Origin of electric dipole moments in free niobium clusters

PRL **93**, 246105 (2004)

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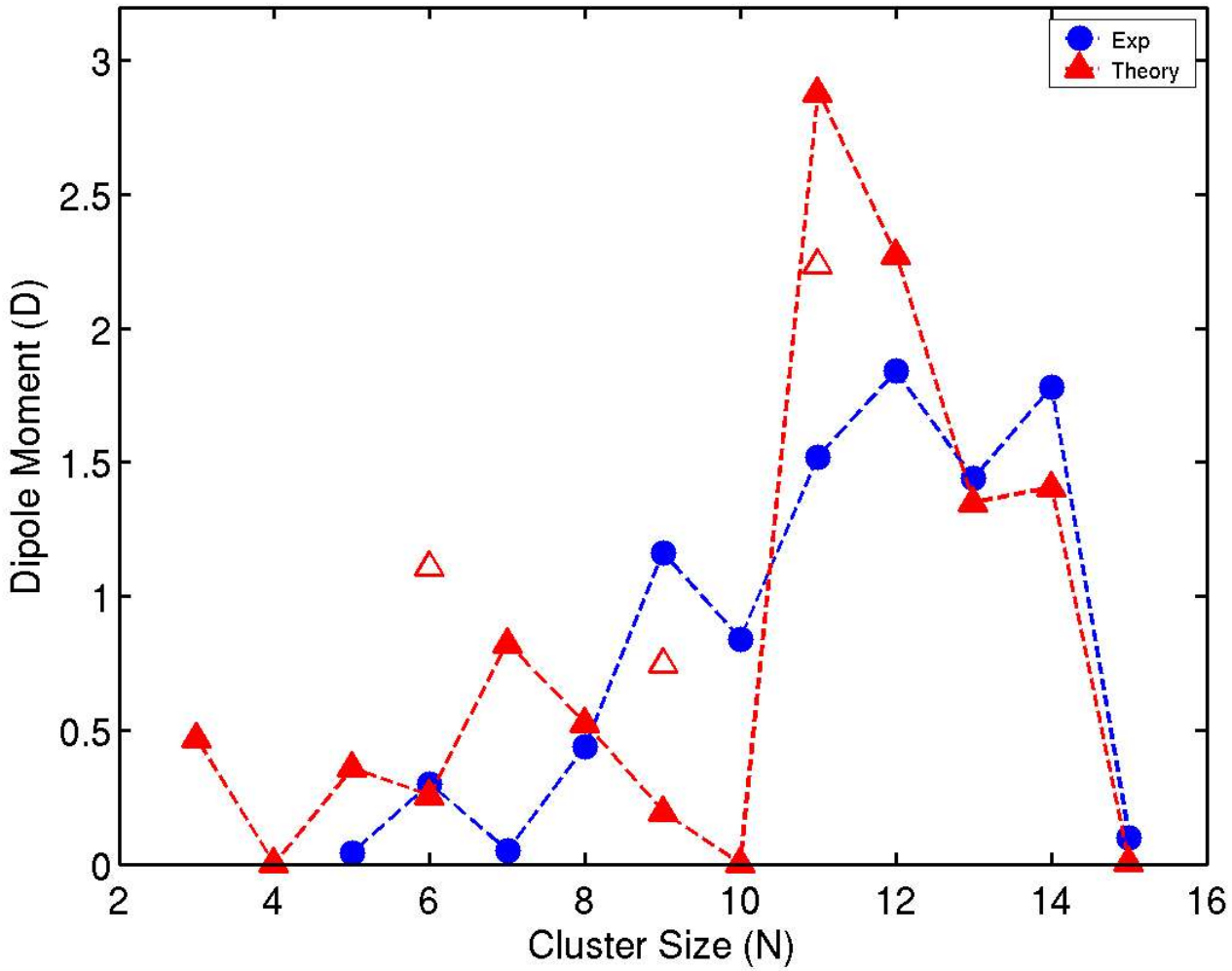
Motivation

- "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: $Nb_{13} \rightarrow$ new structure

Electric Dipole
Comparison to Experiment



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

Trends

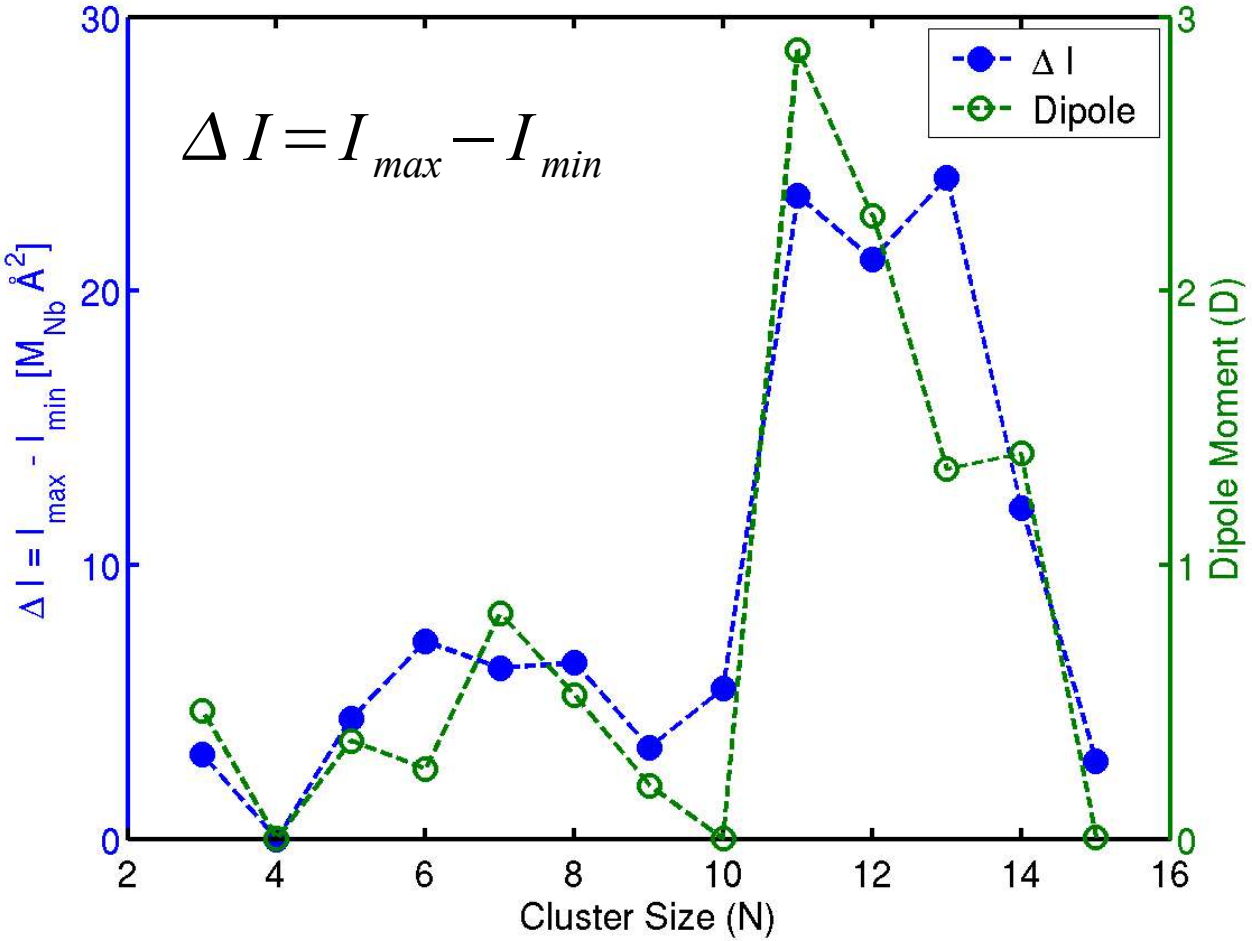
Large Moment
Nb_{11}-Nb_{14}

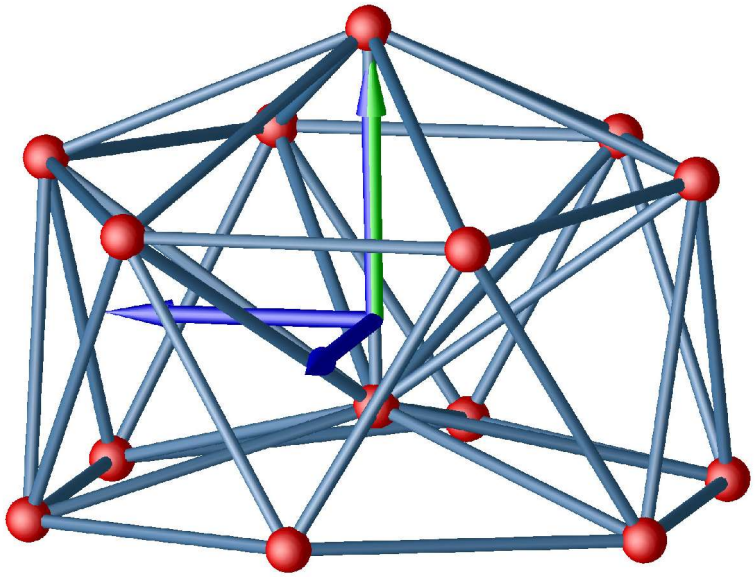
Moderate Moment
Nb_5-Nb_9

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

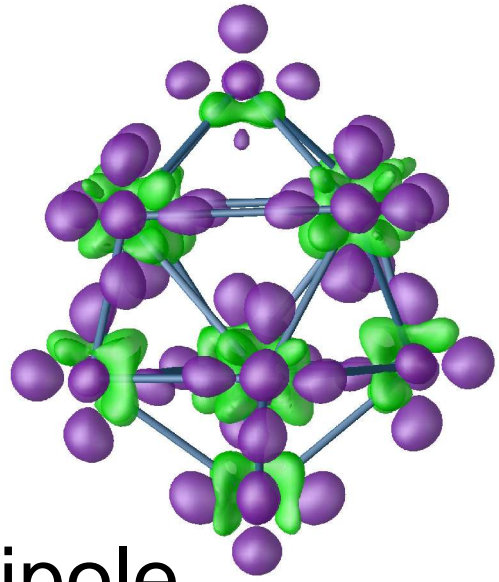




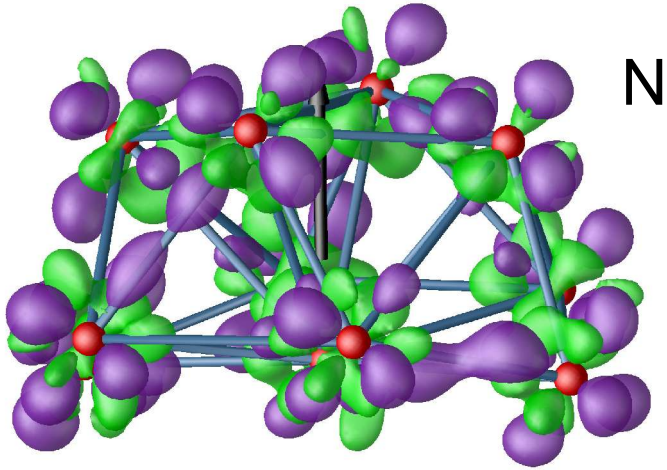
Nb_{14}

Bond Charge

Nb_{10}

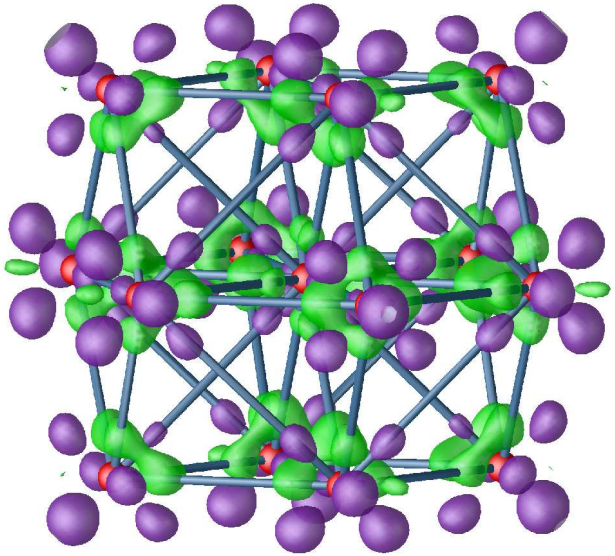


No Dipole

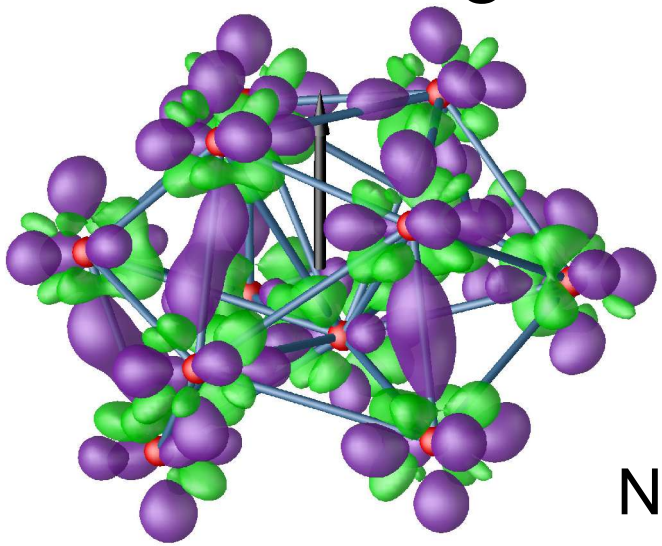


Nb_{11}(2.9 D)

Large Moment

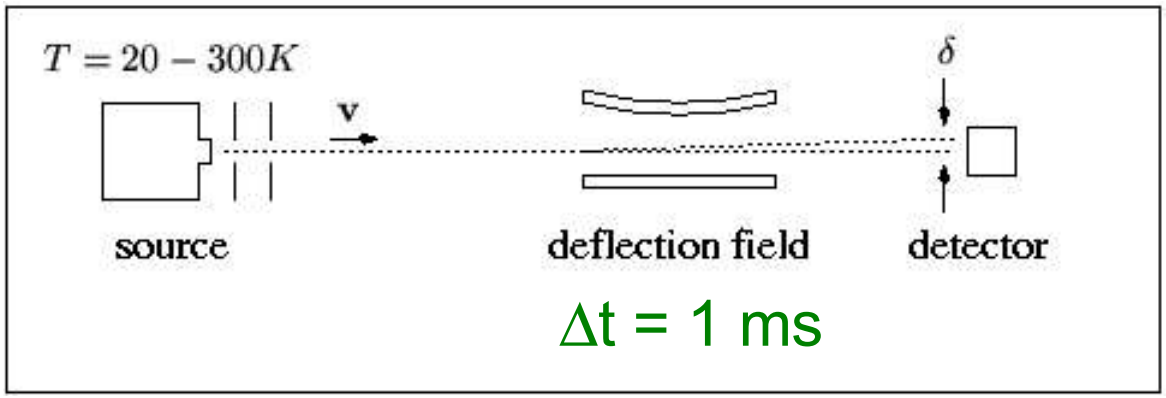


Nb_{15}



Nb_{12} (2.3 D)

Energy and Time Scales



T(*N*) = Transition Temp

T(11) = 110 K

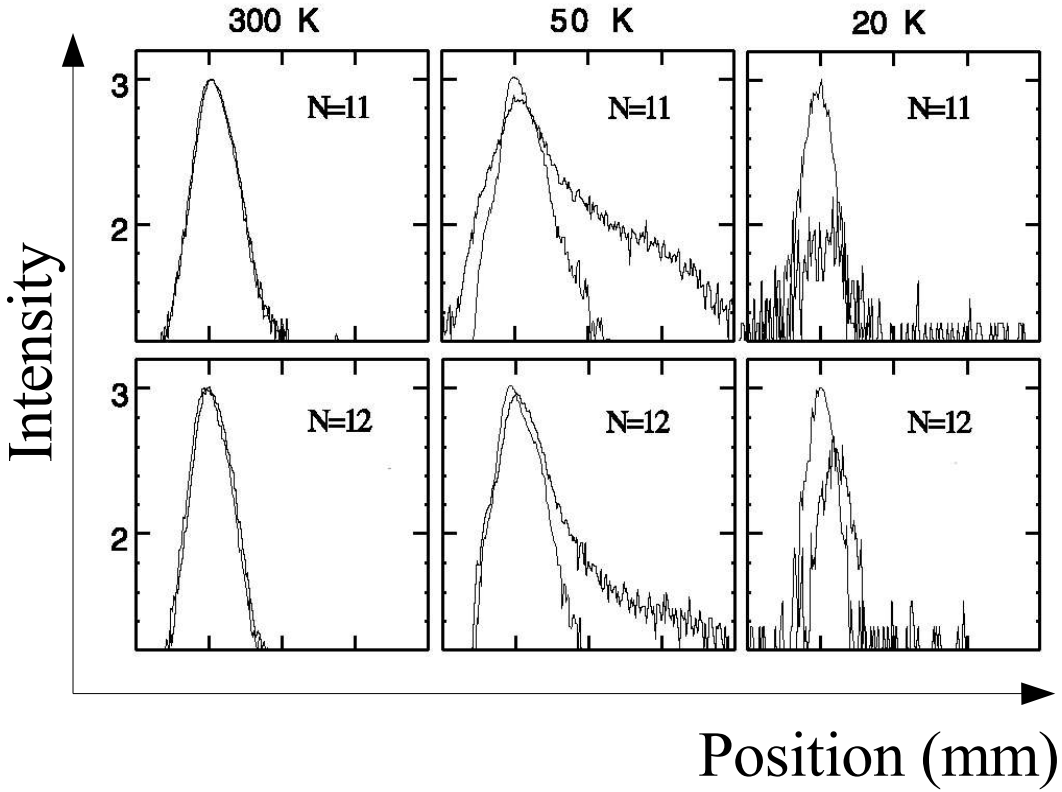
T(100) = 10 K

Thermal Energy	20–300 K
Dipole Energy (μE)	1 K (per Debye)
Vibrational Energy ($hc\nu_{min}$)	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 K)
Period of Rotation (τ)	10^{-11} s

Temperature Dependence

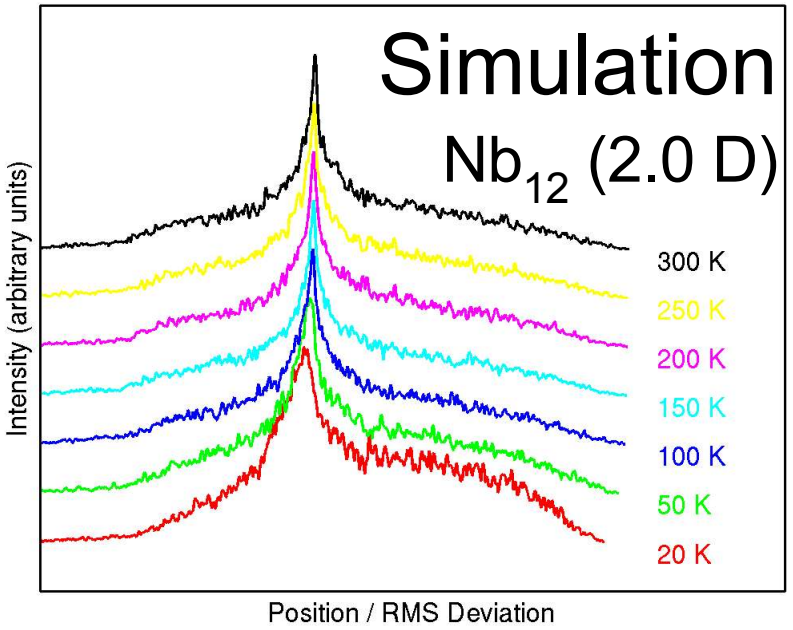
Classical Simulations

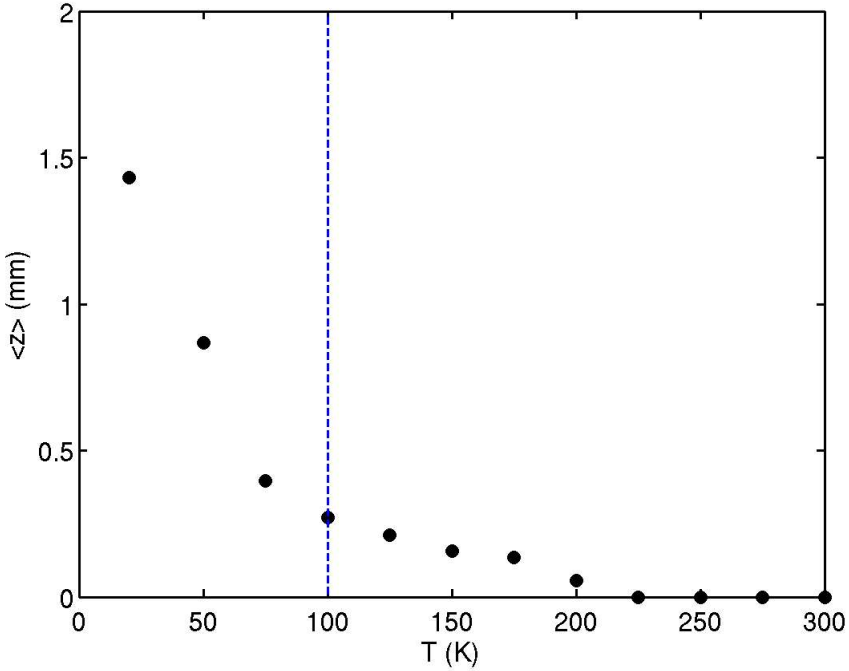
Experiment



Simulation

Nb_{12} (2.0 D)





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.