Covalent bonding in approximants of quasicrystals and the electronic transport

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Decagonal Al-Ni-Co

Interesting Issues

- ***quasiperiodic*** and ***periodic*** structures co-exist
  - ***period*** >4Å due to Ni/Co redistribution [1]?
- ***hybridization*** of Al with Co/Ni
  - Co-*d* ***below*** Ni-*d* [2,3]? Pseudogap at ϵ_F [2]?
  - Is there a Ni/Co ***network*** linked by Al ?
- ***anisotropic*** electronic [4] and thermal [5] transport
  - anisotropic Lorenz number ?

This Work

Energy-optimized approximants close to d-$Al_{69}Ni_{22}Co_9$ [6] are theoretically examined with respect to

- the ***spectral electronic properties*** and
- the ***valence charge density***.

Methods Applied

ASA-LMTO [8] (special **k**-sets) $\Longrightarrow$ valence band states $|i\rangle$, ϵ_i, state density $\widehat{n}(\epsilon)$ after gaussian broadening

ABINIT [9] (GTH/TM pseudopotentials) $\Longrightarrow$ valence-charge densities

Linear-response theory

- **Kubo-Greenwood** with LMTO band states [11] $\Longrightarrow$ spectral conductivities $\widehat{\sigma}_{\alpha\alpha}(\epsilon)$, α = xyz
- **Einstein relation** $\Longrightarrow$ spectral diffusivties $\widehat{D}_{\alpha\alpha}(\epsilon)$
- **CTKG formulas** [11] $\Longrightarrow$ conductivities $\sigma_{\alpha\alpha}(T)$, thermopowers $S_{\alpha\alpha}(T)$, and Lorenz numbers $L_{\alpha\alpha}(T)$

$$\mathcal{L}^{ij}_{\alpha\alpha}(T) = (-1)^{i+j}\int d\epsilon\, \widehat{\sigma}_{\alpha\alpha}(\epsilon)\,(\epsilon-\mu)^{i+j-2}\left(-\frac{\partial f(\epsilon,\mu,T)}{\partial\epsilon}\right)$$

$$\mu(T) \approx \epsilon_F - (k_B T)^2\,\frac{\pi^2}{6}\left[\frac{1}{n(\epsilon)}\,\frac{dn(\epsilon)}{d\epsilon}\right]_{\epsilon_F}$$

$$\sigma_{\alpha\alpha}(T) = \mathcal{L}^{11}_{\alpha\alpha}(T) \qquad S_{\alpha\alpha}(T) = \frac{1}{|e|T}\frac{\mathcal{L}^{12}_{\alpha\alpha}(T)}{\sigma_{\alpha\alpha}(T)} \qquad \frac{L_{\alpha\alpha}(T)}{L_0} = 3\left(\frac{e}{\pi k_B}\right)^2\left(\frac{\mathcal{L}^{22}_{\alpha\alpha}(T)}{e^2T^2\sigma_{\alpha\alpha}(T)} - S_{\alpha\alpha}(T)^2\right)$$

icosahedral Al-TM-Approximants

Motivation

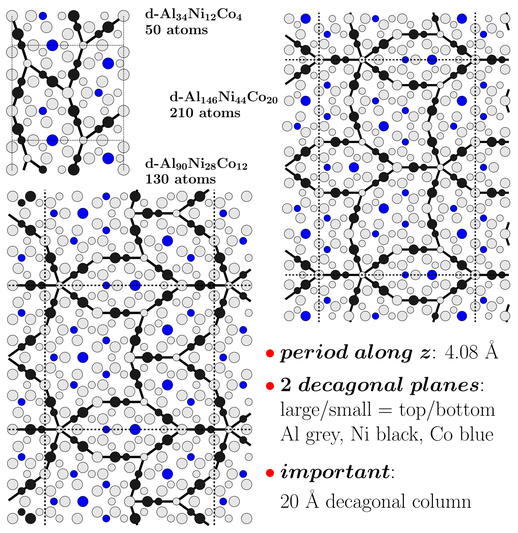
- recent experimental results of Kirihara *et al.* [7] show the ***appearence of covalent bonds*** in $Al_{102}Mn_{24}Si_{12}$ and $Al_{102}Re_{24}Si_{12}$ approximants
- leading questions:
  - relation between ***covalent*** bonding and ***anomal transport*** properties ?
  - mechanisms of stablizing the elementary clusters and a ***bcc–network*** of these clusters ?

Paths of Investigation

- confirmation of high electron density ($\rho > 0.04\,e/\text{Å}^3$) along certain bond lines
- response of these bonds to chemical or geometrical ***disturbtion***
- comparison with common ***crystalline systems***

Three Approximants: 50, 130, 210 atoms

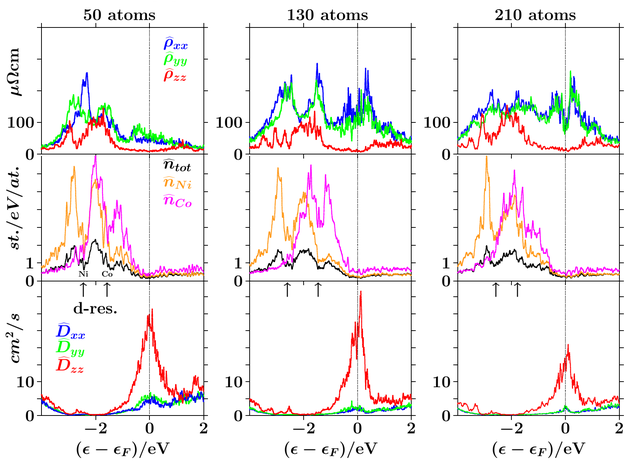
Monte-Carlo, Pair Potentials [6]



- ***period along z***: 4.08 Å
- **2** ***decagonal planes***: large/small = top/bottom Al grey, Ni black, Co blue
- ***important***: 20 Å decagonal column

Spectral Curves: resistivity, state density, diffusivity

ASA-LMTO [8] and Kubo-Greewood

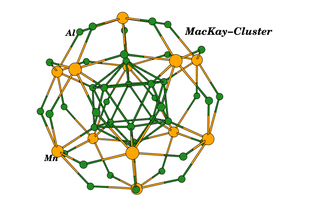


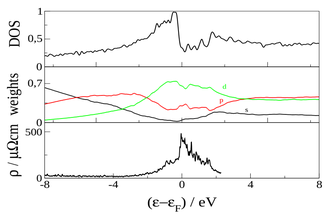
- ***pseudogap close to*** ϵ_F: less pronounced
- ***d resonances***: Ni below Co with overlap Ni antibonding - Co bonding
- ***diffusivities***: decreasing $\widehat{D}_{dec}$, $\widehat{D}_{per}$

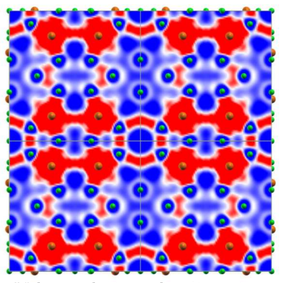
Three Types of Stabilizing Covalent Bonds

- model structure of the 1/1-*AlMnSi*-Approximant [7], all *Si* substituted by *Al*
- ***MacKay cluster*** as bcc-ordered elementary module
- ***deep pseudogap*** in the DOS and ***high resistivity*** ($> 500\mu\Omega cm$)
- classification of the bonds according to the charge distribution

Type of bonds	Bond-distance	Role
Mn-Mn	4.5 Å	cluster network
Al-Mn	2.4 Å	MacKay cluster
Al-Al	2.4 Å	innner MacKay shell



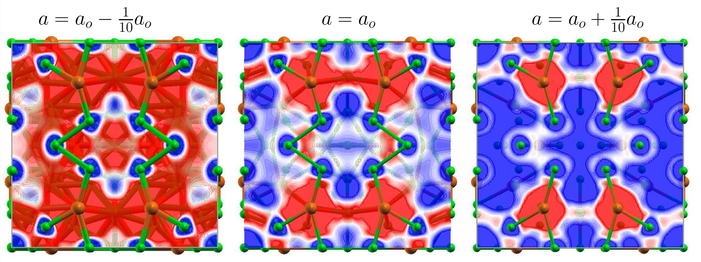




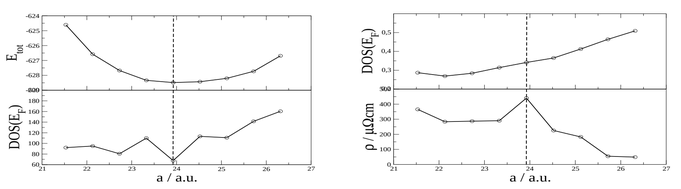
Valence-electron density cut: 0.02-0.04 $e/\text{Å}^3$
ABINIT [9], **XCRYSDEN** [10]

Structural Influences on the Bonds

A. No Influence of Lattice Constant on Hybridization Behavior



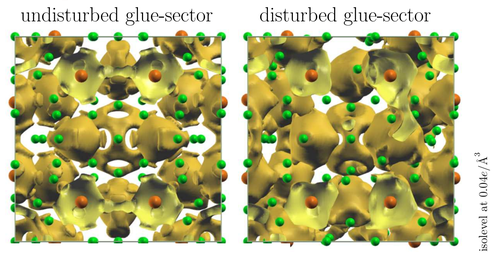
- real strurcture is the ***most stable*** structure of this type
- ***no influence*** of the lattice constant on bonding structure
- highest resistivity in two cases: smallest a and the realistic case $a = a_0$

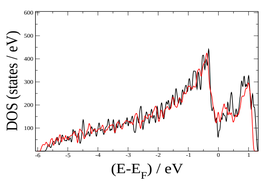


Left : Total energy and $DOS(E_F)$, ABINIT [9]
Right : $DOS(E_F)$ and resistivity, ASA-LMTO [8] / Kubo-Greenwood [11]

B. Importance of the Glue-Atom Positions

undisturbed glue-sector — disturbed glue-sector



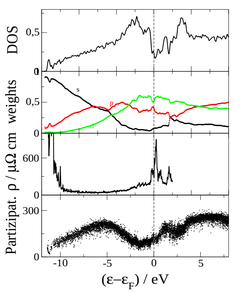


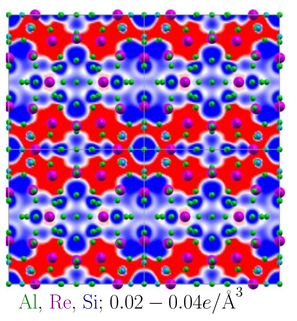
Black Curve: DOS of the original cluster
Red Curve: DOS of the varied cluster

→ ***vanishing*** of the deep pseudogap at E_f in the case of glue-sector variation

- relaxing the glue-atom positions by a Morse potential
- ***Mn-Mn bridges*** very senitive to the glue positions
- mutual stabilization of the MacKays by order of the glue-sector

C. Altering Decoration / AlReSi



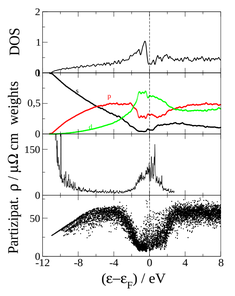


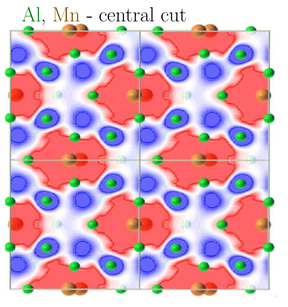
Al, Re, Si; $0.02 - 0.04 e/\text{Å}^3$

- model-cluster → all Si on sc-MacKay positions
- similar bonding behavior compared with AlMn
- ***Si atoms stabilize*** the MacKay-clusters
- very high resistivity peak at E_F ($900.\mu\Omega cm$)

Common Crystal Al_6Mn

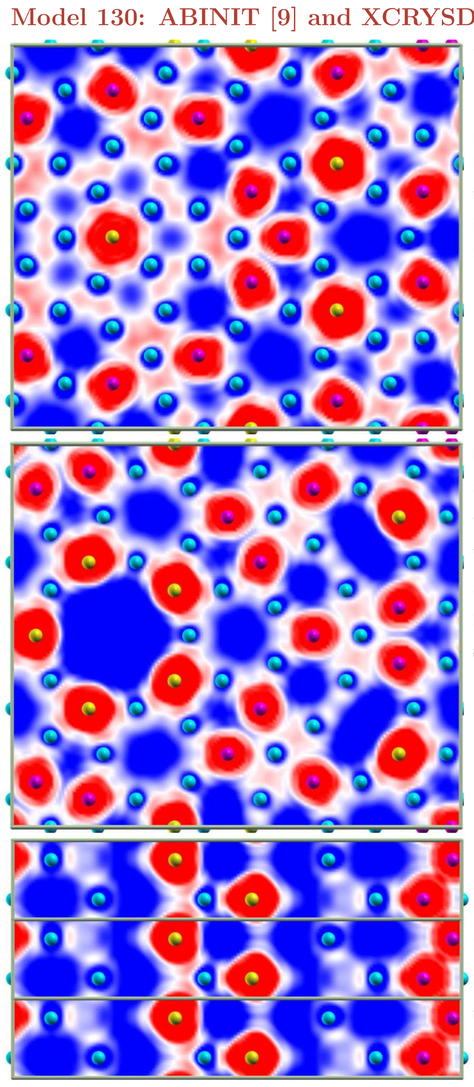
- broad Hume-Rothery pseudogap in the DOS, $\rho < 100\mu\Omega cm$
- strong Mn-Al bonds and weak Al-Al bonds
- ***no Mn-Mn bridges***
- hybridization behavior similar to the approximants





Valence Charge Density: level 0.02 - 0.06 e/Å^3

Model 130: ABINIT [9] and XCRYSDEN [10]



top view
Al Ni Co

coordination: Co-Al higher than Ni-Al, Co-Ni and Co-Co avoided, 3-Ni triangles.

bottom view

bonds: TM network with Al bridges

holes: large pentagons, small triangles

side view

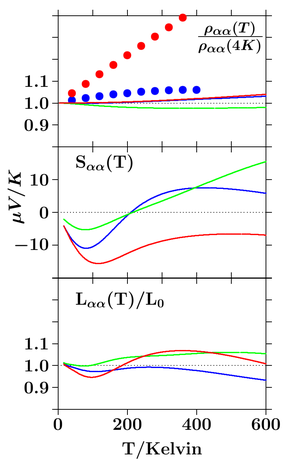
4.08 Å *period*: Ni-Ni attraction Co-Co repulsion

transport: tubes along z for "channeling" ?

Model 130 versus Experiment

A. Temperature Dependence: too Weak

model: $Al_{69}Ni_{22}Co_9$, spiky structure removed, solid curves
experiment [4]: $Al_{73}Ni_{16.7}Co_{10.3}$, bullets
color code: ***x***-decagonal ***y***-decagonal ***z***-periodic



- ***resistivity*** non-metallic behavior less pronounced, considerable phonon scattering required
- ***thermopower*** right behavior, however too small
- ***Lorenz number*** only small deviations from the Wiedemann-Franz law

B. Transport Anisotropy: Realistic

system	$\rho_{per}(300K)$ / μΩcm	$\rho_{dec}(300K)$ / μΩcm	$\frac{\rho_{dec}(300K)}{\rho_{per}(300K)}$
experiment	35	173	5
model 50	10	50	5
model 130	10	103	10
model 210	15	90	6

Approximants to d-AlNiCo?

- Yes, as the structure is concerned [6].
- Yes, as the Al-Ni/Co network is concerned.
- Less clearly as the transport properties are concerned. Decoration problems?

References

[1] K. Saitoh, M. Tanaka, A.P. Tsai Acta Cryst. **A58** (Suppl.), C236 (2002)
[2] E. Belin-Ferré *et al.* J. Phys.: Condens. Matter **8**, 6213 (1996) Z.M. Stadnik *et al.* Phys. Rev. **B51**, 10358 (1995)
[3] M. Krajči, J. Hafner, and M. Mihalkovič Phys. Rev. **B82**, 243 (2000)
[4] Lin Shu-yuan *et al.* Phys. Rev. **B41**, 9625 (1990)
[5] J.A. Barrow *et al.* Phys. Rev. **B68**, 104202 (2003)
[6] M. Mihalkovič *et al.* Phys. Rev. **B65**, 104205 (2002)
[7] K. Kirihara *et al.* Phys. Rev. Letters **85**, 3468 (2000) K. Kirihara *et al.* Phys. Rev. **B68**, 014205 (2003)
[8] O.K. Andersen Phys. Rev. **12**, 3060 (1975)
[9] The ABINIT code is a common project of the Universite Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.pcpm.ucl.ac.be/abinit).
[10] A. Kokalj, J. Mol. Graphics Modelling **17**,176 (1999) A. Kokalj and M. Causa, Proceedings of High Performance Graphics Systems and Applications European Workshop, Bologna, 2000, p. 51-54.
[11] G.V. Chester, A. Thellung Proc. Phys. Soc. **77**, 1005 (1961): K. Kubo J. Phys. Soc. Jap. **12**, 570(1957); D.A. Greenwood Proc. Phys. Soc. **71**, 585(1958)

Conclusions

- **Realistic simulations of materials should consider the valence electrons in two-fold respects, (i) in the static respect on minimizing the total energy, and (ii) in the dynamic respect on reproducing the observed electronic transport parameters.**
- **Monitoring the valence-charge density reveals critical parts of the stabilizing network.**
- **The examined crystalline approximants to quasicrystals bear transition-metal (TM) networks with direct TM-TM links, contrary to related non-approximant systems.**

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