t), \chi_2(t), \dots$, and $S = A_1 X_1 + A_2 X_2 + \dots$, where A_i are constants, the characteristic function $\chi_S(t)$ for S is given by*

$$\chi_S(t) = \chi_1(A_1 t) \chi_2(A_2 t) \dots$$

Probability distribution of local charges II

$p(\delta\eta_i = \xi) = y\delta(\xi + x) + x\delta(\xi - y) \dots$ distribution function of $\delta\eta_i$

$\chi_i(t) = \int_{-\infty}^{\infty} d\xi e^{i\xi t} p(\xi) = ye^{-it} + xe^{it} \dots$ characteristic function of $\delta\eta_i$

$\chi_S(t) = \prod_j' \chi_j(G_{ij}t) = \prod_j' (ye^{-iG_{ij}t} + xe^{iG_{ij}t}) \dots$ char. function of S

$\log \chi_S(t) = \sum_j' \log [xe^{iG_{ij}t} + ye^{-iG_{ij}t}]$

cumulants κ_k are defined by $\log \chi_S(t) = \sum_{k=0}^{+\infty} \kappa_k (it)^k$

$\kappa_0 = 0, \quad \kappa_1 = 0, \quad \kappa_2 = G^{(2)}xy, \quad \kappa_3 = G^{(3)}xy(y - x),$

$\kappa_4 = G^{(4)}xy(1 - 6xy), \quad \kappa_5 = G^{(5)}xy(y - x)(1 - 10xy - 2x^2y^2), \text{ etc.}$

$G^{(n)} = \sum_j' G_{ij}^n$

if $x = y$ then $\kappa_{2n+1} = 0 \dots$ distribution is symmetric

$\kappa_{2n} \neq 0$ for $n > 1 \dots$ distribution is not Gaussian

Probability distribution of local charges III

classical problem of moments: reconstruct distribution from its moments

Pearson system

$$\frac{p'(x)}{p(x)} = \frac{m-x}{a+bx+cx^2}$$

$b = c = 0$... Gaussian distribution

4 constants m, a, b, c and normalization constant ... first 4 central moments

12 types according to values of a, b, c

type I: $p_I(x) = C(x-p)^\alpha(q-x)^\beta$... Beta distribution

CONCLUSIONS

- Bruno, Zingales, and Wang (BZW) model of charge transfer studied in detail
- similarity to single-band tight-binding model of electronic structure
- screened on-site interactions, relation to Hubbard U
- screened Madelung interactions
- Madelung contribution to effective interatomic interactions
- statistics of net charges on A and B atoms

OPEN PROBLEMS

- extension to random on-site interactions - via CPA
- improved expression for the Madelung energy
- combination with the local-field CPA: accurate method for electronic structure calculations with moderate requirements on computer resources
- other screening mechanisms (monopole-dipole, dipole-dipole interactions)