Literature Review - Structures and Magnetism of Rhodium Nanoclusters

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- Group : 9
- Period : 5
- Transition Metals
- Valence electrons : $4d^8\ 5s^1$
- The rarest of all non-radioactive metals on Earth
- Uses
  - Catalyst in industrial processes
  - Use in catalytic converters for cars
  - Hardener for platinum and palladium

Structure and Magnetism of Small Rhodium Clusters

F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, E. O. Berlanga-Ramirez, and A. Vega,

Phys. Rev. B **66**, 224410 (2002).

Abstract

- Rhodium clusters, Rh_N ; $4 \leq N \leq 26$
- To study the structural and magnetic properties of rhodium clusters.
- Structures of global minima
  - Gupta potential
  - Genetic algorithm
- Spin-polarized electronic structures and magnetic properties
  - *spd* tight-binding Hamiltonian

Ref. : F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, E. O. Berlanga-Ramirez, and A. Vega, *Phys. Rev. B* **66**, 224410 (2002).

Geometrical Structure

- 80,000 global optimizations starting from distinct random initial configurations of the atoms.
- Optimization algorithm : Hybrid approach
  - Global genetic algorithm with stochastic moves on potential energy surfaces.
    - Avoid entrapment in high-energy local minima.
  - Local conjugate gradient relaxation.
    - Applied once the global part has reached the lowest-energy minima.

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Gupta Potential

$$V = \sum_{i=1}^{n} \left[A \sum_{j(\neq i)=1}^{n} \exp\left[-p \left(\frac{r_{ij}}{r_{0n}} - 1 \right) \right] - \left(\xi^2 \sum_{j(\neq i)=1}^{n} \exp\left[-2q \left(\frac{r_{ij}}{r_{0n}} - 1 \right) \right] \right)^{\frac{1}{2}} \right]$$

- Parameters used :
  - $p = 18.45$, $q = 1.867$, $\xi = 1.66\text{eV}$, $A = 0.0629\text{eV}$

Ref. : F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, E. O. Berlanga-Ramirez, and A. Vega, *Phys. Rev. B* **66**, 224410 (2002).

Electronic Structure

- Solve tight-binding Hamiltonian for 4*d*, 5s and 5*p* valence electrons in a mean-field approximation.

$$H = \sum_{i\alpha\sigma} \varepsilon_{i\alpha\sigma} \hat{n}_{i\alpha\sigma} + \sum_{\substack{\alpha\beta\sigma \\ i\neq j}} t_{ij}^{\alpha\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma}$$

where $\varepsilon_{i\alpha\sigma} = \varepsilon_{i\alpha}^{0} + z_{\sigma} \sum_{\beta} \frac{J_{\alpha\beta}}{2} \mu_{i\beta} + \Omega_{i\alpha}$

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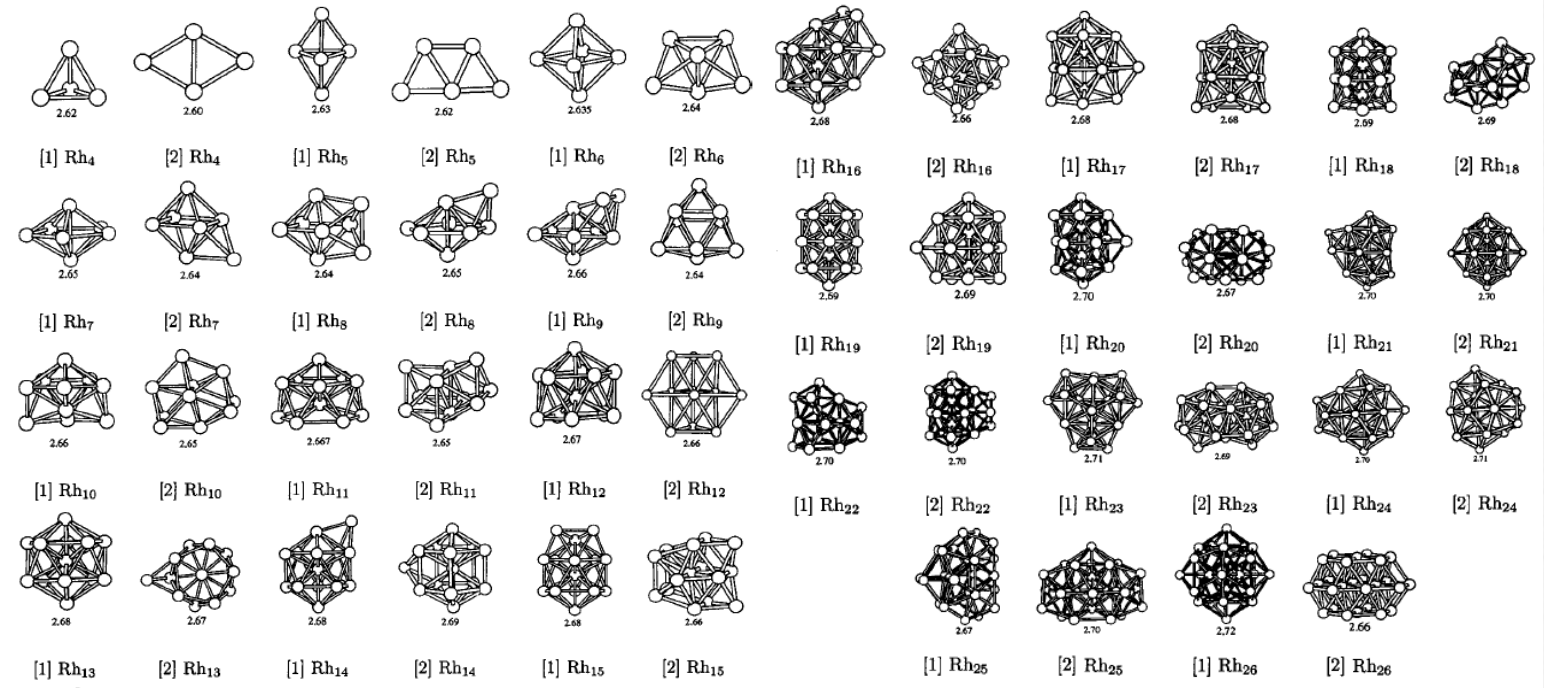
Results and Discussion

- Icosahedral growth pattern for global minima structures for Rh_N up to $N = 26$ atoms.
- Obtained four lowest-energy structures for each cluster size.
- Calculated magnetic moment, relative stability and relative populations for each structure obtained.

Ref. : F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, E. O. Berlanga-Ramirez, and A. Vega, *Phys. Rev. B* **66**, 224410 (2002).

Optimized Geometrical Structures



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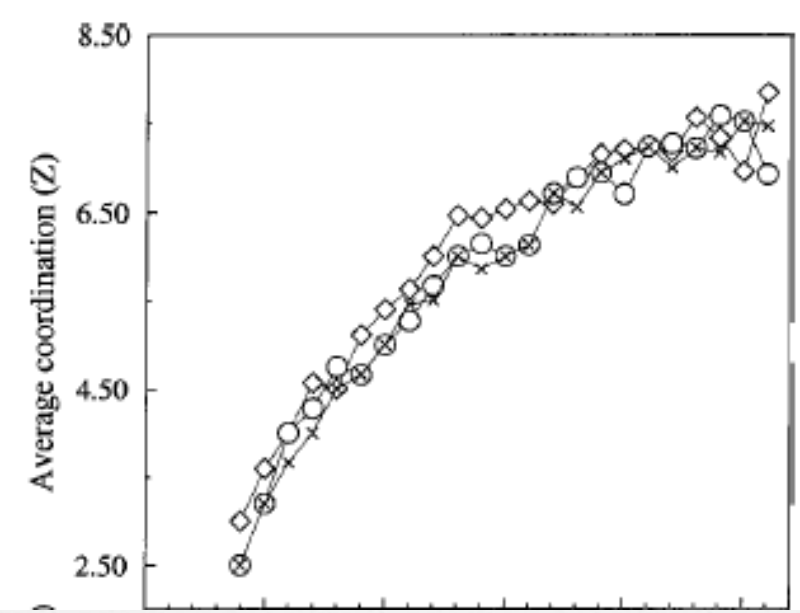
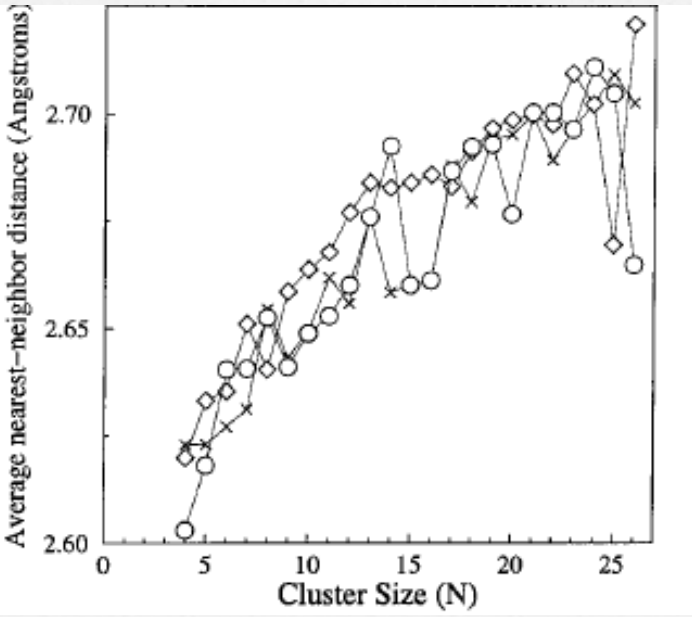
Geometrical Properties





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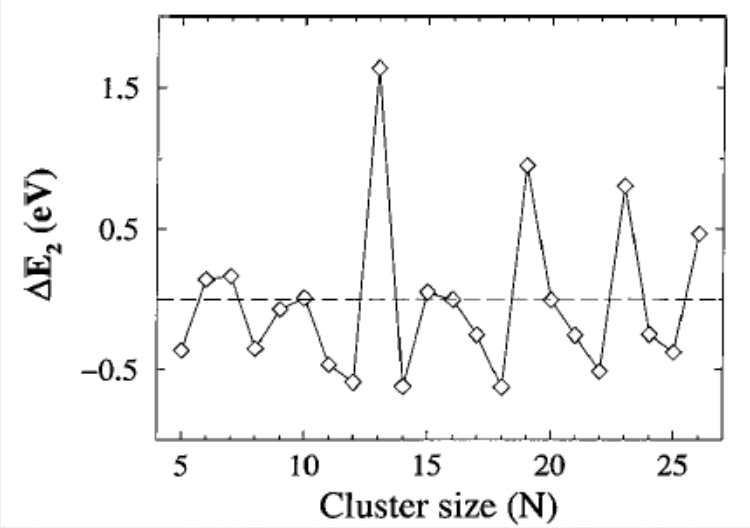
Relative Stability



- Relative stability w.r.t. adjacent clusters Rh_{N-1} *and* Rh_{N+1}
- Maxima at N=13, 19, 23, 26 atoms
  - High stability structures

$$\Delta E_2 = E(N+1) + E(N-1) - 2E(N)$$

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Relative Populations

- Free energy

$$F = V + \sum_i \frac{\hbar\omega_i}{2} + k_B T \sum_i \ln\left[1 - \exp\left(\frac{-\hbar\omega_i}{k_B T}\right)\right]$$

- At most sizes, there should be isomers other than the global minimum at the temperature of experiment.

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Relative Populations

N	$\overline{\mu}^{[1]}$	$RP^{[1]}$	$\overline{\mu}^{[2]}$	$RP^{[2]}$	$RP^{[3]}$	$RP^{[4]}$
4	0.00	1.0	0.5	0.0	0.0	0.0
5	0.59	1.0	0.57	0.0	0.0	0.0
6	0.99	1.0	0.33	0.0	0.0	0.0
7	1.04	1.0	0.43	0.0	0.0	0.0
8	1.15	0.99	0.46	0.01	0.0	0.0
9	0.30	1.0	0.76	0.0	0.0	0.0
10	0.57	1.0	0.13	0.0	0.0	0.0
11	0.48	1.0	0.61	0.0	0.0	0.0
12	1.04	1.0	0.66	0.0	0.0	0.0
13	1.15	1.0	1.00	0.0	0.0	0.0
14	1.14	1.0	0.86	0.0	0.0	0.0
15	0.92	1.0	0.73	0.0	0.0	0.0
16	0.69	1.0	0.48	0.0	0.0	0.0
17	0.45	0.75	0.59	0.14	0.07	0.03
18	0.68	0.86	0.23	0.14	0.0	0.0
19	0.76	1.0	0.59	0.0	0.0	0.0
20	0.74	1.0	0.56	0.0	0.0	0.0
21	0.40	0.8	0.56	0.10	0.1	0.0
22	0.51	0.93	0.35	0.07	0.0	0.0
23	0.25	1.0	0.80	0.0	0.0	0.0
24	0.08	0.64	0.04	0.36	0.0	0.0
25	0.42	0.0	0.41	0.33	0.66	0.01
26	0.34	1.0	0.08	0.0	0.0	0.0

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Magnetic Properties

- 3*d* systems
  - Widely accepted semi-empirical rules that enhance magnetic moments
    - Decreasing coordination
    - Increasing interatomic distance
      - Due to reduce of electron delocalization

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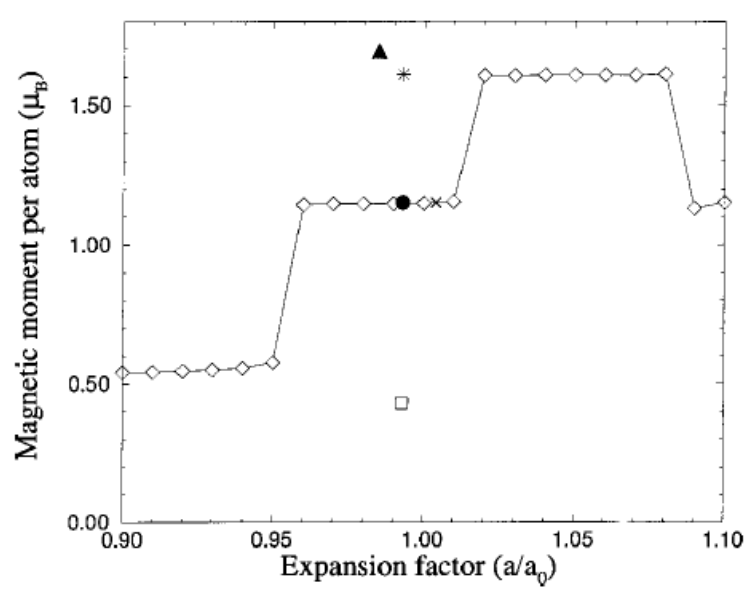
Magnetic Properties



- Magnetic moment per atom for Rh_{13} against interatomic distance
  - Perform uniform compressions and expansions of the global minimum structure.
  - Conclusion: Magnetic moment is not very sensitive to changes in interatomic distance.

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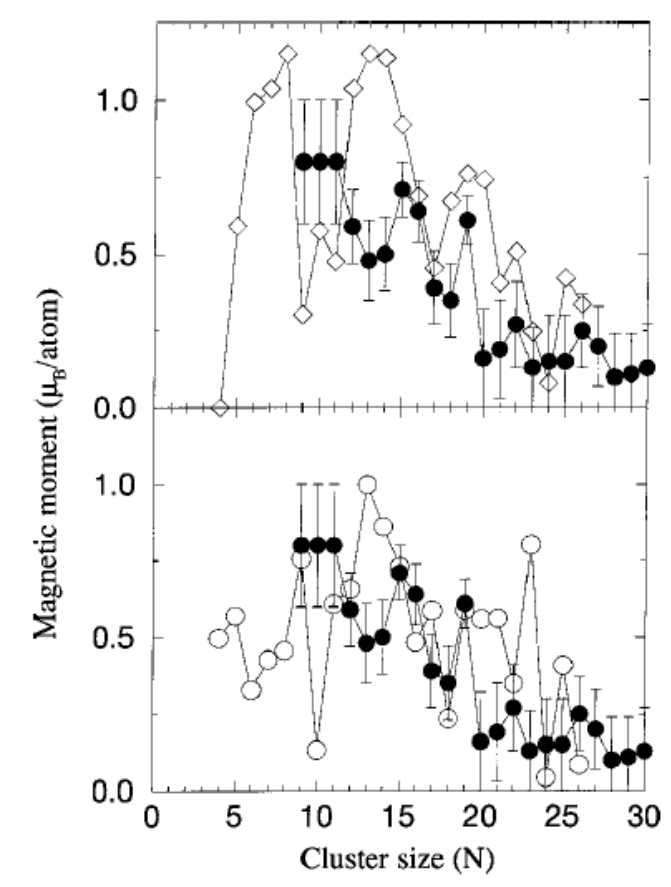
Magnetic Properties



- Average magnetic moment per atom against cluster size
  - Both cases : Decreasing magnetic moment with increasing cluster size.
  - Global minima
  - Second isomers

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Magnetism in clusters of non-magnetic elements: Pd, Rh, and Ru

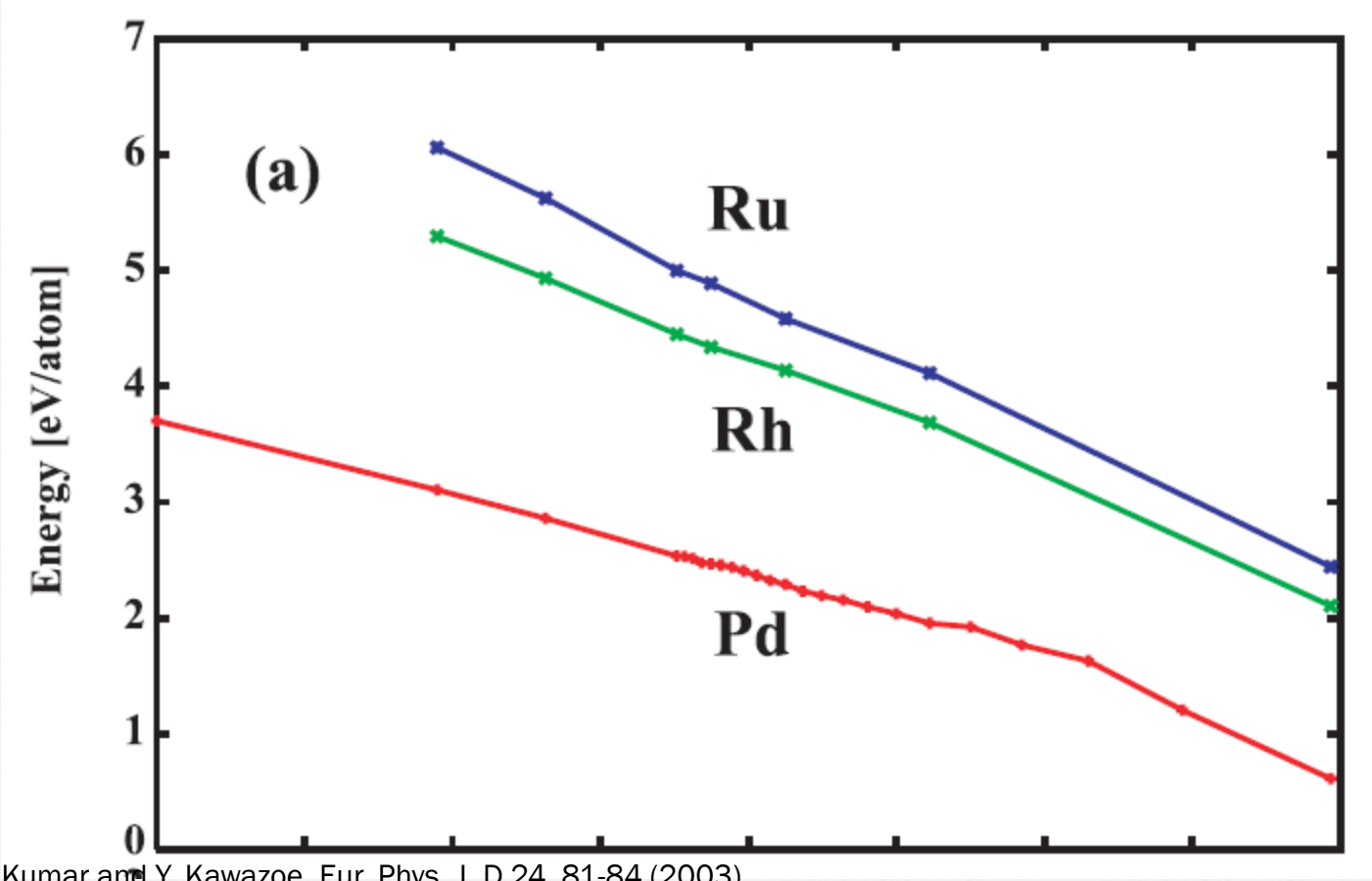
V. Kumar and Y. Kawazoe, *Eur. Phys. J. D* **24**, 81-84 (2003).

Methodology

- *Ab initio* calculations using ultrasoft pseudopotential plane wave method and spin polarized generalized gradient approximation for the exchange-correlation energy.
- Clusters are placed in a simple cubic supercell of side up to 30Å.
- Selected structures are optimized without any symmetry constraint using the conjugate gradient method.

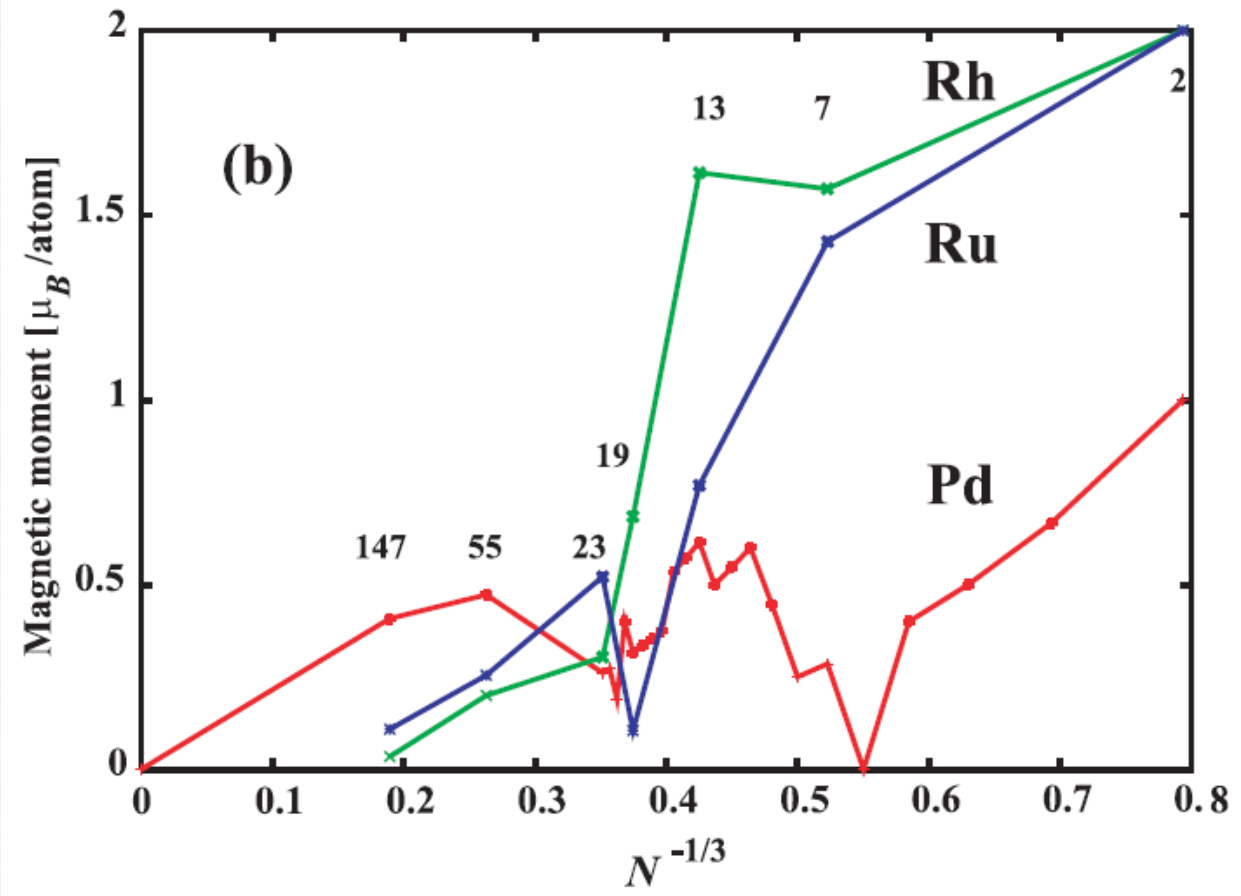
Ref. : V. Kumar and Y. Kawazoe, Eur. Phys. J. D 24, 81-84 (2003).

Results : Binding Energy



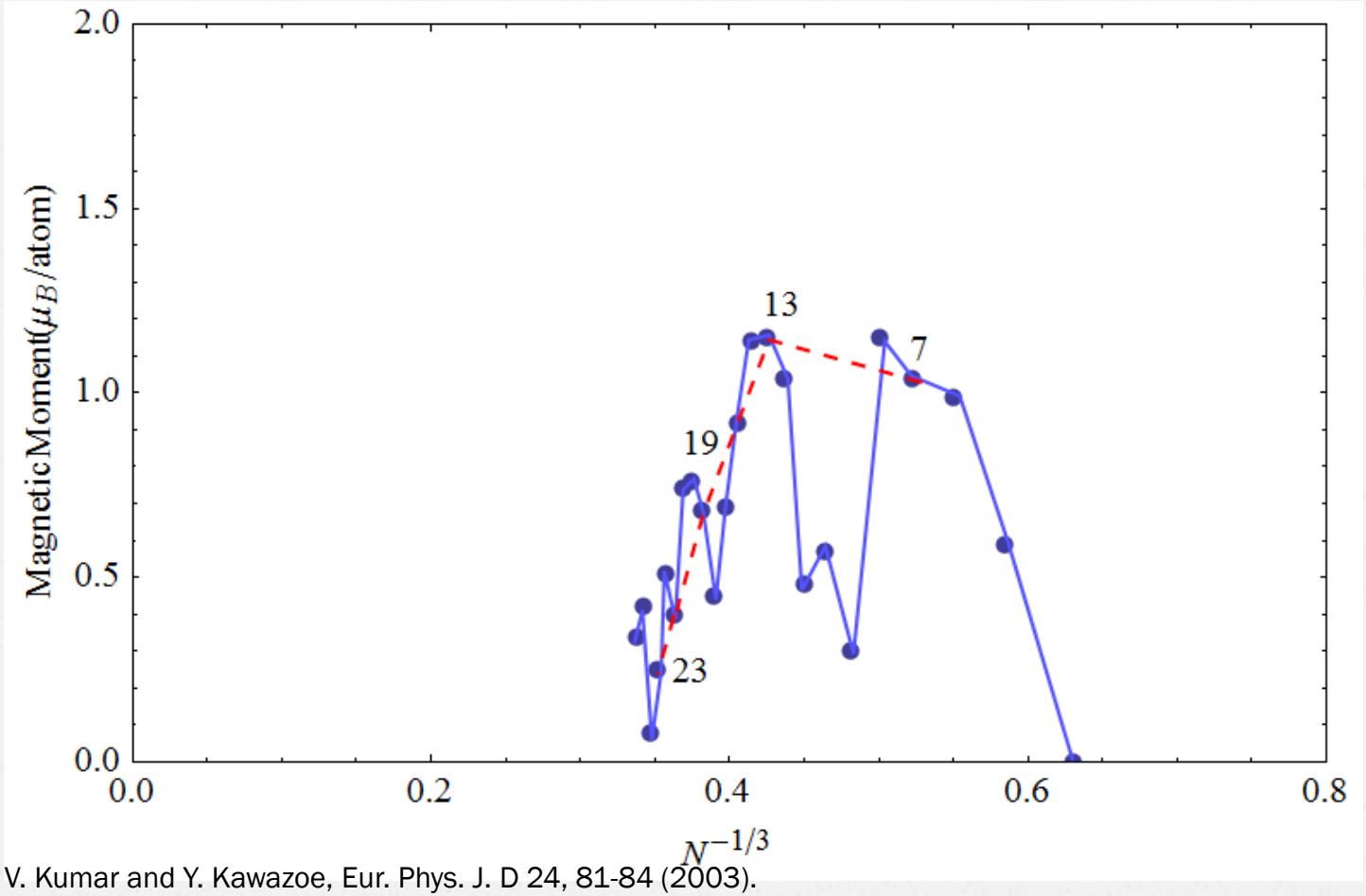
Ref. : V. Kumar and Y. Kawazoe, Eur. Phys. J. D 24, 81-84 (2003).

Results : Magnetic Moment



Ref. : V. Kumar and Y. Kawazoe, Eur. Phys. J. D 24, 81-84 (2003).

Comparison : F. Aguilera-Granja



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Conclusion

1. Determine structures of global minima
2. Calculate electronic structures
3. Observe magnetic properties

The End