Disordered global-minima structures for Zn and Cd nanoclusters

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The most stable isomers of zinc and cadmium nanoclusters of the normally geometrically closed shell, "magic" sizes of 13, 38, 55, 75, and 147 atoms, are found to be of very low symmetry or disordered. The normally global minimum, highly symmetric, ordered icosahedral structures at 13, 55, and 147 atoms, and the Marks decahedral at 75 atoms, are found to be unstable. The 38-atom fcc truncated octahedron is stable for Zn, but unstable for Cd. The lowest energy configurations were obtained using an *n*-body Gupta potential and employing a global, evolutive search algorithm. All structures were relaxed with density-functional theory calculations at both the LDA and GGA levels which confirmed the greater stability of the disordered isomers. Structure factors are given for anticipated comparison with experiment.

We have recently predicted that gold nanoclusters of geometrically closed shell sizes of 38, 55 and 75 atoms (an intermediate subset of the so-called "magic" size clusters), have disordered global minima geometries at all temperatures up to at least 300 K.[1–3] Recent experimental data lend support to this result.[2,4] Since the chemical, electronic, optical, and other properties of these systems are sensitive to the geometrical configurations of the lowest energy isomers, confirmation would have important implication to the applied fields of catalysis[5,6] and nano-electronics/optics.[7–9]

An important question is whether other metals of the Periodic Table are also disordered in their lowest energy nanostructured geometries. There are indications that certain Pt nanoclusters may be disordered,[10,11] and theoretical calculations on the compromise between internal strain and surface atom coordination suggest that indeed they should be.[12] Other first principles investigations on Al clusters[13] also suggest a high degree of structural distortion for the 55 atom, normally icosahedral, structure.

The investigations described here, based on global searches with the *n*-body Gupta potential and further relaxation with density-functional theory (DFT), indicate that only nanoclusters of the transition metals Zn and Cd are disordered in their most stable configuration for all of the magic sizes up to at least 147 atoms, and probably even beyond 192 atoms. This is a surprising result since the sizes of 13, 55, and 147 atoms normally correspond to the ordered, closed-shell icosahedral structure; 38 atoms to the ordered, fcc truncated octahedral; and 75, 146, and 192 atoms to the ordered, Marks decahedral. These are the most stable geometries; for example, for Ni and Ag,[2] for Rh,[14] and for most other transition metals.[15] These normally global minimum ordered structures were in fact found to be unstable for both Zn and Cd, except for the fcc structure of Zn_{38}.

Zn is directly above Cd in the Periodic Table, the two metals falling within the first and second transition series, respectively. Both elements have all electronic shells closed. In the bulk, both Zn and Cd are of the hexagonal close-packed (hcp) structure with an unusually large c/a ratio (1.856 and 1.886, respectively) about 15% greater than the

ideal hcp structure of $c/a = \sqrt{8/3}$. This has been explained through reduction in the band structure energy through lattice distortion.[16] Both metals have relatively low melting temperatures, 692.5 and 594 K respectively. Zn and Cd in the bulk have been used as effective catalysts for many reactions, and recent results of increased activity with metal nanocluster catalysts[5,6] hint at intriguing possibilities for Zn and Cd nanoclusters. Despite their interesting atomic and bulk properties only recently has experimental work begun on elucidating the characteristics of Zn and Cd nanoparticles[17] and, the authors are not aware of any prior theoretical works on these clusters.

The choice of using the *n*-body Gupta potential in the search for other possibly disordered candidate metals from the Periodic Table was based on our good experience with this potential in modeling Ni, Ag, and Au nanoclusters,[1,2] qualified by confirmation using density-functional theory of the geometry and stability of the predicted structures. The Gupta potential[18] is based on a second-moment approximation of the electron density of states of a tight-binding Hamiltonian and has the following form,[19]

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

The free parameters $A, \xi, p,$ and q are fitted to the experimental values of the bulk cohesive energy, lattice parameters and elastic constants. The nearest neighbor distance r_{0n} is a function of the type and number of atoms n in the cluster. In the results presented here, reduced units are used in which $r_{0n} = 1.0$, except in the calculation of the free energies for which DFT calculated distances were used.

The search for nanoclusters of other elements disordered in their most stable geometry consisted of first delineating a region in the "$p-q$" parameter space for which the disordered global minimum geometry found for Au_{38} (Refs. 2 and 3) had a lower energy than the lowest energy ordered struc-
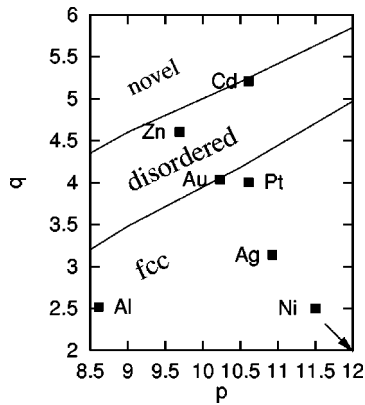
FIG. 1. Plot of the regions in the $p-q$ parameter space of the Gupta potential where the global minimum configuration of 38 atoms corresponds to the "disordered" and "fcc" structures. Of all the transition metals, only Zn, Cd, and Au lie within the disordered region. See text for an explanation of the "novel" region.

ture, which is the fcc truncated octahedron. The most extensive parameterizations of the Gupta potential by Cleri and Rosato for transition metals[19] indicate that apart from Au, only Zn and Cd have the appropriate combination of p and q (Fig. 1). Surprisingly, neither the parameterization of Pt, nor that of Al, suggest that they should be disordered in their lowest energy configuration of 38 atoms. The region labeled "novel" in the figure corresponds to a region within which neither the disordered nor the ordered structures are stable (see Ref. 2), here the stable structures are clusters of dimers and trimers.

Using the parametrizations of Cleri and Rosato (Table I) an exhaustive global search for the lowest energy isomers of Zn and Cd was then performed on the Gupta potential energy surface. The search employed a symbiotic algorithm,[20] an efficient variant of the genetic algorithm, followed by a conjugate gradient relaxation. 100 000 such global searches were performed, starting from different random initial configurations of the atoms, for each element and for each cluster size. An additional 20 000 searches were performed, starting from the geometries of the lowest energy isomers thus found, for the largest sizes of 75, 146, 147, and 192 atoms. This search produced an extensive distribution of low energy minima (Fig. 2) and confirmed that the global minima at all magic sizes were indeed disordered. A further search, of roughly the same CPU time, was performed for the global minima candidates with the basin-hopping algorithm.[15] This search confirmed the global minima at 13 and 38 atoms, found a lower minimum at 55 atoms, but did not find the candidates (nor structures lower in energy) at 75 and 147 atoms.

Figure 3 presents two mutually perpendicular views of the geometry of the lowest energy isomer found for each metal at each cluster size. Although the sizes of 13, 38, and 55

TABLE I. Parametrization of the Gupta potential used in this work (Ref. 19).

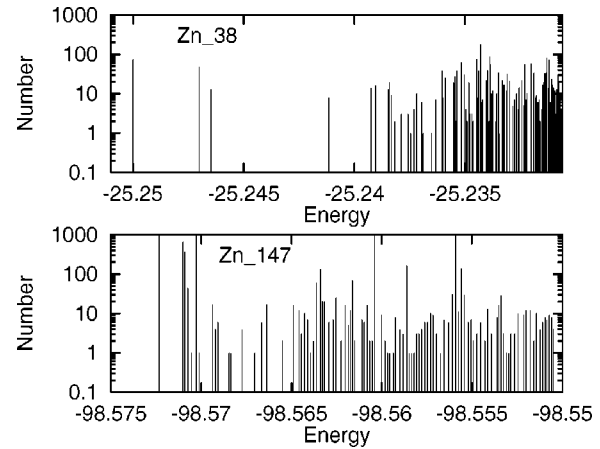|	A [eV]	ξ [eV]	p	q
Zn	0.1477	0.8900	9.689	4.602
Cd	0.1420	0.8117	10.612	5.206

FIG. 2. Energy distribution of the 100 lowest energy stationary configurations found in 100000 and 120000 runs of the symbiotic algorithm for Zn_{38} and Zn_{147}, respectively. The number of times the configuration was found is plotted on a logarithmic scale on the y axis.

atoms have one plane of symmetry, there is no other discernible order. The normally global minimum ordered structures are given for comparison. All the icosahedral structures and the Marks decahedral structures for both metals are unstable. Although all are stationary points, they have very small negative eigenvalues in the Hessian which cause them to deform upon tight relaxation (using the potential) into very distorted versions of high energy with respect to the disordered global minima appearing to the left in Fig. 3. The fcc truncated octahedron of 38 atoms is unstable for Cd but stable for Zn.

The binding energies of the three lowest energy isomers found (all disordered) are listed in Table II. The disordered nature of the global minima for the Zn and Cd nanoclusters can be appreciated by comparing their pair distribution functions with the more discrete distributions of the normally global minimum ordered structure of the same number of atoms (Fig. 4). Another indication of their disordered nature is that none of the global minima presented in Fig. 3 (except Cd_{38}) have degenerate vibrational normal modes.

We verified the potential model predictions for the stability, geometry, and energy ordering of all structures by con-

TABLE II. Gupta potential binding energies (eV) of the three lowest energy isomers found for each cluster size.

	Isomer		
	1	2	3
Zn_{13}	−17.03214	−17.03168	−17.02912
Cd_{13}	−14.9603	−14.96018	−14.95902
Zn_{38}	−50.49998	−50.49402	−50.49294
Cd_{38}	−43.96762	−43.96570	−43.96562
Zn_{55}	−73.30973	−73.30285	−73.30166
Cd_{55}	−63.71104	−63.70700	−63.70696
Zn_{75}	−100.18498	−100.18406	−100.18268
Cd_{75}	−86.94018	−86.93930	−86.93682
Zn_{147}	−197.14463	−197.14202	−197.14184
Cd_{147}	−170.66888	−170.66846	−170.66578

13 atoms

C_S

Zn(1), Cd(1)

I_h

Zn(φ), Cd(φ)

38 atoms

C_S

Zn(1), Cd(2)

O_h

Zn(>1537), Cd(φ)

D_{2d}

Zn(3), Cd(1)

55 atoms

C_S

Zn(1), Cd(1)

I_h

Zn(φ), Cd(φ)

75 atoms

C_1

Zn(1), Cd(1)

D_{5h}

Zn(φ), Cd(φ)

147 atoms

C_1

Zn(1), Cd(1) similar

I_h

Zn(φ), Cd(φ)
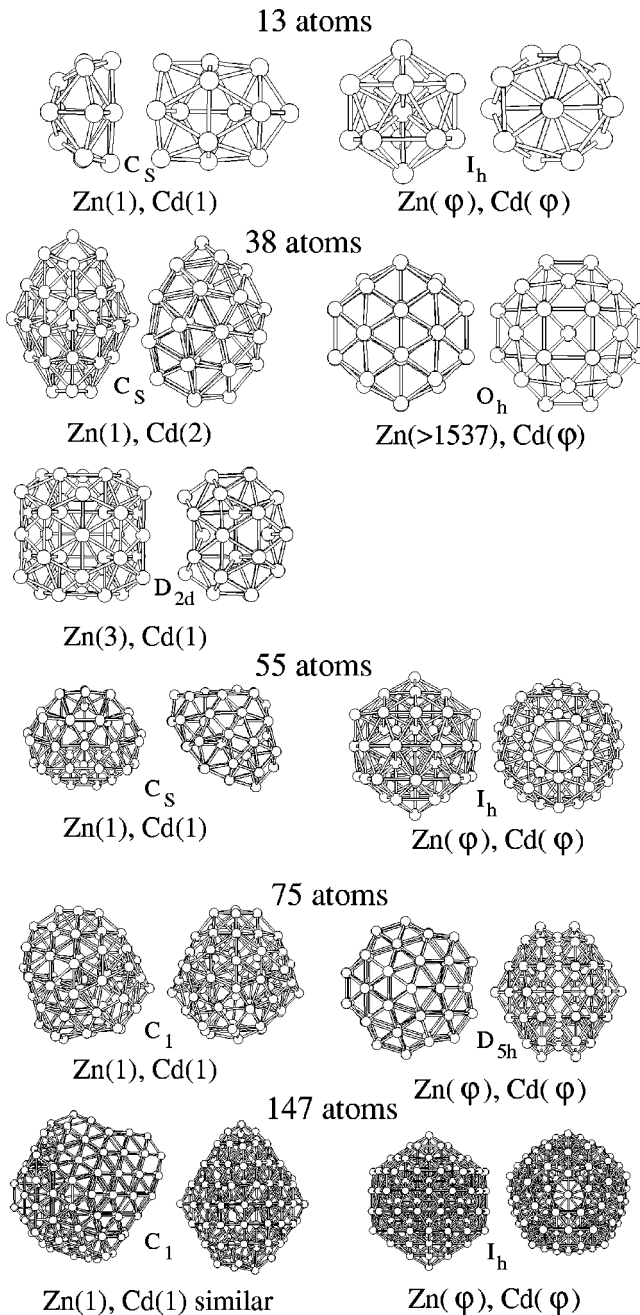
FIG. 3. Two perpendicular views of the geometry of the lowest energy isomer found for each cluster size. The normally global minimum ordered structures (although predicted to be unstable in most cases) are shown on the right for comparison. The isomer number (in parentheses) for the stable ordered structure of Zn_{38} is given as a lower limit since it is not likely that all the intervening isomers have been found. The symbol φ denotes that the configuration is unstable or inviable with respect to the Gupta potential and DFT calculations. The point group symmetry of each structure is given.

jugate gradient relaxation of the geometries using density-functional theory at both the local spin (LDA) and the gradient corrected spin density (GGA) levels, as implemented in the SIESTA program.[21] Standard norm conserving pseudo-potentials[22] were used in their fully non-local form.[23] A linear combination of numerical pseudo-atomic orbitals
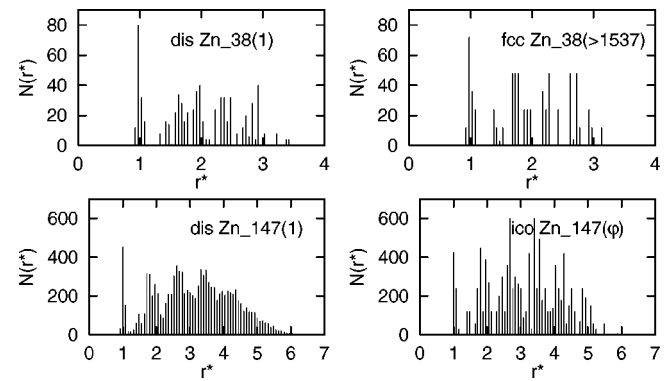

FIG. 4. The atomic pair distribution function in reduced units ($r^* = r_{ij}/r_{0n}$) for the disordered and ordered isomers of Zn_{38} and Zn_{147}. The number in parentheses is the isomer number. Results for the Cd clusters are similar.

was used as the basis set, allowing for multiple ζ and polarization orbitals, slightly excited by a common energy shift of 0.001 Ry, and truncated at a resulting radial node.[24,25] Tests of the bulk were first performed within these approximations (Table III).

Table IV lists the binding energies and free energies of the stable fcc ordered geometry for Zn_{38} with respect to the global-minimum disordered structure found using both the Gupta potential and density-functional theory. The free energies were calculated in the harmonic approximation, and include the zero point energy and only the most important vibrational contribution to the entropy.[27] The disordered structure for Zn_{38} is the most stable up to a temperature of slightly over 165 K, after which the fcc truncated octahedral structure is favored. Note that using the DFT calculated binding energies, at all temperatures and all sizes, and for both metals, the disordered structures are the most stable. In fact, the DFT ordered structures, where stable, have such high energies (>0.03 eV/atom extra) with respect to the disordered global minima, as to make them inviable at any temperature up to at least 300 K.

The structure factors (Ref. 2 for details) of the disordered global minima and those of the normally global minimum closed shell ordered structures are given in Fig. 5 for comparison with anticipated experimental data. Notable differences exist between the structure factors of the disordered and ordered isomers.

In conclusion, we predict that the most stable structures of Zn and Cd nanoclusters of the magic number sizes (n = 13,38,55,75, and 147) are disordered or of very low symmetry (except for Cd_{38}). Since the closed shell magic num-

TABLE III. Predicted unit cell volumes (Å^3) and bulk moduli ($N \times 10^{11}/m^2$) obtained with DFT (GGA) compared with experimental results (Ref. 26). The errors in the bulk moduli result from interpolation between the volume versus energy points.

	V DFT	Expt.	Bm DFT	Expt.
Zn	30.317	30.33	0.728±0.026	0.598
Cd	43.224	43.22	0.472±0.032	0.467

TABLE IV. Free energy differences (eV) of the Zn, 38 atom fcc ordered structure with respect to the global minimum disordered structure obtained with density functional theory (GGA) at a temperature of 0 K and with the Gupta potential at 0, 77, and 300 K.

	DFT	Gupta		
	0 K	0 K	77 K	300 K
fcc Zn_{38}	$+2.018$	$+0.140$	$+0.076$	-0.110

ber clusters normally have the highest binding energy per atom of the symmetric structures, the implicit prediction is that at most sizes Zn and Cd have low symmetry global minima. The geometry and stability of these structures was confirmed with density functional theory at both the LDA and the GGA levels. The usual global minimum high symmetry ordered structures were found to be unstable or inviable, except for the fcc structure of Zn_{38}, up to a temperature of at least 300 K. Results obtained with the Gupta potential also indicate that the magic sizes of 146 and 192 have disordered global minima, but this result remains to be confirmed with DFT. It is noted that these new structures are not merely Jahn-Teller deformations. We have shown in Ref. 12 that Jahn-Teller effects are very small (for example, for Au_{38}, atomic displacements of approximately 0.02 angstroms and total energies of approximately 0.1 eV) and cannot explain the preferred stability of these very different structures. The structure factors obtained for the ordered and disordered geometries suggest that the two forms should be easily distinguished, thus facilitating the experimental con-
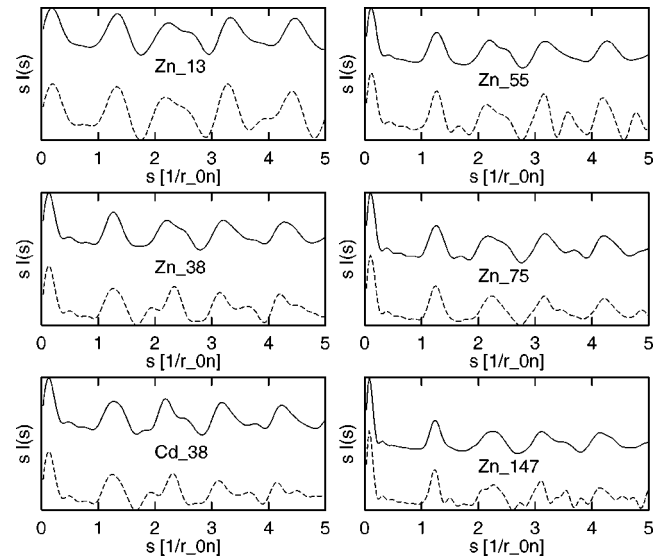

FIG. 5. The structure factor of the global minimum disordered configuration (solid curve) compared with the ordered structures (dashed curve). The spectra were obtained using the geometries given in Fig. 3. Results are similar for the Cd clusters, except for Cd_{38} which is shown.

firmation or rejection of this prediction. The electronic and thermodynamic properties of these nanoclusters will be presented in a forthcoming paper.

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