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著者	Andersen Kristopher E., Kumar Vijay, Kawazoe Yoshiyuki, Pickett Warren E.
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## Origin of Spontaneous Electric Dipoles in Homonuclear Niobium Clusters

Kristopher E. Andersen,<sup>1</sup> Vijay Kumar,<sup>2,3</sup> Yoshiyuki Kawazoe,<sup>3</sup> and Warren E. Pickett<sup>1,\*</sup>

<sup>1</sup>*Department of Physics, University of California, Davis, CA 95616-8677, USA*

<sup>2</sup>*Dr. Vijay Kumar Foundation, 45 Bazaar Street, Chennai 600 078, India*

<sup>3</sup>*Institute for Materials Research, Tohoku University, 2-1-1 Katahira Aoba-ku, Sendai 980-8577, Japan*

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Surprisingly large, spontaneous electric dipole moments recently observed in homonuclear niobium clusters below 100 K (Moro *et al.*, 2003) are explained using first-principles electronic structure calculations. The calculated moments for  $\text{Nb}_n$  ( $n \leq 15$ ) generally agree with the experimental data. A strong correlation is found between the geometrical asymmetry of the cluster and electric dipole: its magnitude is proportional to the spread in the principal moments of inertia and its direction aligns with the axis of the largest principal moment. Charge deformation densities reveal directional, partially covalent bonds that stabilize structural asymmetry. Classical simulations of the deflection of a cluster in a molecular beam reveal that the electronic dipole may persist at higher temperatures, but is masked by the rotational dynamics of the cluster.

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Though the response of nanoparticles to an external electric field has been actively studied for several years, the recent observation of permanent electric dipoles on the order of several debye (D) in free  $\text{Nb}_n$  clusters ( $n \sim 10$ –100) has introduced an entirely new and unexpected dimension. That the intrinsic moment is only observed below temperatures  $T \approx 100$  K for  $n \sim 10$  [1] has led to speculation that the origin of large electric dipoles might be related to superconductivity in bulk Nb (rather robust at  $T_c = 9$  K) and that the dependence on temperature may signal a nanoscale “ferroelectric” transition. Permanent dipoles in mixed clusters and molecules, including canonical polar molecules like  $\text{H}_2\text{O}$  and HF, are well understood in terms of charge transfer between unlike atoms. However, it is more challenging to envision what forces could drive the underlying charge separation in homonuclear clusters of metal atoms. This unexpected and non-intuitive dielectric behavior in Nb clusters [1] has also attracted attention to the conceptually related question of quantum dipoles in symmetric clusters [2,3].

A fundamental requirement for the occurrence of a permanent dipole is the lack of a center of inversion. For a homonuclear system, however, the issue is more complex because disproportionation into charged ions is energetically disfavored. These questions are more perplexing in clusters that are going to become metals (which support no charge separation) as their size increases. Our calculations demonstrate that the origin of these large dipoles does not require a new state of matter related to superconductivity as suggested in Ref. [1], but is explained directly in terms of directional partially covalent bonds that favor the formation of clusters with low symmetry. The resulting charge separation, which implies internal electric fields on the order of  $10^6$  V/cm [1], is sustained by the chemical forces of the Nb bonding. By performing classical simulations of the rotational dynamics of the clusters in a molecular beam, we provide

evidence that thermal averaging, instead of a loss of intrinsic moment, accounts for the observed temperature dependence.

The atomic and electronic structures of neutral  $\text{Nb}_n$  clusters ( $n \leq 23$ ) have been extensively studied using first-principles electronic structure methods [4–7], but there has been no theoretical study of their dielectric properties. In this Letter, the electric dipole moments of  $\text{Nb}_n$  clusters ( $n \leq 15$ ) are analyzed in terms of their asymmetry and charge deformation using the electronic structure codes GAUSSIAN98 [8] and ABINIT [9]. Calculations with GAUSSIAN98 used Stuttgart-Dresden effective core potentials [10] and the B3PW91 [11,12] hybrid exchange-correlation functional. Calculations with ABINIT [9] used the plane wave (norm-conserving) pseudopotential method [13] and Perdew-Burke-Ernzerhof [15] generalized gradient approximation functional. The lowest energy structures as well as isomers close in energy (within 25 meV/atom) obtained by Kumar and Kawazoe [7] were used, except for  $\text{Nb}_{13}$ , for which a new structure lower in energy was found. Isomers of  $\text{Nb}_n^+$  clusters have been observed in spectroscopic [16] and reactivity [17] experiments.

The calculated permanent electric dipoles (Table I) are compared in Fig. 1 with the reported values [1] for Nb clusters emitted after reaching thermal equilibrium with He gas at 50 K. Considering the many uncertainties in presenting such a comparison, the level of agreement is satisfying: moderate moments are found for  $3 \leq n \leq 9$ , large moments for  $11 \leq n \leq 14$ , and essentially zero moments for  $n = 4, 10$ , and 15. The only notable discrepancy is  $\text{Nb}_{10}$  for which experiments show significant dipole moment while theoretically it is zero because of the symmetric nature of the lowest energy structure. A general feature in Fig. 1 is the larger calculated dipole moment in comparison to experiment. This difference may be due to the neglect of rotational dynamics in the ex-

TABLE I. Principal moments of inertia  $I_1$ – $I_3$  ( $M_{\text{Nb}} \text{Å}^2$ ) and dipole moment  $\mu$  (D) for  $\text{Nb}_n$ .

$n$	$I_1$	$I_2$	$I_3$	$\mu$
2	0.00	2.21	2.21	0.0
3	2.69	3.09	5.78	0.5
4	6.33	6.33	6.33	0.0
5	7.60	11.43	12.01	0.4
6	10.50	16.06	17.71	0.3
7	16.78	17.25	23.02	0.8
8	21.24	23.63	27.67	0.5
9	28.89	29.29	32.21	0.2
10	32.54	38.03	38.03	0.0
11	34.51	48.51	57.99	2.9
12	42.97	55.26	64.14	2.3
13	51.28	61.35	75.42	1.4
14	64.32	64.38	76.39	1.4
15	73.59	76.44	76.45	0.0

perimental analysis [1]. Calculations on isomers, such as  $\text{Nb}_{9b}$  and  $\text{Nb}_{11b}$ , whose binding energies are lower by 1 and 9 meV/atom, respectively, show dipole moments closer to the experimental data [1], which may be an indication of isomers in the experimental conditions. However,  $\text{Nb}_{6a}$  is in good agreement with experiment in comparison to  $\text{Nb}_{6b}$ , whose binding energy is also only moderately lower (20 meV/atom).

For  $n > 2$ , only in the case of  $\text{Nb}_4$ , which is a regular tetrahedron [7], does symmetry strictly forbid an electric dipole. Other cases of vanishing dipole moment, such as  $\text{Nb}_{10}$  and  $\text{Nb}_{15}$ , are attributed to near symmetries.  $\text{Nb}_{10}$  has an approximate  $D_{4d}$  symmetry, whereas  $\text{Nb}_{15}$  has near inversion symmetry with a cubic structure. These symmetries are reflected in the cluster's principal moments of inertia  $I_1$ ,  $I_2$ , and  $I_3$  (Table I).  $\text{Nb}_4$ , for example, is a spherical top ( $I_1 = I_2 = I_3$ ), and  $\text{Nb}_{10}$  and  $\text{Nb}_{15}$  are sym-

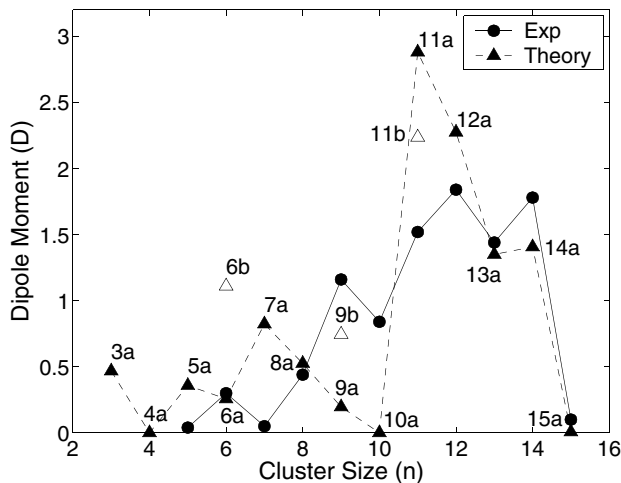


FIG. 1. Comparison of the calculated dipole moments and “low-temperature” (50 K) experimental data from Fig. 2 of Ref. [1] ( $1 \text{ D} = 0.20819e\text{Å}$ ). Higher energy structures are labeled in alphabetical order, following the notation of Ref. [7].

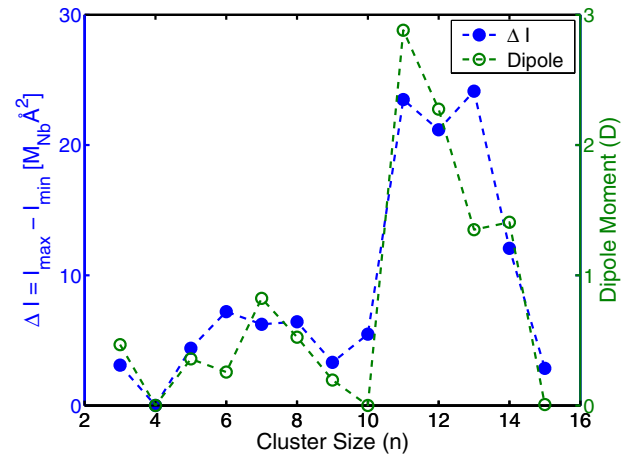


FIG. 2 (color online). The strong correlation between the dipole moment and asymmetry of the cluster, as quantified by the difference between the largest  $I_{\text{max}}$  and smallest  $I_{\text{min}}$  principal moments of inertia.

metrical tops ( $I_2 = I_3 \neq I_1$ ). The rest of the clusters studied are asymmetrical tops ( $I_1 \neq I_2 \neq I_3$ ). One measure of the degree of asymmetry is the spread  $\Delta I = I_{\text{max}} - I_{\text{min}}$ , where  $I_{\text{max}}$  ( $I_{\text{min}}$ ) is the largest (smallest) principal moment of inertia. Figure 2 shows the strong correlation between  $\Delta I$  and the calculated electric dipole. Since the principal moments of inertia map the dynamics of a rigid body to that of an ellipsoid,  $\Delta I$  can be interpreted as quantifying the existence of a preferred structural axis in the cluster. This interpretation is supported by the alignment of the electric dipole. In cases where  $\Delta I$  is large ( $\text{Nb}_{11}$ – $\text{Nb}_{14}$ ), the direction of the dipole moment and the principal axis corresponding to  $I_{\text{max}}$  are close to collinear. The  $26^\circ$  deviation from collinearity of  $\text{Nb}_{12}$  is the only exception to this otherwise near-perfect (within  $5^\circ$ ) collinearity.

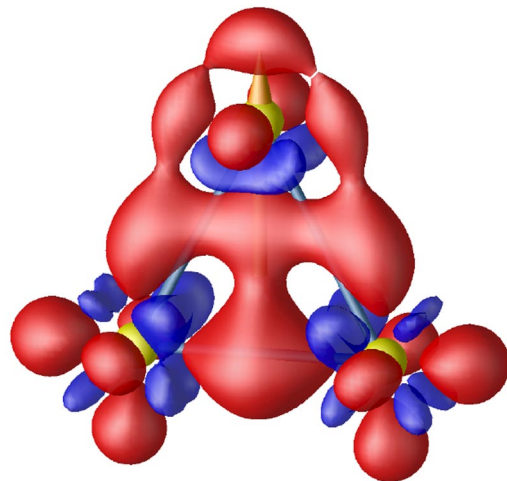


FIG. 3 (color online). Charge deformation of  $\text{Nb}_3$  (0.5 D). Because of the mirror symmetry, the dipole moment (orange arrow) is restricted to lie on the symmetry axis.

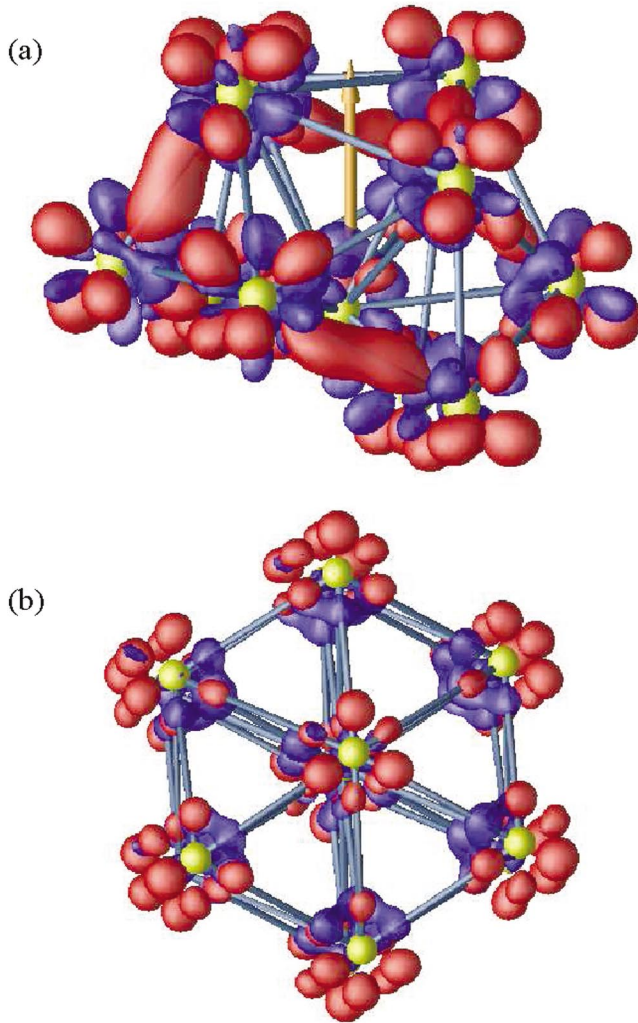


FIG. 4 (color). Charge deformation for (a)  $\text{Nb}_{12}$  (2.3 D) and (b)  $\text{Nb}_{15}$  (no dipole). The direction of the dipole moment is represented by the orange arrow. Note the formation of covalent bonding. Unlike systems with a large dipole moment, no asymmetric covalency is seen in  $\text{Nb}_{15}$ . Instead, the charge deformation density is entirely intra-atomic.

To understand the origin of the electric dipole, we consider the charge deformation density due to bonding, that is, the difference between the charge density of the cluster and that of isostructural spherical neutral atoms, for which the dipole moment vanishes. Figure 3 shows the charge deformation for the simple and illustrative case of  $\text{Nb}_3$  [18], an isosceles triangle [7] with a dipole moment of 0.5 D. In Fig. 3, two isosurfaces are shown. The blue (red) surface corresponds to a negative (positive) isocontour of value  $-2.0e/\text{\AA}^3$  ( $+2.0e/\text{\AA}^3$ ). Taken together, these isosurfaces show how charge redistributes during the formation of bonds. Two general features can be discerned. First is the formation of a few specific covalent bonds as revealed by the charge buildup between ions, which reflects charge being pulled in from elsewhere in the cluster. Second, some charge is pushed outward at each surface site due to Coulomb repulsion.

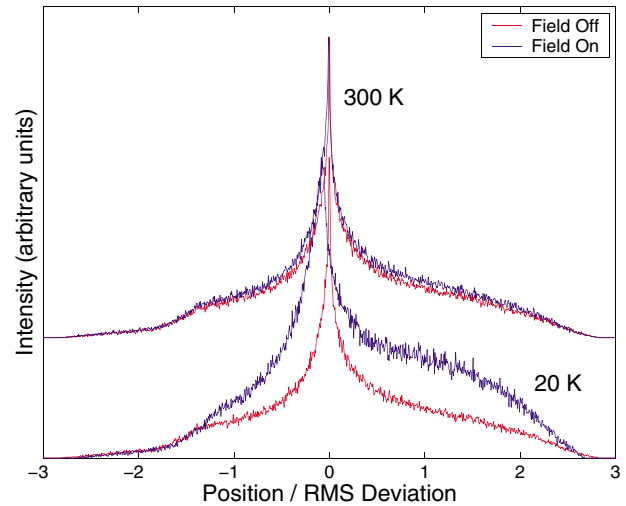


FIG. 5 (color). Classical deflection of a model  $\text{Nb}_{12}$  cluster with a dipole moment  $\mu = 2$  D at 300 K (top) and 20 K (bottom). At higher temperatures, the rotational dynamics masks the permanent dipole moment.

Figure 4 shows the charge deformation for  $\text{Nb}_{12}$  and  $\text{Nb}_{15}$ , which are representative of clusters with large dipole moment and no dipole moment, respectively. The same color scheme and isocontour values are used as in Fig. 3 and the general features remain. Only in cases with a dipole moment, such as  $\text{Nb}_{12}$ , is there an asymmetric character to the deformation density. This reveals how strong directional bonding in isolated regions of the cluster leads to the formation of low symmetry geometries, and thereby to the intrinsic charge separation giving rise to the permanent dipole moment.

An additional aspect of the experiments of Moro *et al.* is the disappearance of the dipole (i.e., a change in the deflection of the cluster beam) when the clusters are formed at higher temperatures [1], which has been likened to a ferroelectric transition. One possible mechanism for the disappearance of the polarized electric state is the thermal excitation of vibrational modes within the cluster, which should be directly related to the temperature at which the clusters are formed. The charge response to vibrations might disturb the intrinsic charge separation in the static cluster at equilibrium. In addition, if the direction of the dipole moment were to fluctuate, this charge separation, if still in existence, could become unobservable if the time average of the dipole moment  $\langle \vec{\mu} \rangle$  were sufficiently reduced. Such vibration-induced fluctuations of the dipole moment are known to be important in weakly bound molecules [19].

To quantify the influence of vibrations, we calculated the vibrational spectrum for  $\text{Nb}_{12}$ , a cluster with a large permanent electric dipole (2.3 D), and looked at the excitation of the six lowest energy vibrational modes between 60–105  $\text{cm}^{-1}$ . These are in the range of those that would be excited during the experimentally observed transition, which occurs at a temperature on the order of

100 K. The atomic displacements associated with these vibrations are less than 0.1 Å and are unable to significantly alter the charge density or the permanent dipole, with relative changes of less than 3% or 0.1 D in magnitude and a few degrees in direction. This implies that another mechanism, beyond harmonic vibrations, is needed to explain the disappearance of the dipole moment.

Classical simulations by Dugourd *et al.* [20], using the thermal occupation of rotational states, were able to reproduce the molecular beam deflection of TiC<sub>60</sub> clusters, but full temperature dependence was not studied. Figure 5 shows the classical deflection of a representative niobium cluster (Nb<sub>12</sub>) with a dipole moment of 2 D at 20 and 300 K when the homogeneous electric field is on and off. These profiles were obtained by numerically evaluating the deflection [20] of 10<sup>6</sup> random initial configurations (orientation and rotational energy) of a cluster with symmetric inertial moments  $I_1 = I_2 = 45M_{\text{Nb}} \text{ \AA}^2$  and  $I_3 = 65M_{\text{Nb}} \text{ \AA}^2$ . The deflection due to the induced dipole, which would shift each profile a constant distance, has been ignored by setting the electric polarization  $\alpha = 0$ . In addition, the broadening of the profile due simply to the cluster's reduced translational velocity at lower temperature has been divided out.

The classical deflection profile Fig. 5 and the experimental profiles in Ref. [1] agree qualitatively. In particular, the asymmetric shape at lower temperatures, which is an experimental signature of the permanent moment [1], is clearly seen in the profile at 20 K. At 300 K the deflection profile is more symmetric, which has been interpreted as a loss of the intrinsic moment [1], but in this simulation is the effect of additional thermal averaging.

Finally we return to the question of (a lack of) symmetry with which we began. Our calculations have traced the origin of large spontaneous electric dipoles to the structural asymmetry of Nb<sub>n</sub> clusters that is enhanced by the directional bonding favored by *d* electrons. These correlations can be sharpened. First, the asymmetric inertial moments observed in systems with large electric dipole moment result from oblate, not prolate, cluster shapes. Second, although the magnitude and direction of the electric dipole correlate very strongly with an (asymmetric) imbalance of inertial moments, this cannot be the whole story, since breaking reflection symmetry—of which the inertial moments themselves provide no information—is required for dipole formation.

That much of the apparent temperature dependence of the electric dipole can be explained classically implies a more rigorous treatment of rotational dynamics [21] may be required to distinguish induced versus permanent dipole effects in experiment accurately. However, because the structure of the deflection profile is richer at low

temperatures, and depends directly on the inertial moments of the cluster, future low-temperature molecular beam experiments combined with detailed modeling of the dynamics have the potential to extract structural information that is directly comparable to theoretical predictions.

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\*Electronic address: pickett@physics.ucdavis.edu

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