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‘Madelung model’ prediction for dependence of lattice parameter on nanocrystal size

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Abstract

The competition between the long-range Coulomb attractive and the short-range repulsive interaction in ionic nanocrystals creates an effective negative pressure, which causes the lattice parameter a to increase with decreasing nanoparticle size d . A simple ‘Madelung model’ is used to predict the dependence of the lattice parameter for CeO₂ and BaTiO₃ on d , $\delta a/a = \alpha/d$, for $\alpha = 0.22$ and 0.18 Å, respectively. The model predictions are compared with experimental results. © 2002 Elsevier Science Ltd. All rights reserved.

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How properties of ionic crystals change when their surface to volume ratio becomes large is an active area of research [1–7]. The ceria nanoparticles CeO₂ have been studied experimentally using Raman, X-ray diffraction, photo-absorption, high resolution transmission electron microscopy (HRTEM) [1,2], and transmission electron microscopy [3–5]. The fascinating property of ionic nanoparticles is the lattice parameter increase with nanoparticle decreasing size [1,4,5]. Intuitively one would expect the lattice parameter to decrease as a result of surface stress as was observed in gold nanoparticles [8].

Nanocrystal properties are significantly different from their bulk counterparts. Previous theoretical treatments [6,7] used realistic potentials for small Ce_nO_{2n} cluster calculations. It was shown that fluorite structure for ceria was not achieved for $n < 50$. In the present work we investigate lattice parameter dependence on a cluster size for $d = 4–20$ nm or $n = 10^3–10^5$. Charge neutral octahedra nanocrystals are surface terminated with oxygen anion layers along the eight {111} faces. The balance between the

long-range Coulomb and the short-range atomic interactions leads to the optimal lattice parameter a_0 dependent on the size of the cluster. The volume energy per formula unit in the bulk material is usually modeled as

$$\varepsilon_v = \frac{BV_0}{2} \left(\frac{V}{V_0} - 1 \right)^2, \quad (1)$$

where B is the bulk modulus and $E_v = N\varepsilon_v$ the volume energy of N formula units of CeO₂, each filling volume space $V_0 = a_0^3/4$. In the infinite crystal Eq. (1) is the total free energy which is minimum at the bulk lattice parameter a_0 . In the nanocrystal the balance between the Coulomb and short-range forces is altered due to the surface. The surface Coulomb energy creates a negative pressure which leads to the lattice parameter expansion in the nanocrystal in accord with observation [1].

To calculate the Coulomb energy in ionic nanoparticles we use the same procedure as Madelung energy calculation in bulk material [9]. In the fluorite (CaF₂) structure the Ce⁴⁺ ions occupy a fcc sublattice and O²⁻ ions occupy the tetrahedral interstitial sites forming a simple cubic sublattice of length $a_0/2$. This gives a Madelung energy per formula unit $\varepsilon_{\text{Mad}} = \beta_{\text{bulk}} e^2/a$, where $\beta_{\text{bulk}} = -46.55$. The value of $\beta = Mz_i z_j / r_0$ is related to the Madelung constant $M = 2.52$ for the CaF₂ crystal structure [10], where ionic charges are

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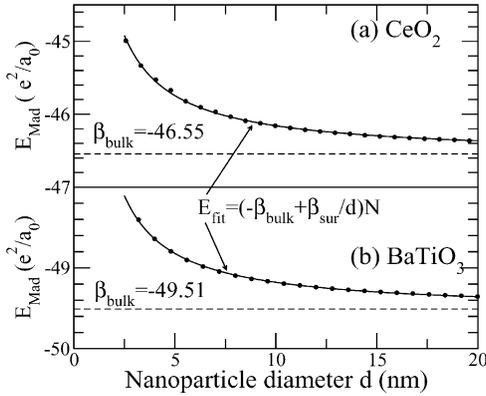


Fig. 1. Closed circles are model calculations of the Madelung energy on ionic (a) CeO₂ and (b) BaTiO₃ nanocrystals. The CeO₂ nanocrystal was terminated by eighth (111) planes and BaTiO₃ by six (100) planes. The solid lines are the best fits using Eq. (2).

$z_i = 2$, $z_j = 4$ and the nearest neighbor distance is $r_0 = \sqrt{3}/4$ in units of a . To calculate the surface Madelung energy we use a finite size cluster of Ce⁴⁺ and O²⁻ ions terminated by the oxygen layers along the eight (111) planes. The surface energy is proportional to the area of nanoparticle $\sim N^{2/3}$. The diameter $d = (3N/2\pi)^{1/3}a_0$ is related to the number of Ce atoms N such that the sphere of equal diameter contains an equal volume NV_0 . The Madelung energy of a cluster (with a uniform lattice parameter) can be calculated for different diameters. The results are shown in Fig. 1(a), which are well fitted by

$$\frac{E_{\text{Mad}}}{N} = \left(-\beta_{\text{bulk}} + \frac{\beta_{\text{sur}}}{d} \right) \frac{e^2}{a} \quad (2)$$

with two parameters $\beta_{\text{bulk}} = 46.55$ and $\beta_{\text{sur}} = 4.13$ nm.

The uniform lattice parameter expansion reduces the surface Madelung energy creating the stress in the nanocrystal estimated with Eq. (1). The total energy per Ce atom on the nanoparticle is

$$\frac{E_{\text{tot}}}{N} = \frac{BV_0}{2} \left(\frac{a^3}{a_0^3} - 1 \right) + \frac{\beta_{\text{sur}}}{d} \frac{e^2}{a}. \quad (3)$$

Here the first term is the volume contribution, which includes the Madelung energy of the infinite crystal, and the second term is the surface Coulomb energy from Eq. (2). Minimization of the total energy with respect to the lattice parameter for fixed N gives

$$\frac{\delta a}{a_0} = \frac{1}{9BV_0} \frac{e^2}{a_0} \frac{\beta_{\text{sur}}}{d} = \frac{\alpha}{d}. \quad (4)$$

The bulk modulus $B = 230 \pm 10$ GPa has been measured by high-pressure X-ray diffraction [10]. Taking $a_0 = 5.409$ Å we obtain the relation $\delta a/a_0 = 0.22$ Å/d for the lattice parameter expansion shown in Fig. 2. The experimental lattice parameter (also shown in Fig. 2) expands with a larger slope $\alpha = 0.37$ Å. Our model predicts 60% of the measured value of α . The missing 40% of the lattice

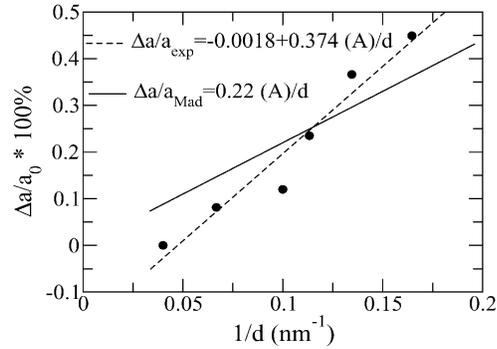


Fig. 2. Filled circles are experimental lattice parameters versus inverse diameter of CeO₂ nanoparticle. Dashed line is the best fit for the experimental data [1]. Solid line is a Madelung model prediction $\delta a/a = 0.22$ Å/d.

parameter expansion might be assigned to the formation of point defects. These defects are oxygen vacancies and simultaneous reduction of two ions of Ce⁴⁺ to Ce³⁺ for each oxygen vacancy formed, maintaining charge neutrality. Electron spectroscopy [11] and X-ray photoelectron spectroscopy [3] show the presence of a Ce³⁺ component in nanocrystals. Since Ce³⁺ has a larger radius compared to Ce⁴⁺ there may be a lattice expansion accompanying the replacement of (Ce⁴⁺)₂O²⁻ by Ce³⁺V where V is a neutral oxygen vacancy. An upper limit in the Ce³⁺ contribution to expansion was estimated [1] by interpolation of published results of the variation in ceria lattice parameter with RE³⁺ radii from doping with different rare earth oxides (RE₂O₃) [12,13]. Recent neutron diffraction measurements on nanoscale powder of CeO₂ [14] suggest associated oxygen defect formation (involving oxygen vacancies and self-interstitials) in the fluorite structure. Such defects are not included in our model and may alter the surface Madelung energy estimation.

The Madelung model is valid for any ionic nanocrystal. We apply it for the BaTiO₃ nanoparticles to calculate the competition between the long-range Coulomb and the short-range atomic interactions. The results are shown in Fig. 1(b). Ionic charges Ba²⁺, Ti⁴⁺ and O²⁻ were used to calculate the surface energy of the nanoparticle. To preserve charge neutrality the cubic nanocrystal with size d was terminated by the three BaO and three TiO₂ {100} planes. The calculated value of $\beta_{\text{sur}} = 3.6$ nm along with the experimental lattice parameter $a_0 = 3.996$ Å and bulk modulus $B = 196$ GPa [15] predicts $\delta a/a_0 = 0.18$ Å/d. Existing data [5] on BaTiO₃ nanoparticles are not sufficient to verify the relationship Eq. (4) and further experiments are needed.

In conclusion we propose a mechanism for lattice parameter expansion of ionic nanocrystals due to the effective negative Madelung pressure. Using the experimental bulk modulus we quantitatively explain a lattice parameter expansion in ionic materials. A discrepancy between the model prediction and observed effect in CeO₂ can be attributed to the Ce³⁺ component [3,4] and other

defects not included in our model. The Ce^{3+} concentration deduced from magnetic measurements [4] suggests a much smaller value than expected from lattice expansion measurements in accord with our theory. A non-uniform lattice parameter expansion and structural defect formation [14] would change the quantitative answer, but not the conclusion that an effective negative Madelung pressure is significant in ionic nanocrystals.

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