

Origin of electric dipole moments in free niobium clusters

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Motivation

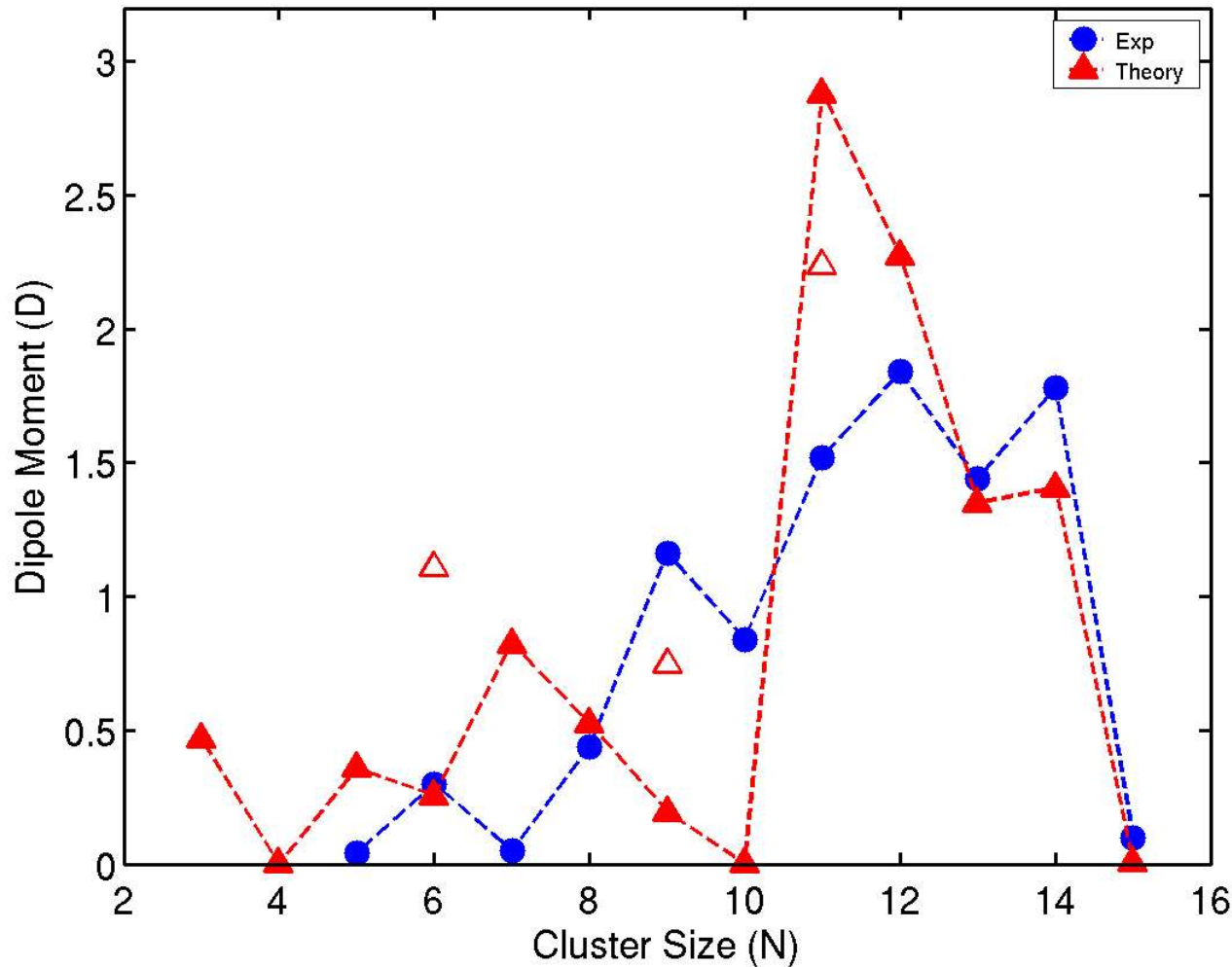
- “Ferroelectric” Nb_N ($5 \leq N \leq 200$) clusters
 - Moro *et al.*, Science **300**, 1265 (2003)
 - Moro *et al.*, PRL **93**, 086803 (2004)
- What's the origin of the electric dipole moment?
- How does it depend on temperature?
- Possible connections to...
 - Mesoscopic superconductivity (Moro *et al.*)
 - Metallic ferroelectricity (Batista *et al.*)
 - Quantum electric dipoles (Allen *et al.*)

Methods

- First-principles density functional theory
 - Planewave method using Abinit 4.2.4
 - PBE96 GGA functional
 - Nb (4s, 4p, 4d) norm-conserving pseudopotential
 - Generated with FHI98PP
 - 45 E_H planewave cutoff energy
 - All-electron method using Gaussian98
 - B3PW91 Hybrid Functional
- Relaxed (locally optimized) structures $N \leq 15$
 - V. Kumar and Y. Kawazoe, PRB **65**, 125403 (2002)
 - Exception: Nb₁₃ → new structure

Electric Dipole

Comparison to Experiment



Data: Moro *et al.*, Science **300**, 1265 (2003)

Trends

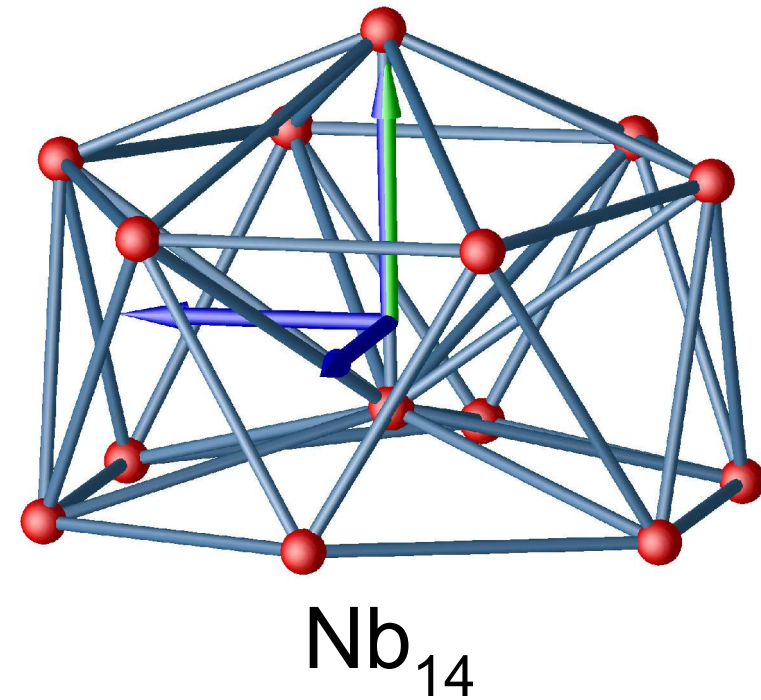
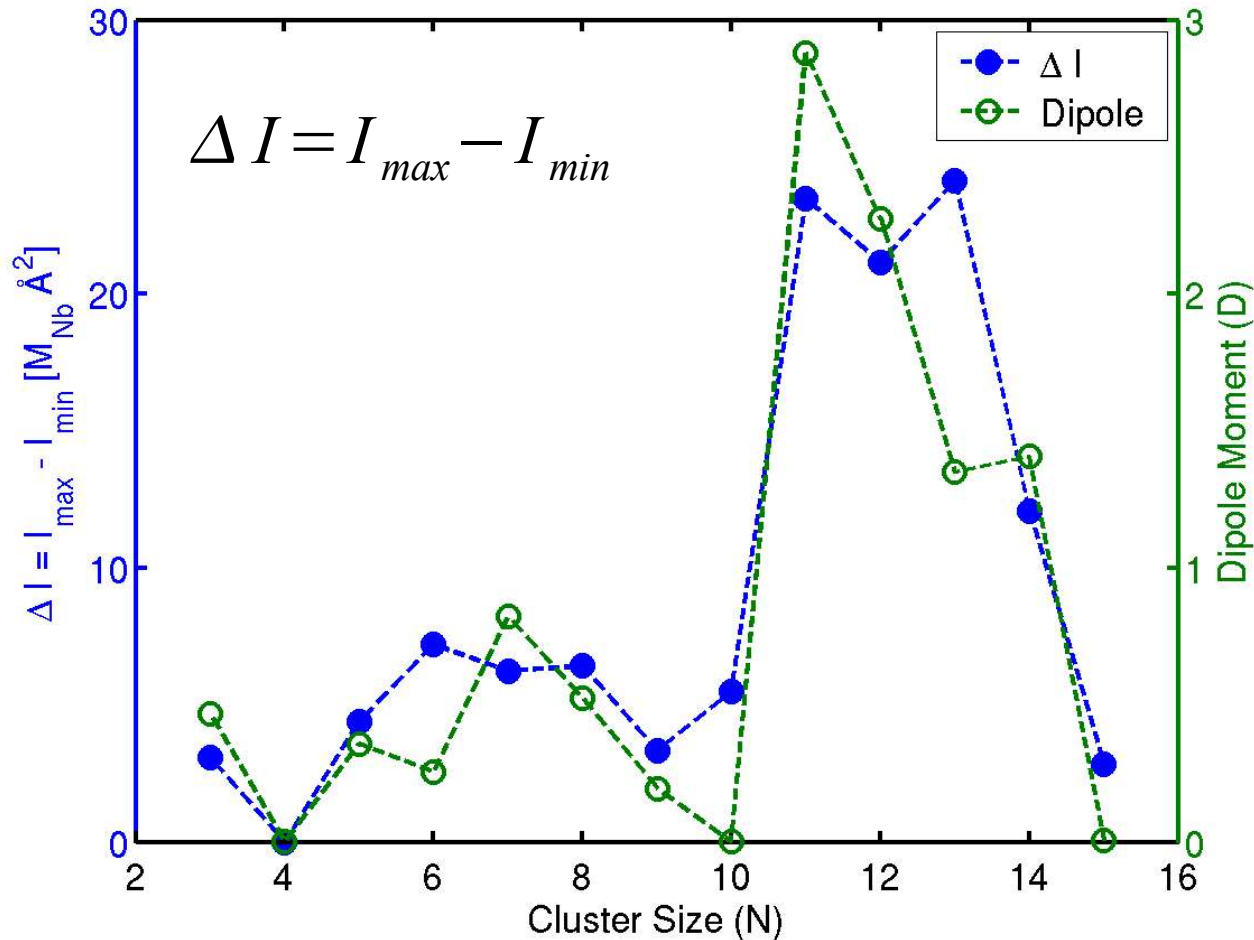
Large Moment
 Nb_{11} - Nb_{14}

Moderate Moment
 Nb_5 - Nb_9

High Symmetry
 Nb_4 , Nb_{10} , Nb_{15}

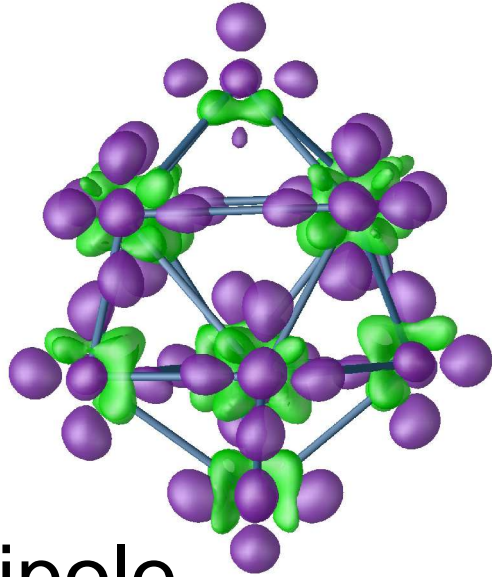
Asymmetry

Principal moments of inertia and axes correlate with the magnitude and *direction* of the electric dipole



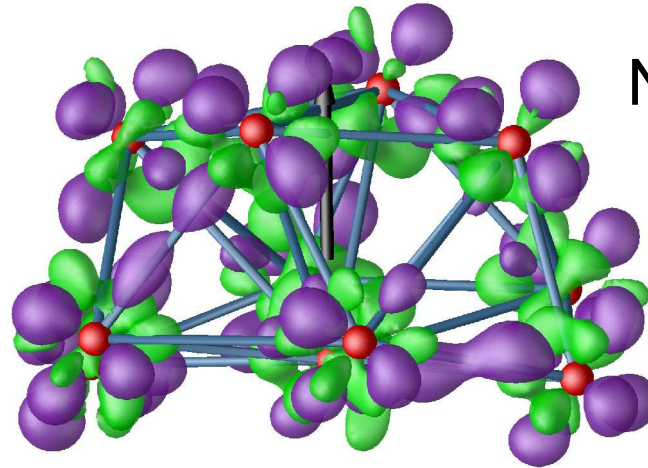
Bond Charge

Nb₁₀



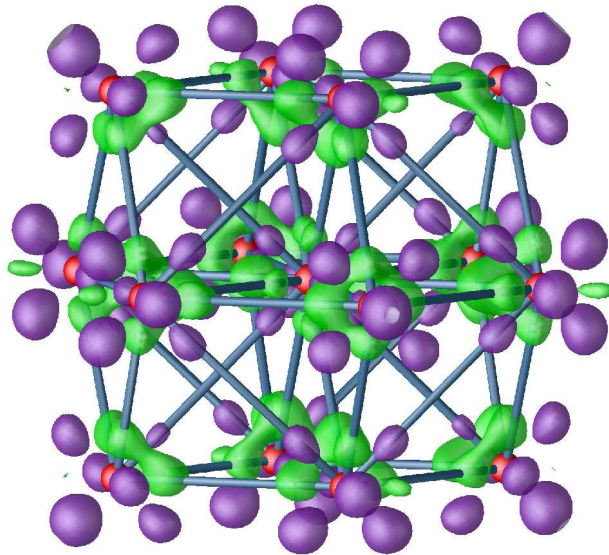
No Dipole

Nb₁₁ (2.9 D)

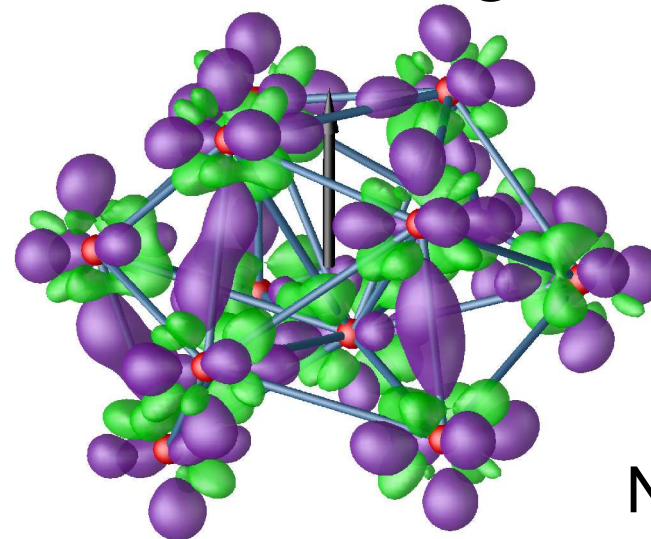


Large Moment

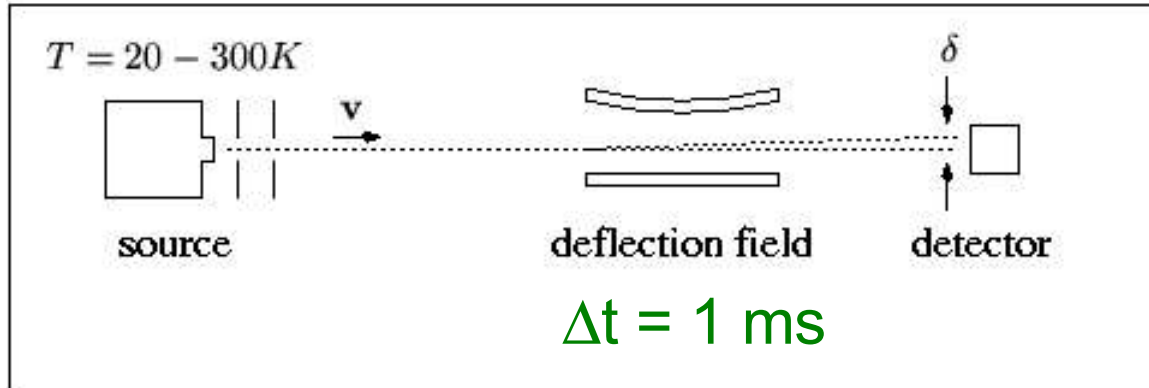
Nb₁₅



Nb₁₂ (2.3 D)



Energy and Time Scales



$T(N)$ = Transition Temp

$T(11) = 110 \text{ K}$

$T(100) = 10 \text{ K}$

Thermal Energy

20–300 K

Dipole Energy (μE)

1 K (per Debye)

Vibrational Energy ($h\nu_{\min}$)

65 K

Magnetic Anisotropy

2 K

Electric Energy Level Spacing Δ_E

1000 K

Rotational Energy Level Spacing Δ_R

0.2 K (at $T = 20 \text{ K}$)

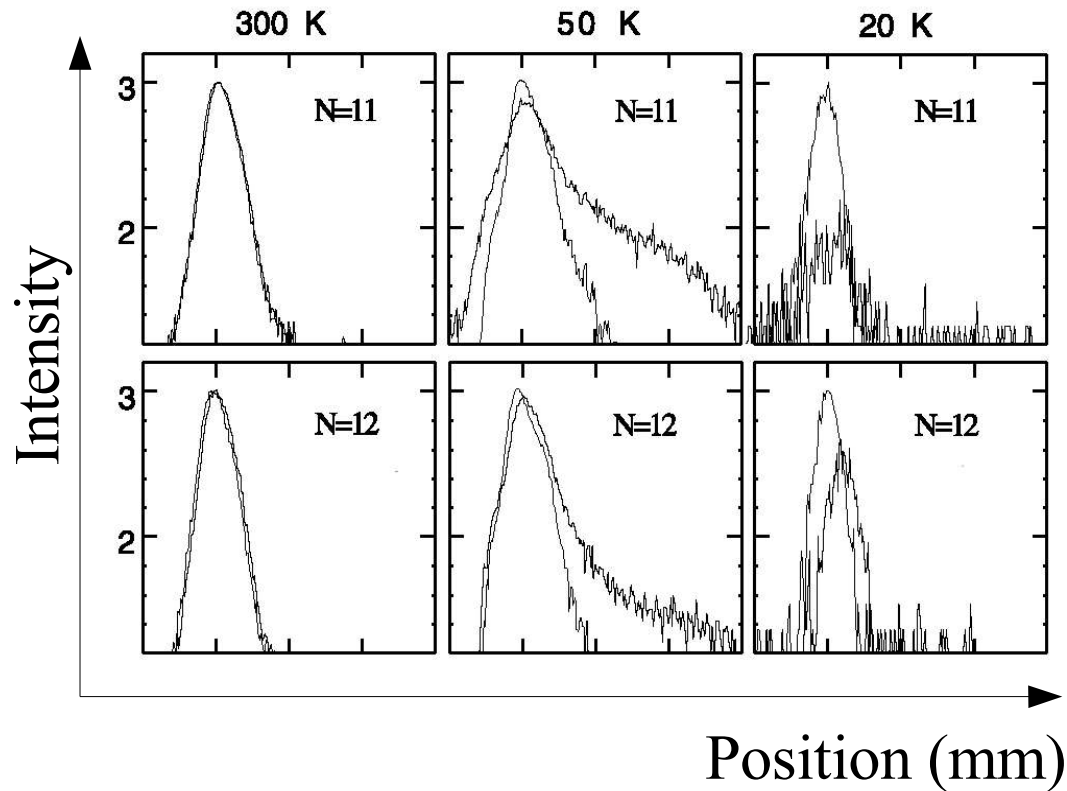
Period of Rotation (τ)

10^{-11} s

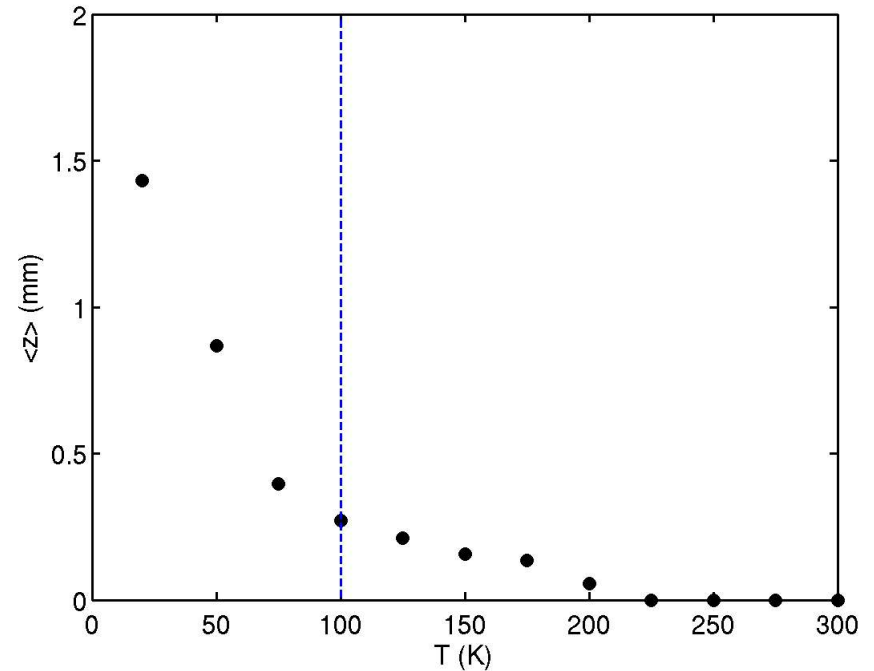
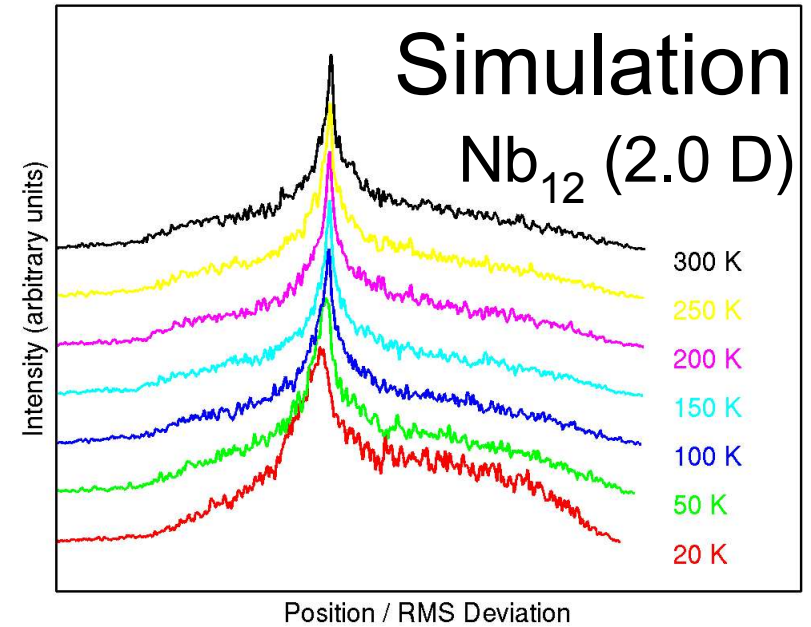
Temperature Dependence

Classical Simulations

Experiment



Source: Moro *et al.*, Science **300** 1265 (2003)



Reference: Dugourd *et al.*, Chem. Phys. Lett. **336**, 511 (2001)

Conclusion

- Calculated permanent electric dipoles generally agree with experiment.
- Dipole moment strongly correlates with the asymmetry of the cluster.
 - Quantified using inertial moments.
 - Asymmetry is enhanced by directional bonding.
- Electric dipole may be masked at higher temperatures due to thermal averaging.
 - Vibrational excitations are negligible.