Screening, charge distribution, and electron correlations in metallic alloys

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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

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

- screened impurity model (SIM)

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

- screened CPA ($\beta = 1$)
- neutral atomic spheres

  good only for small charge transfer

POLYMORPHOUS CPA

q_i and V_i assume individual values for each atom

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

- 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

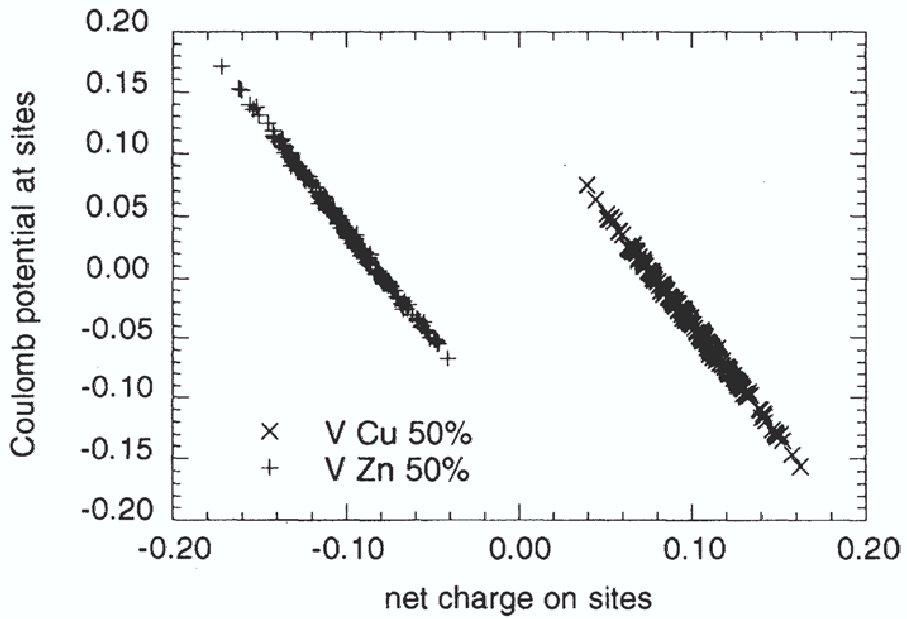


FIG. 1. The Coulomb potential V^i versus the charges q^i on the 432 sites in the cell for a 50% Cu-Zn alloy with the bcc crystal structure. The plus signs are the data points for sites that have a Zn atom on them and the crosses are for Cu. The potentials and charges are in dimensionless atomic units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

J.S. Faulkner, Y. Wang, and G.M. Stocks, Phys. Rev B **52** (1995), 17106.

statistics of net charges

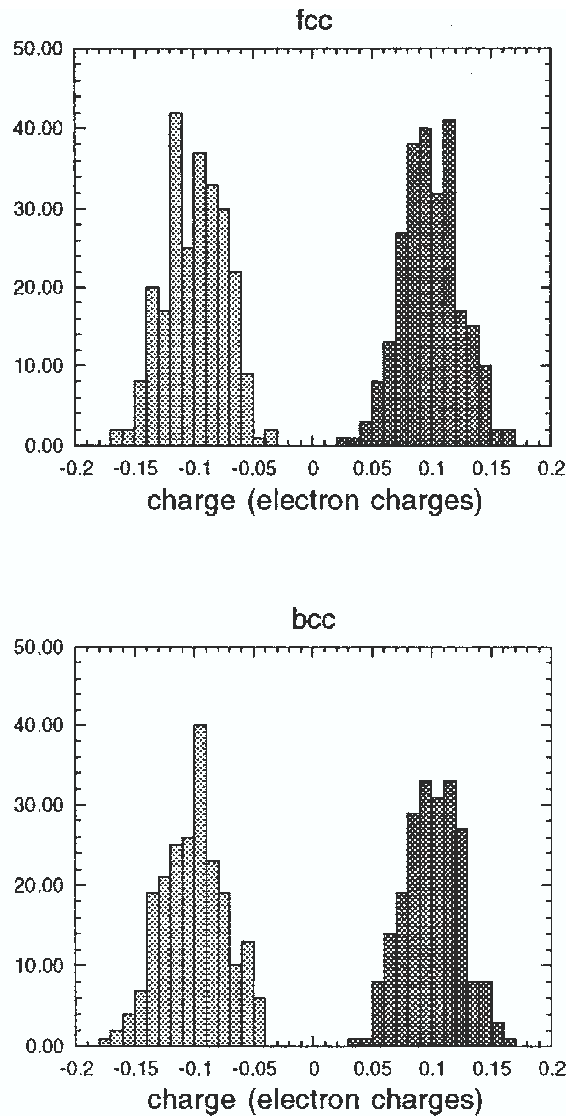


FIG. 1. A histogram distribution showing the charges on the sites of two 50% copper-zinc disordered alloys. The charges with positive sign correspond to copper atoms, which gain electronic charge in the alloy. The negative charges are associated with the zinc atoms. The upper panel is for models of fcc 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, Moghadam, Wang, and Stocks, PRB **57** (1998), 7653.

MODEL

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

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

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:

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

$$q_i = \sum_j G_{ij} a_j b_j$$

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

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

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

Ewald summation technique:

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

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

comments

- asymptotics for $|\mathbf{k}| \to 0$: $M(\mathbf{k}) \approx \frac{4\pi}{\Omega_0}\frac{1}{|\mathbf{k}|^2}$, $M(\mathbf{k}) = \frac{4\pi}{\Omega_0}\frac{1}{|\mathbf{k}|^2} + m(\mathbf{k})$
- 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_xB_y $(y = 1 - x)$
- random case: $a_i = a^A$ or a^B can be solved using the CPA
- randomness usually rather weak
- linear qV-relation $a_i q_i + V_i = k_i$ is built in the model

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

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

compare with Hubbard U

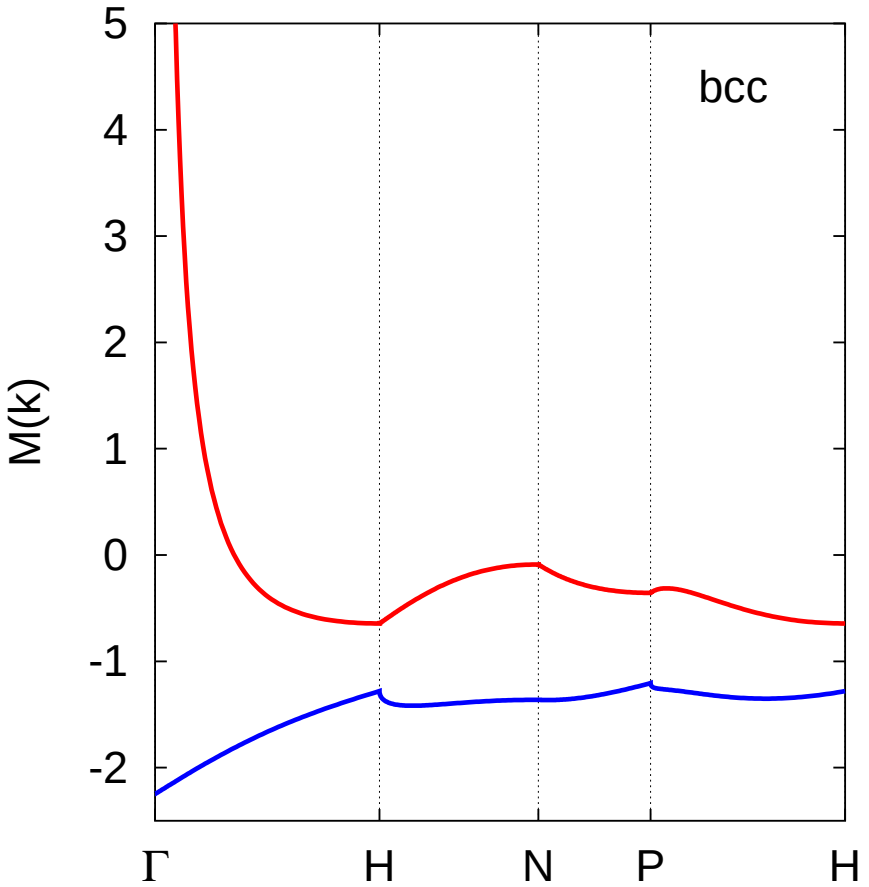
$$E_{\rm int} = \tfrac{1}{2} U N_d (N_d - 1)\,, \quad U = \frac{\partial^2 E_{\rm int}}{\partial N_d^2}$$

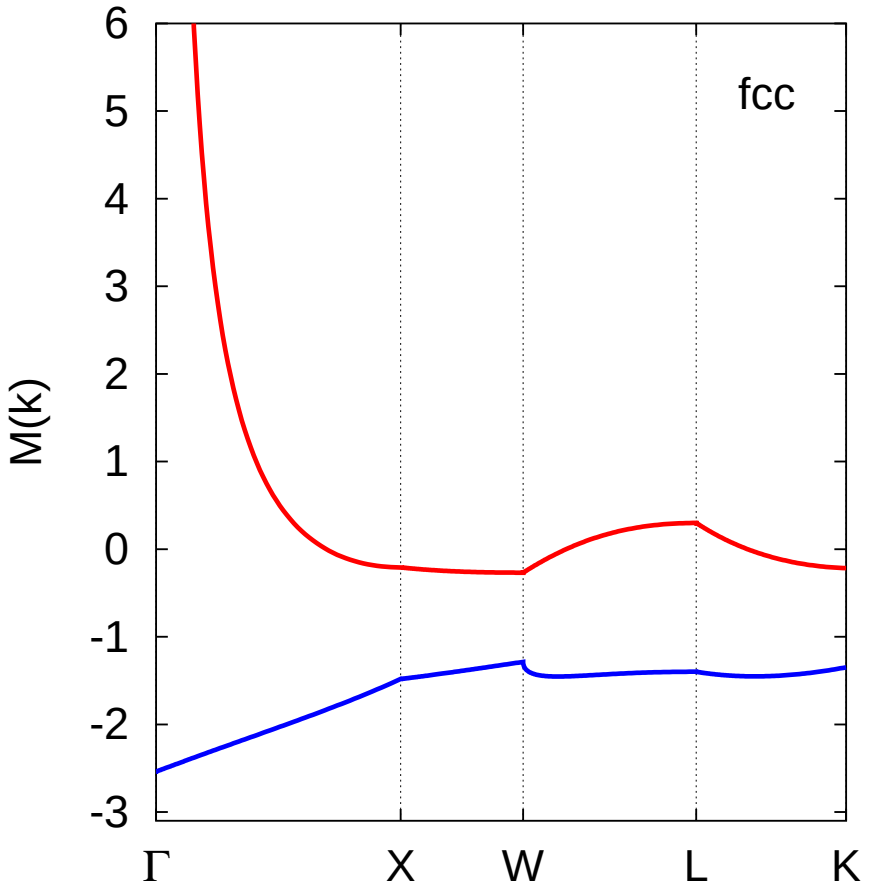
$$U = E(d^{n+1}s^0) + E(d^{n-1}s^2) - 2E(d^n s^1)$$

... *constant net charge and thus efficient intraatomic screening*

b_i ... bare net charges: $a_i q_i + V_i = k_i = a_i b_i$

”Band structure” of the Madelung matrix

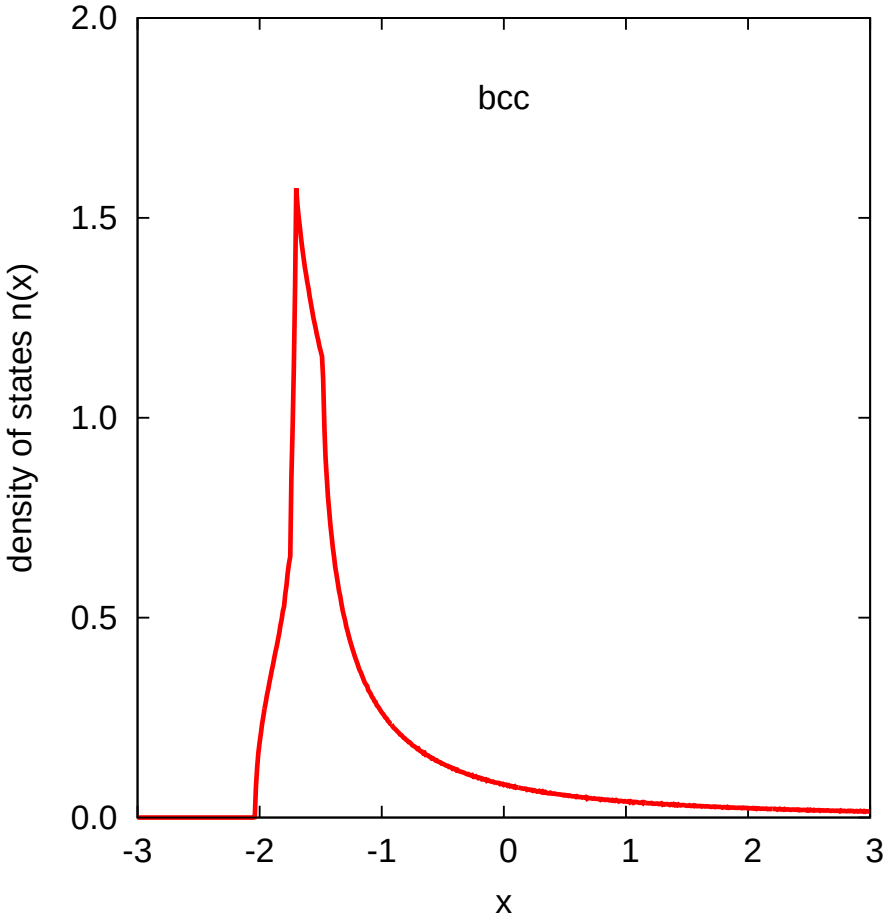


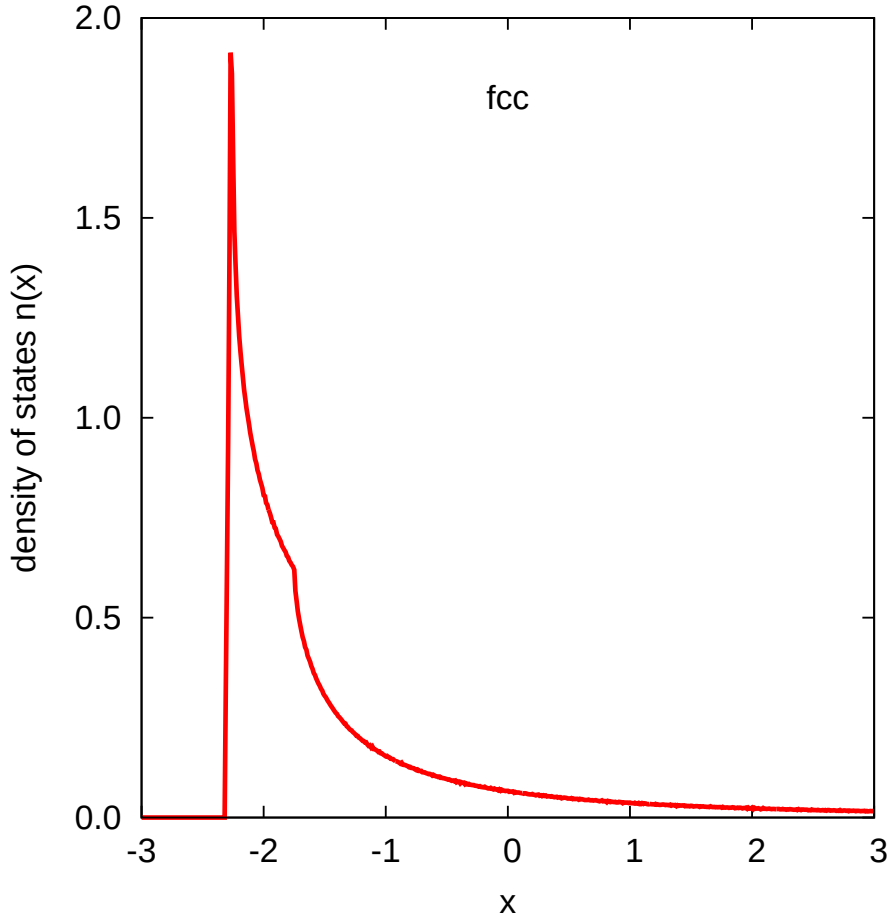


$$a_{\mathrm{latt}} = 1$$

”Density of states” of the Madelung matrix

$$a_{\mathrm{latt}} = 1$$





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

SCREENING

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

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

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

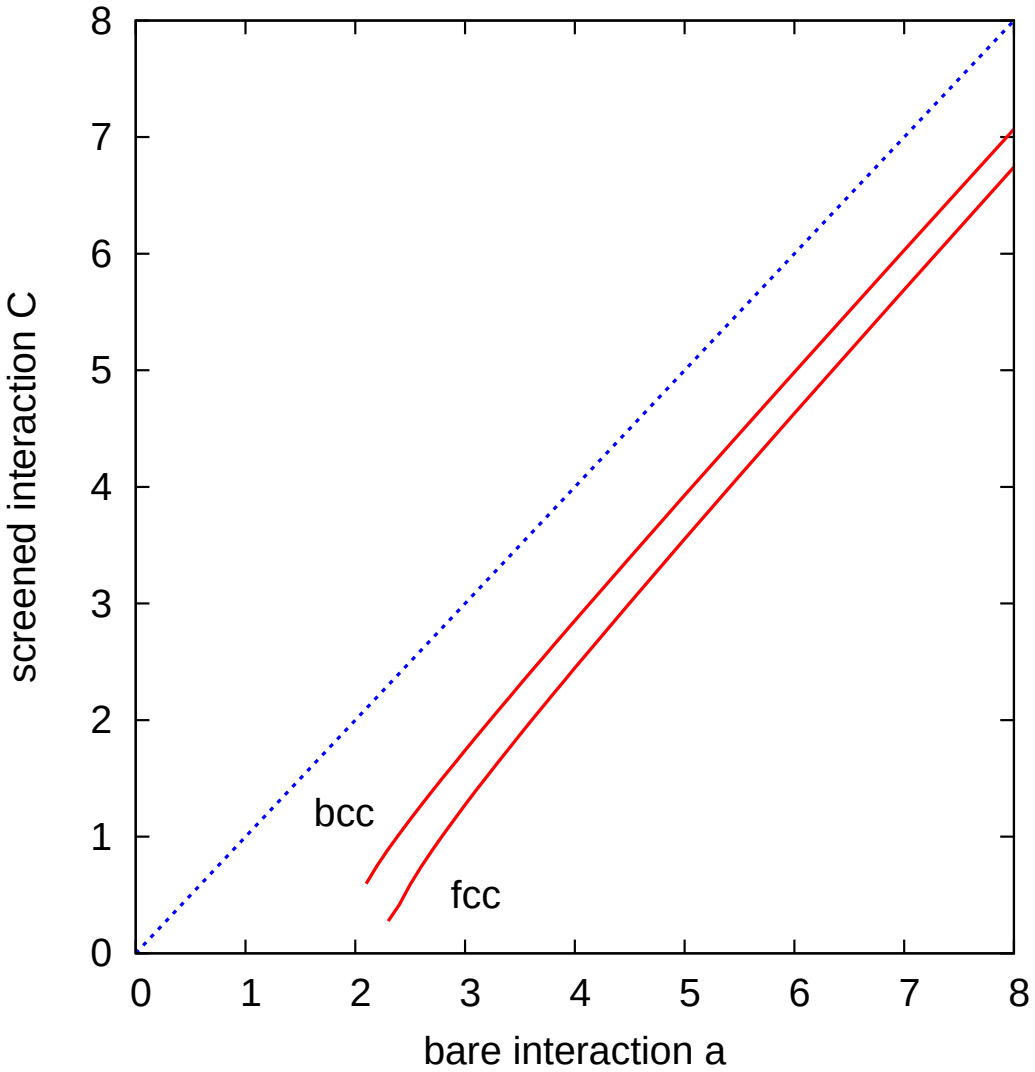
$$M_{ij}^{\mathrm{scr}} = \left[\frac{\partial^2 E(\{q_i\})}{\partial q_i \partial q_j} \right]_{\mathrm{relaxed}} = -\frac{G_{ij}}{G_{ii}G_{jj} - G_{ij}G_{ji}}$$

generally: cluster P: $M_{ij}^{\mathrm{scr}} = \frac{P}{G_{PP}} \,, \quad P$ ... projector onto cluster

Madelung contribution to Ising Hamiltonian parameters

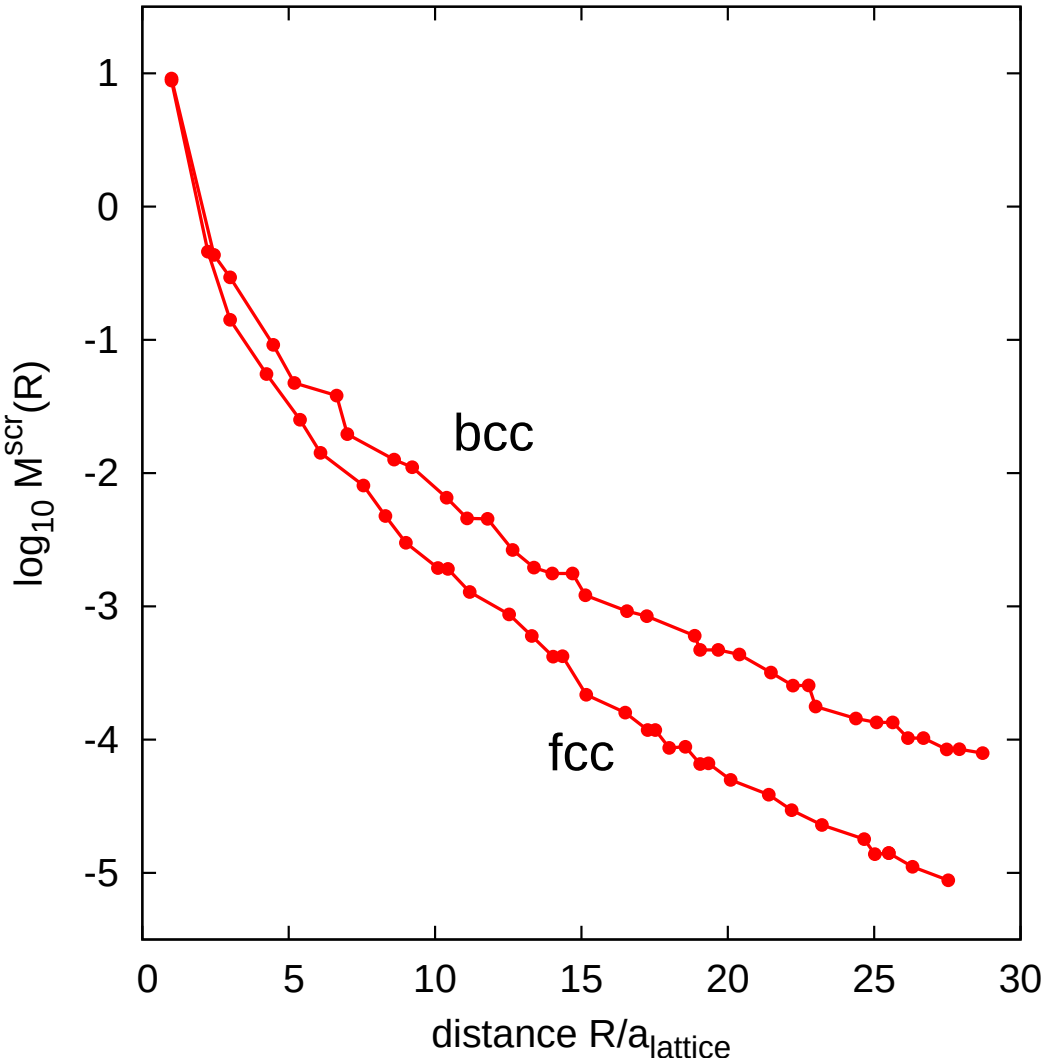
$$V_{ij}^{\mathrm{Mad}} = V_{ij}^{\mathrm{AA}} + V_{ij}^{\mathrm{BB}} - 2V_{ij}^{\mathrm{AB}} = M_{ij}^{\mathrm{scr}} (q^A - q^B)^2$$

Screened on-site interaction



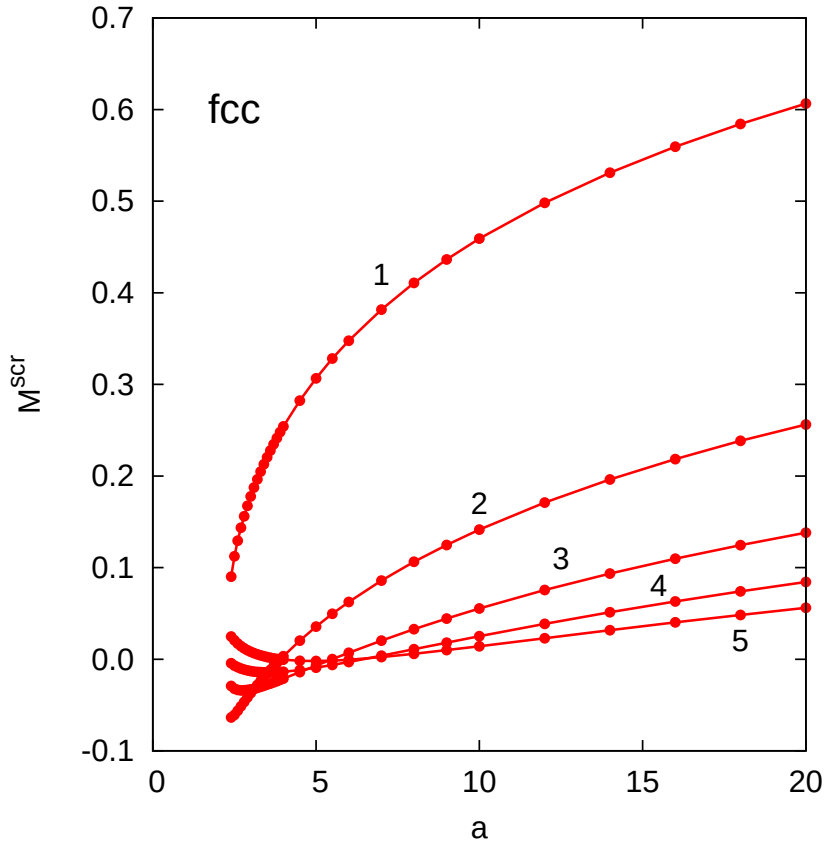
Screened electrostatic interaction

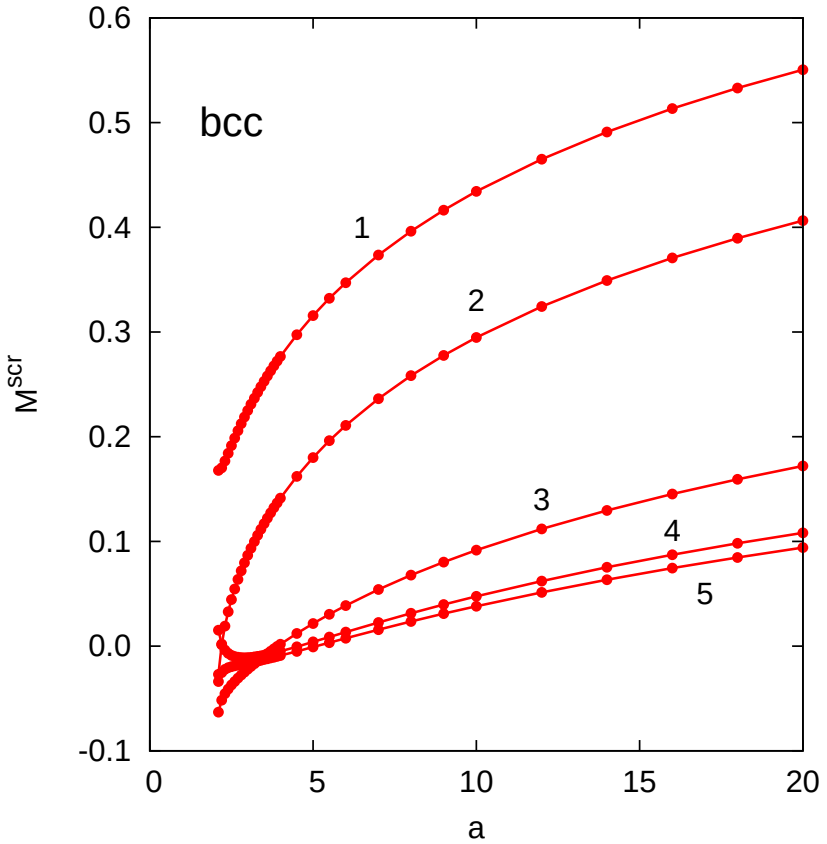
as a function of distance, interaction strength $a = 10$



Screened electrostatic interaction

as a function of interaction strength, lattice constant $a_{\mathrm{latt}} = 1$





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

Probability distribution of local charges I

for simplicity: $a_i = a$ for all i ... nonrandom

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

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

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

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

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

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

$\chi_S(t) = \chi_1(A_1 t)\chi_2(A_2 t) \ldots$.

Probability distribution of local charges II

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

$\chi_i(t) = \int_{-\infty}^{\infty} \mathrm{d}\xi\, e^{i\xi t} p(\xi) = ye^{-ixt} + xe^{iyt}$ ... characteristic function of $\delta\eta_i$

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

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

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

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

$\kappa_4 = G^{(4)}xy(1-6xy)\,, \quad \kappa_5 = G^{(5)}xy(y-x)(1-12xy)$, etc.

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

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

$\kappa_{2n} \neq 0$ for $n > 1$ ... distribution is not Gaussian, finite support

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

$p_I(x) \neq 0$ for $p < x < Q$

MADELUNG ENERGY OF THE ALLOY

$E^{\mathrm{Mad}} = \frac{1}{2}\frac{1}{N}\sum_{i,j} M_{ij} q_i q_j = \frac{1}{N}\sum_i V_i q_i$ per atom

$V_i = \sum_j M_{ij} q_j$

$E^{\mathrm{Mad}} = \frac{1}{2}\langle \bar{q}^Q \bar{V}^Q \rangle - \frac{1}{2}\langle a^Q m_2^Q \rangle$

$m_2^Q = \kappa_2^Q$

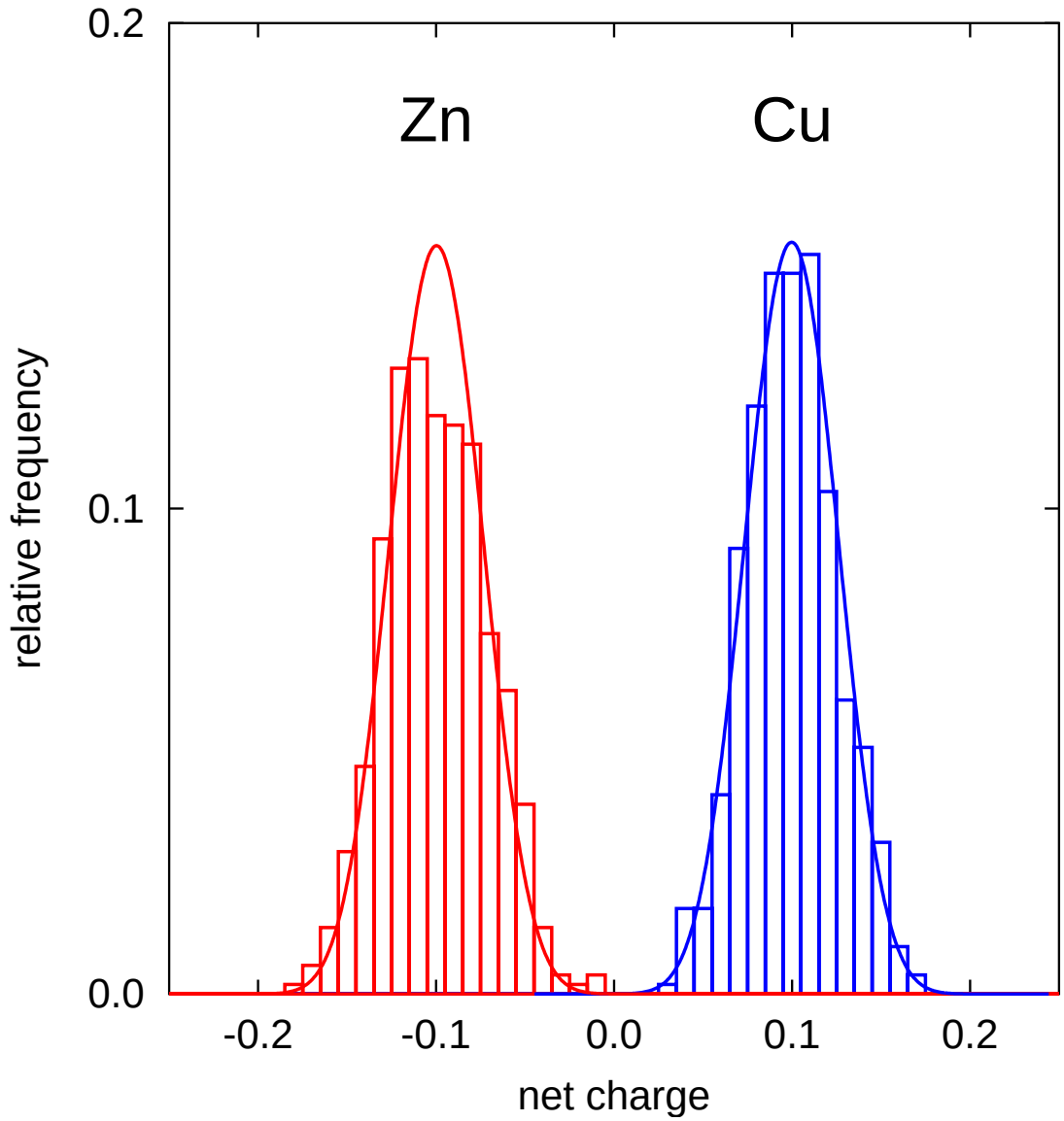
Case study: $Cu_{50}Zn_{50}$ bcc alloy

J.S. Faulkner, Y. Wang, and G.M. Stocks, Phys. Rev. B **55** (1997), 7942.

512 Zn atoms and 512 Cu atoms

atom	k [Ry]	a [Ry]	b [1]	$\bar{q}$[1]
Cu	0.14533	1.83915	0.07902	0.099783
Zn	-0.14350	1.82082	-0.07810	-0.099783

Comparison with supercell



Comparison with supercell

	Cu		Zn	
cumulant	supercell	model	supercell	model
κ_2	6.35×10^{-4}	6.33×10^{-4}	7.91×10^{-4}	6.39×10^{-4}
κ_3	1.45×10^{-6}	0.0	3.26×10^{-6}	0.0
κ_4	-9.16×10^{-8}	-6.88×10^{-8}	-1.02×10^{-7}	-7.01×10^{-8}
κ_5	-3.74×10^{-9}	0.0	-4.03×10^{-9}	0.0
κ_6	-1.50×10^{-10}	3.29×10^{-11}	1.86×10^{-10}	3.39×10^{-11}

$$\kappa_2^{Cu} ... - 0.05\sigma, \quad \kappa_2^{Zn} ... - 3.06\sigma$$

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
- improved expression for Madelung energy
- statistics of net charges on A and B atoms
- explanation and range of validity of simple approximations (SIM, screened CPA, charge correlated model, etc.) on a systematic basis

FUTURE

- combination with the local-fi eld CPA: accurate method for electronic structure calculations with moderate requirements on computer resources
- other screening mechanisms (monopole-dipole, dipole-dipole interactions)

ANNALEN
DER
PHYSIK.

BEGRÜNDET UND FORTGEFÜHRT DURCH
F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. u. E. WIEDEMANN, P. DRUDE.

VIERTE FOLGE.

BAND 64.

DER GANZEN REIHE 369. BAND.

KURATORIUM:
M. PLANCK, G. QUINCKE, W. C. RÖNTGEN,
E. WARBURG.

UNTER MITWIRKUNG
DER DEUTSCHEN PHYSIKALISCHEN GESELLSCHAFT

HERAUSGEGEBEN VON
W. WIEN UND **M. PLANCK.**

MIT EINER FIGURENTAFEL.

LEIPZIG, 1921.
VERLAG VON JOHANN AMBROSIUS BARTH.

3. *Die Berechnung optischer und elektrostatischer Gitterpotentiale;*
von P. P. Ewald.

Inhalt: I. 1. Elektrostatische Potentiale. 2. Elektrodynamische Potentiale. 3. Ziel der Arbeit. — II. 1. Thetafunktionen einer Veränderlichen. Zusammenhang zwischen Thetafunktionen und Gitterproblemen. 2. Ableitung der Transformationsformel für Thetafunktionen von 3 Veränderlichen. — III. 1. Potentiale als Summen von Einzelwirkungen (randloser Kristall). 2. Potentialumformung, Trennungsstelle E. Gesamtpotential eines einfachen Gitters. 3. Erregendes Potential eines einfachen Gitters. 4. Gesamtes und erregendes Potential im zusammengesetzten Gitter, Strukturfaktor. — IV. 1. Übergang zu elektrostatischen Potentialen, dimensionslose Größen. 2. Beispiel: Gitterenergie von Steinsalz. 3. Beispiel: Gitterenergie von Flußspat.

I.

1. Bei den Untersuchungen über den Aufbau der Kristalle und ihre Eigenschaften tritt die Notwendigkeit auf, gewisse Potentiale nicht nur als allgemeinen Ausdruck zu kennen, sondern ihren Zahlenwert an irgendeiner Stelle des vom Gitter erfüllten Raumes zu ermitteln. *Das elektrostatische Potential* eines Ionengitters z. B. ist

$$\varphi(P) = \sum \frac{\varepsilon_{P'}}{R_{PP'}}, \tag{1}$$

wo unter P' ein Atom des Gitterverbandes, unter $\varepsilon_{P'}$ seine Ladung, und unter $R_{PP'}$ sein Abstand vom Aufpunkt P verstanden ist und das Summenzeichen sich auf alle Atome P' bezieht. Dies Potential gibt die Arbeit an, die notwendig ist, um eine positive Einheitsladung (wir benutzen gewöhnliche elektrostatische Einheiten) aus dem Unendlichen an den Ort P zu bringen. Wünscht man die Energie zu kennen, die im ganzen Gitterverband aufgespeichert ist, so ist diese[1])

1) Vgl. etwa M. Born und A. Landé, Berl. Ber. 45. S. 1048 bis 1068. 1918.

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  Cause of death: unspecified
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- **Professor: Technische Hochschule, Stuttgart (1921-)**
  Professor: Physics, Brooklyn Polytechnic Institute (1949-59)
- **Max Planck Medal 1978**
- **Author of books:**
  The Physics of Solids and Fluids
  (1930, with Pöschl and Prandtl)